SUPPORTING INFORMATION

α-Sulfonylated ketazine synthesis from vinyl azides and sodium sulfinates using CAN: Radical C-S/N-N coupling cascade as a key reaction pathway

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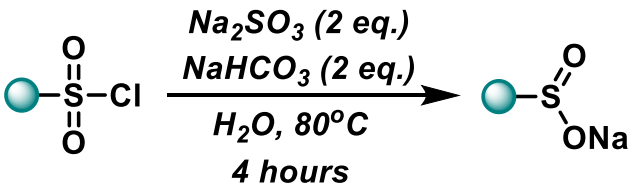
General

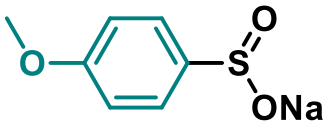
NMR spectra were registered on Bruker Avance II 300 MHz instrument. Chemical shifts were measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.0 ($CDCl_3$) or δ 2.50 and δ 39.0 (DMSO-d6). The TLC analyses were carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Column chromatography was performed on silica gel (60-200 mesh). 4-Methoxybenzenesulfonyl chloride, 4-acetamidobenzenesulfonyl chloride, 4-fluorobenzenesulfonyl chloride, 4-chlorobenzenesulfonyl chloride, naphthalene-2-sulfonyl chloride, thiophene-2-sulfonyl chloride, mesyl chloride (MsCl), ethanesulfonyl chloride, propane-2-sulfonyl chloride, cyclopropanesulfonyl chloride, sodium benzenesulfinate, styrene, 1-methyl-4-vinylbenzene, 1-isopropyl-4-vinylbenzene, 1-(tert-butyl)-4-vinylbenzene, 1-methoxy-4-vinylbenzene, 1-fluoro-4-vinylbenzene, 1-chloro-4-vinylbenzene, 1-bromo-4-vinylbenzene, 1-(chloromethyl)-4-vinylbenzene, 4-ethynylbenzonitrile, 1-ethynyl-4-nitrobenzene, 1-methyl-3-vinylbenzene, 1-chloro-3-vinylbenzene, 1-bromo-3-vinylbenzene, 1-chloro-2-vinylbenzene, 1-fluoro-2-vinylbenzene, 2-vinylnaphthalene, 1,2-dihydronaphthalene, 1-ethynylcyclohexan-1-ol, oct-1-yne, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), 2,6-Di-tert-butyl-4-methylphenol (BHT), Na_2SO_4, $MgSO_4$, Na_2SO_3, $NaHCO_3$, $Na_2S_2O_3$, NaN_3, $AgNO_3$, $Mn(OAc)_2{\cdot}4H_2O$, $(NH_4)_2[Ce(NO_3)_6]$ (CAN), t-BuOK, Et_3N, trimethylsilyl azide, ICl, Br_2, concentrated hydrochloric acid, petroleum ether (PE, 40/70), ethyl acetate (EA), THF, DMSO, MeOH, Et_2O, MeCN, EtOH, DCM, $CHCl_3$ were purchased from commercial sources and were used as is.

Synthesis of the starting compounds

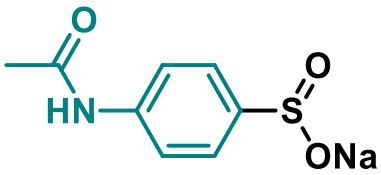
Synthesis of sodium sulfinates 2c-2l.



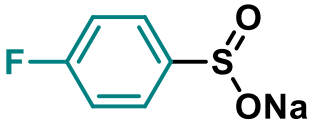
Following the slightly modified literature procedure,[1] Na_2SO_3 (20 mmol, 2 eq.), $NaHCO_3$ (20 mmol, 2 eq.) and the corresponding aryl sulfonyl chloride (10 mmol, 1 eq.) was dissolved in H_2O (9.6 mL). After that the resulting mixture was stirred for 4 hours at 80°C. After the competition of the reaction water was evaporated under reduced pressure. Then the resulted solid was dissolved in 50 mL of EtOH and stayed under magnetic stirring for 20 minutes at room temperature. Formed precipitate was removed by vacuum filtration, and resulted supernatant was evaporated under reduced pressure. The residue was used as is without purification to give pure sodium sulfinate.



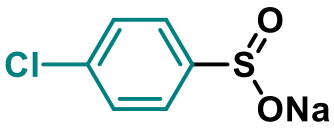
Sodium 4-methoxybenzenesulfinate (2c).[1] 4-methoxybenzenesulfonyl chloride (2.07 g, 10 mmol) gave the title compound as a colorless solid (1.70 g), yield 87%. ^{1}H NMR (D_2O), δ: 3.88 (s, 3H), 7.08-7.13 (m, 2H), 7.60-7.65 (m, 2H). ^{13}C NMR, (D_2O), δ: 55.5, 114.4, 125.2, 146.0, 160.5.



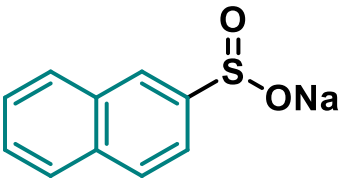
Sodium 4-acetamidobenzenesulfinate (2d).[2] 4-acetamidobenzenesulfonyl chloride (2.34 g, 10 mmol) gave the title compound as a colorless solid (1.81 g), yield 82%. ^{1}H NMR (D_2O), δ: 2.14 (s, 3H), 7.49 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H).^{13}C NMR, (D_2O), δ: 23.1, 121.5, 124.4, 138.8, 149.8, 172.8.



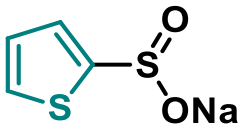
Sodium 4-fluorobenzenesulfinate (2e).[1] 4-fluorobenzenesulfonyl chloride (3.89 g, 10 mmol) gave the title compound as a colorless solid (2.70 g), yield 74%. ^{1}H NMR (D_2O), δ: 7.24-7.31 (m, 2H), 7.65-7.71 (m, 2H).^{13}C NMR, (D_2O), δ: 115.8 (d, *J* = 22.2 Hz), 125.8 (d, *J* = 9.0 Hz), 149.5 (d, *J* = 2.5 Hz), 163.7 (d, *J* = 246.4 Hz).



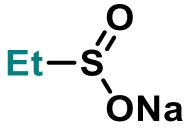
Sodium 4-chlorobenzenesulfinate (2f).[3] 4-chlorobenzenesulfonyl chloride (2.11 g, 10 mmol) gave the title compound as a a colorless solid (1.87 g), yield 95%. ^{1}H NMR (D_2O), δ: 7.51-7.56 (m, 2H), 7.59-7.63 (m, 2H).^{13}C NMR, (D_2O), δ: 125.1, 129.0, 135.7, 152.1. doi/10.1021/jacs.0c03239



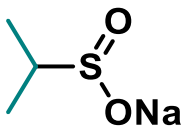
Sodium naphthalene-2-sulfinate (2g).[1] naphthalene-2-sulfonyl chloride (2,27 g, 10 mmol) gave the title compound as a colorless solid (1.79 g), yield 84%. ^{1}H NMR (D_2O), δ: 7.51-7.57 (m, 2H), 7.74 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.86-7.98 (m, 3H), 8.05 (s, 1H).^{13}C NMR, (D_2O), δ: 120.0, 123.5, 126.9, 127.4, 127.8, 128.6, 129.2, 132.5, 133.9, 150.6.



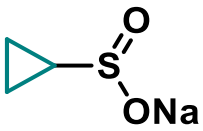
Sodium thiophene-2-sulfinate (2h).[4] thiophene-2-sulfonyl chloride (1.83 g, 10 mmol) gave the title compound as a colorless solid (1.53 g), yield 90%. ^{1}H NMR (D_2O), δ: 7.15 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.36 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.62 (dd, *J* = 4.8, 1.1 Hz, 1H).^{13}C NMR, (D_2O), δ: 126.4, 127.6, 128.5, 158.4.



Sodium ethanesulfinate (2j).[5] ethanesulfonyl chloride (1.29 g, 10 mmol) gave the title compound as a colorless solid (0.99 g), yield 85%. ^{1}H NMR (D_2O), δ: 1.12 (t, *J* = 7.6 Hz, 3H), 2.38 (q, *J* = 7.6 Hz, 2H).^{13}C NMR, (D_2O), δ: 5.3, 53.8.

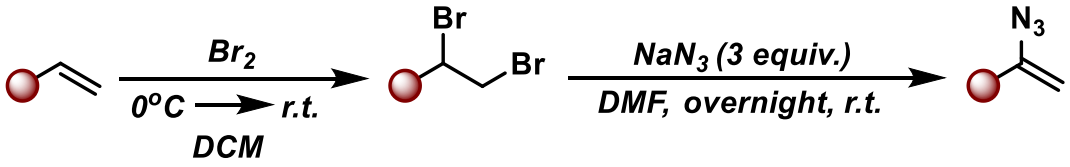


Sodium propane-2-sulfinate (2k).[5] propane-2-sulfonyl chloride (1.43 g, 10 mmol) gave the title compound as a colorless solid (1.20 g), yield 92%. ^{1}H NMR (D_2O), δ: 1.12 (d, *J* = 7.0 Hz, 6H), 2.25 (sep, *J* = 7.0, 1H). ^{13}C NMR, (D_2O), δ: 13.3, 56.0.



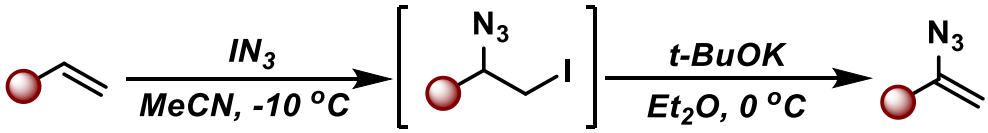
Sodium cyclopropanesulfinate (2l).[6] cyclopropanesulfonyl chloride (1.83 g, 10 mmol) gave the title compound as a colorless solid (1.17 g), yield 91%. ^{1}H NMR (D_2O), δ: 0.75-0.83 (m, 4H), 1.98 (tt, *J* = 7.9, 5.3 Hz, 1H).^{13}C NMR, (D_2O), δ: 0.6, 36.0.

Synthesis of vinyl azides 1a-1d, 1f, 1g and 1i-1n.



Following the literature procedure,[7] the corresponding styrene (28.8 mmol) was dissolved in DCM (10 mL) and the mixture was cooled to 0°C. Bromine (4.61 g, 28.8 mmol) was dissolved in DCM (10 mL) and was added dropwise to the styrene solution under magnetic stirring at 0°C. Then, the reaction mixture was stirred for 1 h at room temperature. A saturated solution of $Na_2S_2O_3$ was added until the color of bromine faded. The resulting mixture was washed with water (2×10 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The resulting dibromide was dissolved in DMF (20 mL) and NaN_3 (5.62 g, 86.4 mmol) was added under magnetic stirring. The reaction mixture was stirred overnight at room temperature. Then, it was diluted with water (20 mL) and was washed with Et_2O (3×10 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified using column chromatography (eluent - PE) to give pure vinyl azide.

Synthesis of vinyl azides 1e, 1h, 1o and 1p.

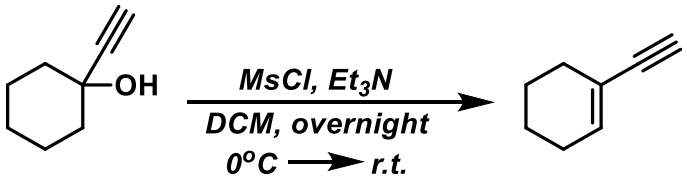


Following the slightly modified literature procedure,[8] to a suspension of NaN_3 (3.26 g, 50.2 mmol) in acetonitrile (16 mL) a solution of ICl (4.06 g, 25 mmol) in acetonitrile (8 mL) was added dropwise at – 10 °C and the mixture was stirred at the same temperature for 30 min. After that a solution of alkene (20 mmol) in acetonitrile (8 mL) was added slowly, and the mixture was stirred at room temperature for 30 min. Then, the reaction mixture was quenched portionwise with saturated aqueous solution of $Na_2S_2O_3$, and the organic phase was extracted twice with Et_2O (20 mL). The combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation of solvent, resulting crude materials were used immediately for the next step without purification.

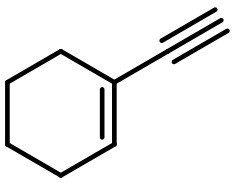
To the solution of obtained compound in Et_2O (40 mL) at 0 °C t-BuOK (2.30 g, 20.5 mmol) was added, and the mixture was stirred for 90 min at the same temperature. After completition of the reaction resulted mixture was quenched with water (50 mL). The

organic phase was extracted twice with Et_2O (20 mL), dried over $MgSO_4$ and evaporated under reduced pressure. Resulting crude materials were purified by column chromatography (eluent - PE) to give pure vinyl azide.

Synthesis of 1-ethynylcyclohex-1-ene (X).



Following the literature procedure,[9] the solution of 1-ethynylcyclohexan-1-ol (3.11 g, 25 mmol) in DCM (22 mL) was added Et_3N (17.5 mL, 125 mmol). Then MsCl (4.8 mL, 62.5 mmol) in DCM (7 mL) was slowly added to the mixture under 0°C. The mixture was warmed to room temperature and stirred overnight. Then the mixture was quenched with H_2O (50 mL). The organic layer was separated and washed with brine (2×10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The residue was subjected to flash column chromatography for purification using petroleum ether as eluent to give 1-ethynylcyclohex-1-ene **X** (1.96 g, 63%) as colourless oil.



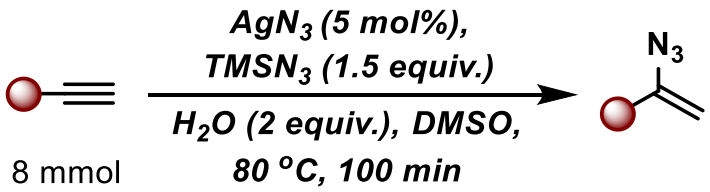
1-ethynylcyclohex-1-ene (X).[9] 1-ethynylcyclohexan-1-ol (3.11 g, 25 mmol) gave the title compound as a colorless oil (1.96 g), yield 63%. ^{1}H NMR ($CDCl_3$): 1.57 – 1.63 (m, 4H), 2.07 – 2.12 (m, 4H), 2.78 (s, 1H), 6.18 (s, 1H). δ: ^{13}C NMR, ($CDCl_3$), δ: 21.5, 22.3, 25.7, 29.1, 74.4, 85.8, 119.9, 136.5.

Synthesis of AgN_3.

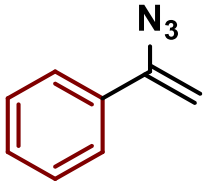
Silver azide was synthesized following literature procedure[10]. A-100 mL round bottom flask was equipped with a magnetic stir bar. During synthesis the flask was protected from the light with aluminum foil. NaN_3 (130 mg, 2 mmol, 1 equiv) was added into this flask and then was dissolved in deionized water (4 mL) under magnetic stirring. $AgNO_3$ (357 mg, 2.1 mmol, 1.05 equiv) was dissolved in deionized water (2 mL). After that solution of silver nitrate was added into the round bottom flask by a syringe and stirred for 10 min at room temperature. When the reaction was completed mixture was filtered

to remove the supernatant. The solid AgN_3 was washed by deionized water (3×10 mL) and anhydrous ethanol (3×5 mL). The sample was dried at 45 °C for 3 h to obtain the product of white silver azide solid in a yield of 90%. The product was stored in dark at room temperature.

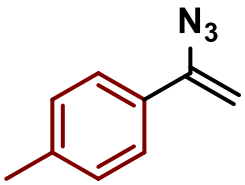
Synthesis of vinyl azides 1j, 1k, 1s and 1t.



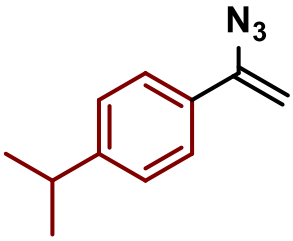
Compounds **1j, 1k, 1s** and **1t** were synthesized according to the literature procedure[10]. A 20-mL sealed tube was equipped with magnetic stir bar, then alkyne (8 mmol, 1 equiv.) and dimethylsulfoxide (DMSO) (8 mL) were added. After that trimethylsilyl azide (1.6 mL, 12 mmol, 1.5 equiv.) was added into this flask through a 2-mL syringe, and water (0.3 mL, 16 mmol, 2 equiv.) was added by using a 1-mL syringe. Finally, the freshly synthesized AgN_3 (60 mg, 0.4 mmol, 5 mol% equiv.) was added and stirred under air. With all reagents added the sealed tube was equipped with silicone rubber septa and then pierced by a needle. The flask was placed in an oil bath at an ambient temperature of 80 °C and was stirred for 100 min. After completition of reaction the mixture was diluted with water (50 mL) and extracted with DCM (3×10 mL). The organic layer was separated and washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was subjected to flash column chromatography for purification using petroleum ether as eluent to give title compound.



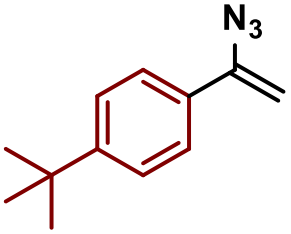
(1-azidovinyl)benzene (1a).[11] styrene (3 g, 28.8 mmol) gave the title compound as a yellow oil (1.96 g), yield 63%. ^{1}H NMR ($CDCl_3$), δ: 4.98 (d, *J* = 2.4 Hz, 1H), 5.45 (d, *J* = 2.4 Hz, 1H), 7.35-7.40 (m, 3H), 7.57-7.60 (m, 2H). ^{13}C NMR, ($CDCl_3$), δ: 98.1, 125.7, 128,6, 129.2, 134.4, 145.2.



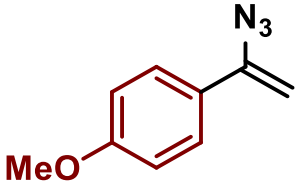
1-(1-azidovinyl)-4-methylbenzene (1b).[12] 1-methyl-4-vinylbenzene (3.4 g, 28.8 mmol) gave the title compound as a yellow oil (2.38 g), yield 52%. ^{1}H NMR ($CDCl_3$), δ: 2.38 (s, 3H), 4.93 (d, *J* = 2.3 Hz, 1H), 5.40 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR, ($CDCl_3$), δ: 21.3, 97.3, 125,6, 129.3, 131.7, 139.3, 145.2.



1-(1-azidovinyl)-4-isopropylbenzene (1c). 1-isopropyl-4-vinylbenzene (4.21 g, 28.8 mmol) gave the title compound as a yellow oil (2.38 g), yield 52%. ^{1}H NMR ($CDCl_3$), δ: 1.26 (d, *J* = 6.9 Hz, 6H), 2.92 (sep, *J* = 7.0 Hz, 1H), 4.92 (d, *J* = 2.3 Hz, 1H), 5.39 (d, *J* = 2.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR, ($CDCl_3$), δ: 24.0, 34.0, 97,4, 125.7, 126.6, 132.0, 145.2, 150.2.

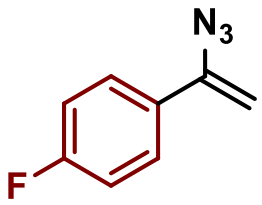


1-(1-azidovinyl)-4-(tert-butyl)benzene (1d).[13] 1-(tert-butyl)-4-vinylbenzene (2.88 g, 18 mmol) gave the title compound as a yellow oil (1.58 g), yield 44%. ^{1}H NMR ($CDCl_3$), δ: 1.35 (s, 9H), 4.94 (d, *J* = 2.3 Hz, 1H), 5.42 (d, *J* = 2.3 Hz, 1H), 7.39 – 7.42 (m, 2H), 7.50 – 7.53 (m, 2H).^{13}C NMR, ($CDCl_3$), δ: 31.4, 34.8, 97,4, 125.4, 125.5, 131.6, 145.1, 152.5.

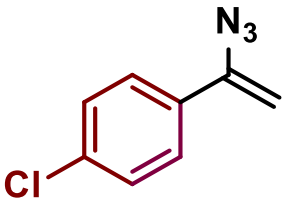


1-(1-azidovinyl)-4-methoxybenzene (1e).[12] 1-methoxy-4-vinylbenzene (2.68 g, 20 mmol) gave the title compound as a white solid (1.82 g), yield 52%. ^{1}H NMR ($CDCl_3$), δ:

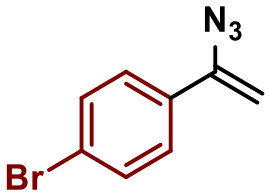
3.82 (s, 3H), 4.86 (d, *J* = 2.2 Hz, 1H), 5.32 (d, *J* = 2.2 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR, ($CDCl_3$), δ: 55.4, 96.3, 113,9, 114.1, 127.0, 144.8, 160.4.



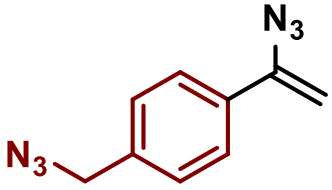
1-(1-azidovinyl)-4-fluorobenzene (1f).[12] 1-fluoro-4-vinylbenzene (1.22 g, 10 mmol) gave the title compound as a yellow oil (865 mg), yield 53%. ^{1}H NMR ($CDCl_3$), δ: 4.94 (d, *J* = 2.4 Hz, 1H), 5.37 (d, *J* = 2.4 Hz, 1H), 7.01 – 7.07 (m, 2H), 7.52 – 7.56 (m, 2H). ^{13}C NMR, ($CDCl_3$), δ: 97.7, 115.5 (d, *J* = 21.7 Hz), 127.6 (d, *J* = 8.3 Hz), 130.6 (d, *J* = 3.0 Hz), 144.3, 163.4 (d, *J* = 248.9 Hz).



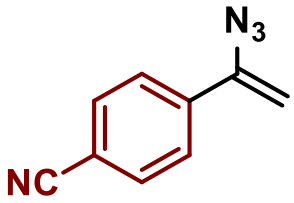
1-(1-azidovinyl)-4-chlorobenzene (1g).[12] 1-chloro-4-vinylbenzene (762 mg, 5.5 mmol) gave the title compound as a yellow oil (542 mg), yield 66%. ^{1}H NMR ($CDCl_3$), δ: 4.97 (d, *J* = 2.6 Hz, 1H), 5.43 (d, *J* = 2.6 Hz, 1H), 7.30 – 7.34 (m, 2H), 7.47 – 7.51 (m, 2H). ^{13}C NMR, ($CDCl_3$), δ: 98.3, 127.0, 128,8, 132.9, 135.2, 144.3.



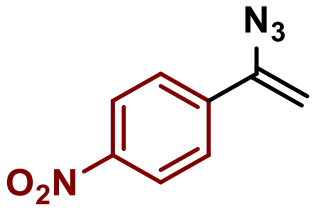
1-(1-azidovinyl)-4-bromobenzene (1h).[11] 1-bromo-4-vinylbenzene (762 mg, 5.5 mmol) gave the title compound as a yellow oil (542 mg), yield 66%. ^{1}H NMR ($CDCl_3$), δ: 4.97 (d, *J* = 2.6 Hz, 1H), 5.44 (d, *J* = 2.6 Hz, 1H), 7.40 – 7.51 (m, 4H).^{13}C NMR, ($CDCl_3$), δ: 98.4, 123.4, 127.3, 131.7, 133.4, 144.3.



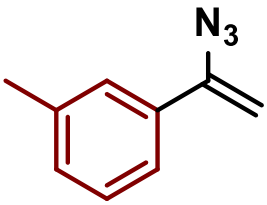
1-(azidomethyl)-4-(1-azidovinyl)benzene (1i).[14] 1-(chloromethyl)-4-vinylbenzene (9.3 g, 61 mmol) gave the title compound as a yellow oil (4.24 g), yield 35%. ^{1}H NMR ($CDCl_3$), δ: 4.35 (s, 2H), 4.99 (d, *J* = 2.5 Hz, 1H), 5.47 (d, *J* = 2.5 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H).^{13}C NMR, ($CDCl_3$), δ: 54.5, 98.4, 126.1, 128.3, 134.4, 136.4, 144.7.



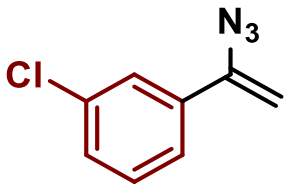
4-(1-azidovinyl)benzonitrile (1j).[15] 4-ethynylbenzonitrile (445 mg, 3.5 mmol) gave the title compound as a colourless solid (304 mg), yield 51%. ^{1}H NMR ($CDCl_3$), δ: 5.11 (d, *J* = 2.9 Hz, 1H), 5.58 (d, *J* = 2.9 Hz, 1H), 7.62 – 7.69 (m, 4H).^{13}C NMR, ($CDCl_3$), δ: 100.5, 112.8, 118.6, 126.2, 132.4, 138.5, 143.7.



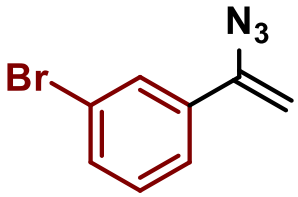
1-(1-azidovinyl)-4-nitrobenzene (1k).[16] 1-ethynyl-4-nitrobenzene (589 mg, 4 mmol) gave the title compound as a yellow solid (311 mg), yield 41%. ^{1}H NMR ($CDCl_3$), δ: 5.15 (d, *J* = 2.7 Hz, 1H), 5.64 (d, *J* = 2.7 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 2H), 8.20 (d, *J* = 8.7 Hz, 2H).^{13}C NMR, ($CDCl_3$), δ: 101.2, 123.9, 126.4, 140.3, 143.5, 148.2.



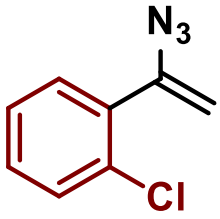
1-(1-azidovinyl)-3-methylbenzene (1l).[12] 1-methyl-3-vinylbenzene (3.4 g, 28.8 mmol) gave the title compound as a yellow oil (1.6 g), yield 35%. ^{1}H NMR ($CDCl_3$), δ: 2.38 (s, 3H), 4.95 (d, *J* = 2.3 Hz, 1H), 5.42 (d, *J* = 2.3 Hz, 1H), 7.16-7.19 (m, 1H), 7.23-7.28 (m, 1H), 7.36-7.39 (m, 2H).^{13}C NMR, ($CDCl_3$), δ: 21.6, 98.0, 122.9, 126.4, 128.5, 130.0, 134.4, 138.2, 145.3.



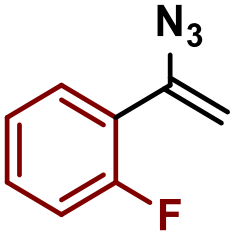
1-(1-azidovinyl)-3-chlorobenzene (1m).[10] 1-chloro-3-vinylbenzene (762 mg, 5.5 mmol) gave the title compound as a yellow oil (622 mg), yield 63%. ^{1}H NMR ($CDCl_3$), δ: 4.98 (d, *J* = 2.7 Hz, 1H), 5.44 (d, *J* = 2.7 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.42 (dt, *J* = 7.2, 1.8 Hz, 1H), 7.54 (t, *J* = 1.8 Hz, 1H). ^{13}C NMR, ($CDCl_3$), δ: 98.9, 123.8, 125.9, 129.2, 129.8, 134.7, 136.2, 144.0.



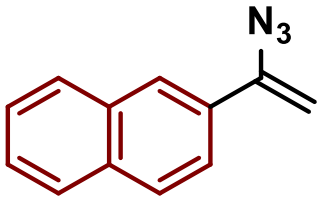
1-(1-azidovinyl)-3-bromobenzene (1n).[17] 1-bromo-3-vinylbenzene (1 g, 5.5 mmol) gave the title compound as a yellow oil (677 mg), yield 55%. ^{1}H NMR ($CDCl_3$), δ: 4.99 (d, *J* = 2.6 Hz, 1H), 5.46 (d, *J* = 2.6 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.46 – 7.50 (m, 2H), 7.72 (t, *J* = 1.5 Hz, 1H). ^{13}C NMR, ($CDCl_3$), δ: 99.0, 122.8, 124.2, 128.8, 130.1, 132.2, 136.4, 143.9.



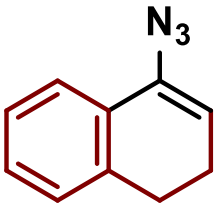
1-(1-azidovinyl)-2-chlorobenzene (1o).[18] 1-chloro-2-vinylbenzene (762 mg, 5.5 mmol) gave the title compound as a yellow oil (217 mg), yield 22%. ^{1}H NMR ($CDCl_3$), δ: 4.91 (d, *J* = 1.0 Hz, 1H), 5.14 (d, *J* = 1.0 Hz, 1H), 7.28 – 7.39 (m, 3H), 7.42 – 7.45 (m, 1H).^{13}C NMR, ($CDCl_3$), δ: 104.2, 127.0, 130.1, 130.5, 131.0, 132.9, 134.3, 143.3.



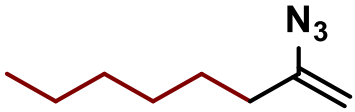
1-(1-azidovinyl)-2-fluorobenzene (1p).[18] 1-fluoro-2-vinylbenzene (672 mg, 5.5 mmol) gave the title compound as a yellow oil (368 mg), yield 41%. ^{1}H NMR ($CDCl_3$), δ: 5.19 - 5.20 (m, 1H), 5.43 (d, *J* = 1.4 Hz, 1H), 7.08 - 7.18 (m, 2H), 7.29 - 7.37 (m, 1H), 7.47 - 7.52 (m, 1H). ^{13}C NMR, ($CDCl_3$), δ: 103.7 (d, *J* = 8.9 Hz), 116.3 (d, *J* = 22.6 Hz), 122.5 (d, *J* = 11.6 Hz), 124.3 (d, *J* = 3.7 Hz), 129.4 (d, *J* = 2.5 Hz), 130.7 (d, *J* = 8.6 Hz), 139.8 (d, *J* = 2.7 Hz), 160.1 (d, *J* = 251.5 Hz).



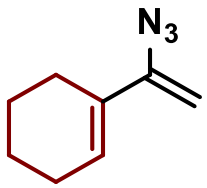
2-(1-azidovinyl)naphthalene (1q).[12] 2-vinylnaphthalene (3.0 g, 20 mmol) gave the title compound as a yellow solid (2.33 g), yield 61%. ^{1}H NMR ($CDCl_3$), δ: 5.09 (d, *J* = 2.5 Hz, 1H), 5.61 (d, *J* = 2.5 Hz, 1H), 7.61 – 7.46 (m, 2H), 7.69 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.93 – 7.78 (m, 3H), 8.08 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR, ($CDCl_3$), δ: 98.4, 123.2, 125.1, 126.6, 126.8, 127.7, 128.3, 128.7, 131.6, 133.2, 133.7, 145.1.



4-azido-1,2-dihydronaphthalene (1r).[16] 1,2-dihydronaphthalene (1.95 g, 15 mmol) gave the title compound as a yellow oil (642 mg), yield 25%. ^{1}H NMR ($CDCl_3$), δ: 2.46 (td, *J* = 8.4, 4.8 Hz, 2H), 2.84 (t, *J* = 8.0 Hz, 2H), 5.73 (t, *J* = 4.8 Hz, 1H), 7.25 – 7.13 (m, 3H), 7.42 – 7.37 (m, 1H).^{13}C NMR, ($CDCl_3$), δ: 22.8, 27.8, 111.9, 122.3, 126.6, 127.5, 128.3, 130.5, 136.0, 136.4.



2-azidooct-1-ene (1s).[10] oct-1-yne (882 mg, 8 mmol) gave the title compound as a colorless oil (777 mg), yield 63%. ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, *J* = 6.5 Hz, 3H), 1.26-1.32 (m, 6H), 1.43-1.50 (m, 2H), 2.07 (t, *J* = 7.5 Hz, 2H), 4.62 (s, 2H). ^{13}C NMR, ($CDCl_3$), δ: 14.2, 22.7, 27.4, 28.7, 31.7, 33.8, 98.1,147.0.

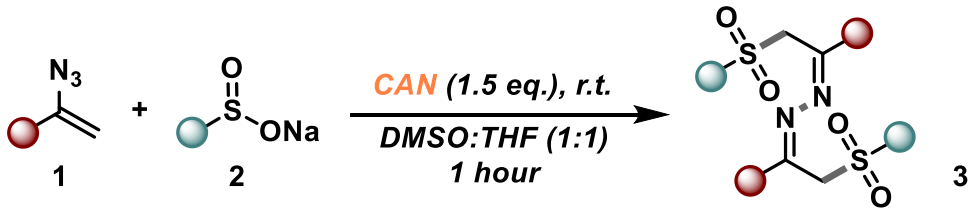


1-(1-azidovinyl)cyclohex-1-ene (1t).[10] 1-ethynylcyclohex-1-ene (849 mg, 8 mmol) gave the title compound as a colorless oil (788 mg), yield 66%. ^{1}H NMR ($CDCl_3$), δ: 1.56-1.70 (m, 4H), 2.14-2.16 (m, 4H), 4.70 (s, 1H), 4.95 (s, 1H), 6.22 (s, 1H).^{13}C NMR, ($CDCl_3$), δ: 22.0, 22.6, 25.4, 25.6, 95.4, 127.3, 130.9, 146.2.

Sulfonylation of vinyl azides with sodium sulfinates

General procedure for the optimization of the reaction conditions for the synthesis of (1Z,2Z)-1,2-bis(1-phenyl-2-(phenylsulfonyl)ethylidene)hydrazine 3aa from (1-azidovinyl)benzene 1a and sodium benzenesulfinate 2a (Table 1): A 50 mL round-bottom flask was equipped with a magnetic stir bar. Sodium benzenesulfinate **2a** (164-246 mg, 1-1.5 mmol, 1.0-1.5 equiv.) and (1-azidovinyl)benzene **1a** (145-218 mg, 1-1.5 mmol, 1.0-2.0 equiv.) were dissolved in 10 mL of appropriate solvent. After that, cerium (IV) ammonium nitrate (274-822 mg, 0.5-1.5 mmol, 0.5-1.5 equiv.) were added in one portion under magnetic stirring and stayed for 30 min (entry 4), 60 min (entries 1-3 and 7-13) or 90 min (entry 5) at room temperature or heated to 40°C (entry 6). When reaction was completed, the reaction mixture was diluted with water (50 mL). The organic materials were extracted with DCM (4×10 mL). Combined organic layer was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The yield of the desired product **3aa** was determined by ^1H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard.

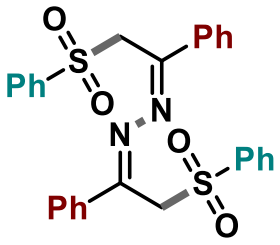
Synthesis of α-sulfonylated ketazines 3aa-3ta (Table 2).



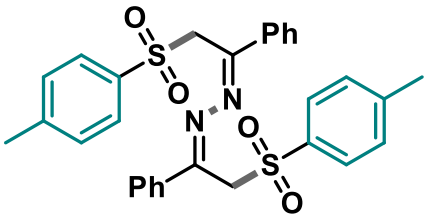
1 2 3

A 50 mL round-bottom flask was equipped with a magnetic stir bar. Vinyl azide **1** (1.5 mmol, 1.5 equiv.) and sodium sulfinate **2** (1 mmol, 1.0 equiv.) were dissolved in 10 mL of THF−DMSO (1:1). After that, cerium (IV) ammonium nitrate (1.5 mmol, 1.5 equiv.) were added in one portion under magnetic stirring and stayed for 60 min at room temperature. When reaction was completed, the reaction mixture was diluted with water (50 mL). The organic materials were extracted with DCM (4×10 mL). Combined organic layer was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The desired products **3aa-3ta** were isolated by chromatography on SiO_2 with elution using $CHCl_3$-EA in a gradient of the latter from 2 to 5 vol%. (***Note:*** *due to low solubility of ketazine* ***3ai*** *isolation procedure should be changed to filtration. After completition of the reaction resulted mixture was diluted with 50 mL of water and filtered by vacuum filtration. Bright yellow precipitate was*

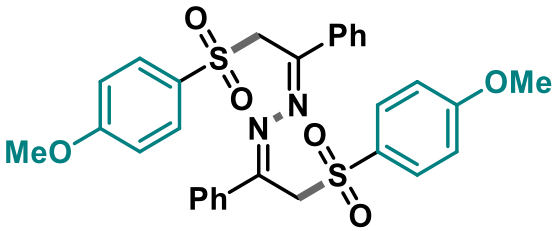
subsequently washed with 20 mL of water, 10 mL of cold EtOH and 20 mL of diethyl ether. Dried precipitate was characterized without any additional purification)



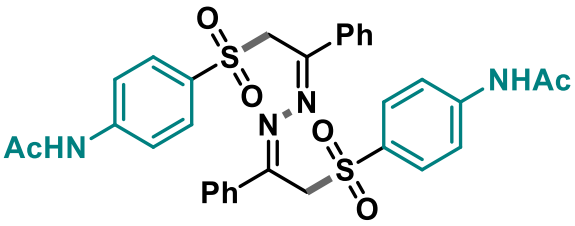
(1Z,2Z)-1,2-bis(1-phenyl-2-(phenylsulfonyl)ethylidene)hydrazine (3aa). Bright orange solid. 222 mg (yield 86%). R_f = 0.33 ($CHCl_3$:EA 50:1), mp = 185.0-186.0°C. ^1H NMR ($CDCl_3$), δ: 4.90 (s, 4H), 7.25-7.31 (m, 4H), 7.38-7.51 (m, 8H), 7.71-7.79 (m, 8H). ^{13}C NMR ($CDCl_3$), δ: 55.2, 128.2, 128.4, 128.6, 129.0, 131.3, 133.8, 135.3, 139.8, 155.6. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{28}H_{24}N_2NaO_4S_2]^+$: 539.1070. Found: 539.1061.



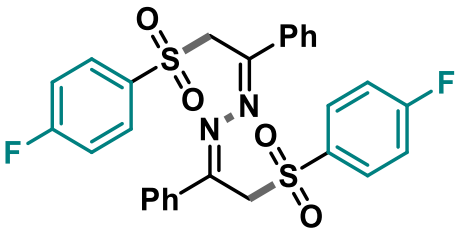
(1Z,2Z)-1,2-bis(1-phenyl-2-tosylethylidene)hydrazine (3ab). Bright orange solid. 229 mg (yield 84%). R_f = 0.41 ($CHCl_3$:EA 50:1), mp = 190.0-192.0°C. ^1H NMR ($CDCl_3$), δ: 2.27 (s, 6H), 4.87 (s, 4H), 7.05 (d, J = 8.1 Hz, 4H), 7.38-7.43 (m, 4H), 7.46-7.51 (m, 2H), 7.59 (d, J = 8.2 Hz, 4H), 7.77 (d, J = 7.4 Hz, 4H), ^{13}C NMR ($CDCl_3$), δ: 21.7, 55.3, 128.2, 128.5, 128.5, 129.6, 131.3, 135.4, 137.0, 144.9, 155.8. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{30}H_{29}N_2O_4S_2]^+$: 545.1563. Found: 545.1565.



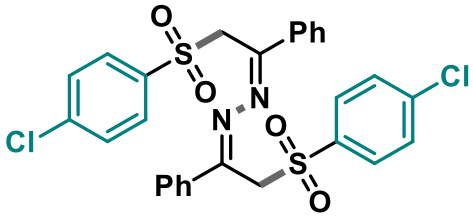
(1Z,2Z)-1,2-bis(2-((4-methoxyphenyl)sulfonyl)-1-phenylethylidene)hydrazine (3ac). Bright orange solid. 225 mg (yield 78%). R_f = 0.34 ($CHCl_3$:EA 50:1), mp = 171.0-173.0°C. ^1H NMR (DMSO-d6), δ: 3.70 (s, 6H), 5.09 (s, 4H), 6.86-6.89 (m, 4H), 7.41-7.46 (m, 4H), 7.49-7.54 (m, 2H), 7.57-7.60 (m, 4H), 7.79-7.82 (m, 4H). ^{13}C NMR, ($CDCl_3$) δ: 54.4, 55.6, 114.3, 128.0, 128.1, 130.0, 130.9, 131.2, 135.3, 155.9, 163.2. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{30}H_{28}N_2NaO_6S_2]^+$: 599.1281. Found: 599.1289.



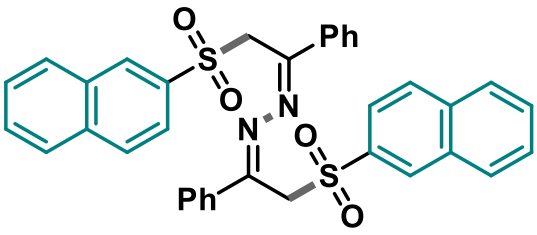
N,N'-(((2Z,2'Z)-hydrazine-1,2-diylidenebis(2-phenylethan-1-yl-2 ylidenesulfonyl))bis(4,1-phenylene))diacetamide (3ad). Bright orange solid. 202 mg (yield 64%). R_f = 0.31 ($CHCl_3$:EA 50:1), mp = 238.0-240.0°C. ^{1}H NMR (DMSO-d6), δ: 2.08 (s, 6H), 5.04 (s, 4H), 7.39-7.44 (m, 4H), 7.48-7.56 (m, 10H), 7.75-7.78 (m, 4H), 10.25 (s, 2H). ^{13}C NMR (DMSO-d6), δ: 24.2, 54.4, 118.5, 128.0, 128.1, 129.0, 130.9, 133.0, 135.1, 144.1, 155.5, 169.0. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{32}H_{31}N_4O_6S_2]^+$: 631.1680. Found: 631.1680.



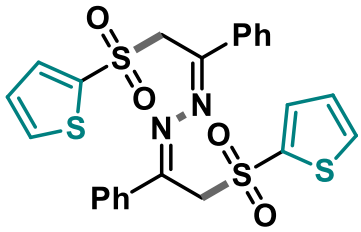
(1Z,2Z)-1,2-bis(2-((4-fluorophenyl)sulfonyl)-1-phenylethylidene)hydrazine (3ae). Bright orange solid. 227 mg (yield 82%). R_f = 0.62 ($CHCl_3$:EA 50:1), mp = 189.0-191.0°C. ^{1}H NMR (DMSO-d6), δ: 5.22 (s, 4H), 7.16-7.22 (m, 4H), 7.41-7.46 (m, 4H), 7.50-7.55 (m, 2H), 7.72-7.77 (m, 4H), 7.79-7.82 (m, 4H). ^{13}C NMR (DMSO-d6), δ: 54.1, 116.3 (d, J = 22.9 Hz), 128.1 (d, J = 9.4 Hz), 131.0, 131.0 131.2, 135.1, 135.8 (d, J = 2.6 Hz), 156.1, 165.0 (d, J = 253.4 Hz). HRMS (ESI) m/z ($M+K^+$) calculated for $[C_{28}H_{22}F_2N_2KO_4S_2]^+$: 591.0621. Found: 591.0624.



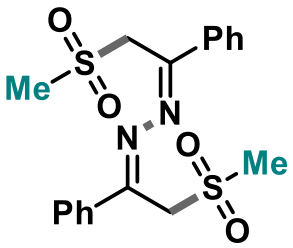
(1Z,2Z)-1,2-bis(2-((4-chlorophenyl)sulfonyl)-1-phenylethylidene)hydrazine (3af). Bright orange solid. 243 mg (yield 83%). R_f = 0.63 ($CHCl_3$:EA 50:1), mp = 249.0-250.0°C. ^{1}H NMR (DMSO-d6), δ: 5.18 (s, 4H), 7.42-7.46 (m, 8H), 7.51-7.53 (m, 2H), 7.68-7.71 (m, 4H), 7.78-7.81 (m, 4H). ^{13}C NMR (DMSO-d6), δ: 54.0, 128.1, 128.2, 129.2, 129.7, 131.0, 135.1, 138.3, 139.1, 156.1. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{28}H_{23}{}^{37}Cl_2N_2O_4S_2]^+$: 587.0443. Found: 587.0440.



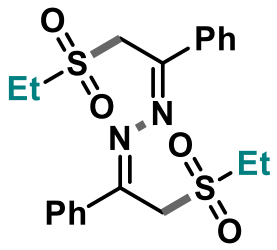
(1Z,2Z)-1,2-bis(2-(naphthalen-2-ylsulfonyl)-1-phenylethylidene)hydrazine (3ag). Bright orange solid. 234 mg (yield 76%). R_f = 0.51 ($CHCl_3$:EA 50:1), mp = 168.0-169.0°C. ^{1}H NMR (DMSO-d6), δ: 5.07 (s, 4H), 7.21-7.26 (m, 4H), 7.36-7.41 (m, 2H), 7.59-7.72 (m, 10H), 7.72-8.00 (m, 6H), 8.37 (d, J = 1.4 Hz, 2H). ^{13}C NMR (DMSO-d6), δ: 54.3, 122.5, 127.6, 127.8, 127.8, 128.0, 129.2, 129.3, 129.4, 129.4, 130.8, 131.5, 134.8, 134.9, 136.8, 155.1. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{36}H_{28}N_2NaO_4S_2]^+$: 639.1383. Found: 639.1381.



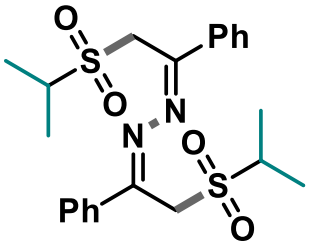
(1Z,2Z)-1,2-bis(1-phenyl-2-(thiophen-2-ylsulfonyl)ethylidene)hydrazine (3ah). Bright orange solid. 193 mg (yield 73%). R_f = 0.36 ($CHCl_3$:EA 50:1), mp = 211.0-212.0°C. ^{1}H NMR (DMSO-d6), δ: 5.27 (s, 4H), 7.02-7.04 (m, 2H), 7.43-7.55 (m, 8H), 7.88-7.92 (m, 6H).^{13}C NMR (DMSO-d6), δ: 55.2, 128.1, 128.1, 128.2, 131.0, 134.8, 135.1, 135.8, 139.9, 155.6. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{24}H_{20}N_2NaO_4S_4]^+$: 551.0198. Found: 551.0184.



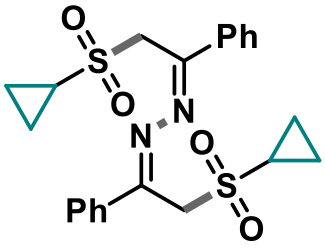
(1Z,2Z)-1,2-bis(2-(methylsulfonyl)-1-phenylethylidene)hydrazine (3ai). Pale yellow solid. 131 mg (yield 68%). R_f = 0.32 ($CHCl_3$:EA 50:1), mp = 262.0-263.0°C. ^{1}H NMR (DMSO-d6), δ: 3.02 (s, 6H), 5.18 (s, 4H), 7.52-7.55 (m, 6H), 8.14-8.17 (m, 4H). ^{13}C NMR (DMSO-d6), δ: 42.6, 52.8, 128.2, 128.5, 131.1, 135.6, 156.4. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{18}H_{21}N_2O_4S_2]^+$: 393.0937. Found: 393.0932.



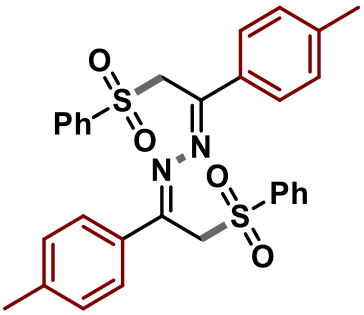
(1Z,2Z)-1,2-bis(2-(ethylsulfonyl)-1-phenylethylidene)hydrazine (3aj). Yellow solid. 182 mg (yield 87%). R_f = 0.36 ($CHCl_3$:EA 30:1), mp = 185.0-186.0°C. ^1H NMR ($CDCl_3$), δ: 1.31 (t, *J* = 7.4 Hz, 6H), 3.07 (q, *J* = 7.4 Hz, 4H), 4.94 (s, 4H), 7.45-7.55 (m, 6H), 8.05-8.07 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 6.7, 49.6, 51.9, 128.1, 129.0, 131.7, 135.7, 156.8. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{20}H_{25}N_2O_4S_2]^+$: 421.1250. Found: 421.1254.



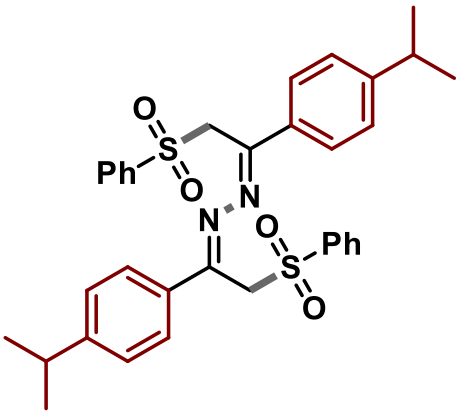
(1Z,2Z)-1,2-bis(2-(isopropylsulfonyl)-1-phenylethylidene)hydrazine (3ak). Bright yellow solid. 128 mg (yield 57%). R_f = 0.41 ($CHCl_3$:EA 30:1), mp = 213.0-214.0°C. ^1H NMR ($CDCl_3$), δ: 1.33 (d, *J* = 6.9 Hz, 12H), 3.25 (sep, *J* = 6.9 Hz, 2H), 4.85 (s, 4H), 7.44-7.53 (m, 6H), 8.03-8.07 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 15.6, 49.5, 55.4, 128.1, 128.8, 131.4, 135.9, 155.8. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{22}H_{29}N_2O_4S_2]^+$: 449.1563. Found: 449.1558.



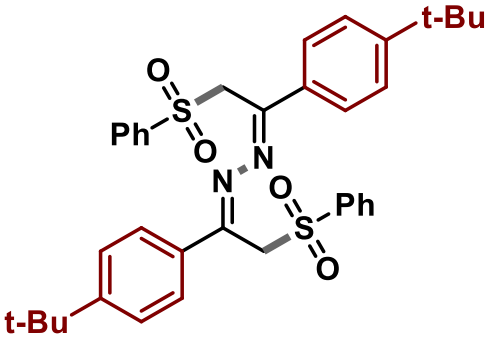
(1Z,2Z)-1,2-bis(2-(cyclopropylsulfonyl)-1-phenylethylidene)hydrazine (3al). Bright yellow solid. 189 mg (yield 85%). R_f = 0.35 ($CHCl_3$:EA 50:1), mp = 204.0-205.0°C. ^1H NMR (DMSO-d6), δ: 0.84-0.94 (m, 8H), 2.69-2.77 (m, 2H), 5.22 (s, 4H), 7.47-7.54 (m, 6H), 8.12-8.16 (m, 4H). ^{13}C NMR (DMSO-d6), δ: 4.8, 31.1, 52.0, 128.2, 128.5, 131.1, 135.6, 155.9. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{22}H_{25}N_2O_4S_2]^+$: 445.1250. Found: 445.1251



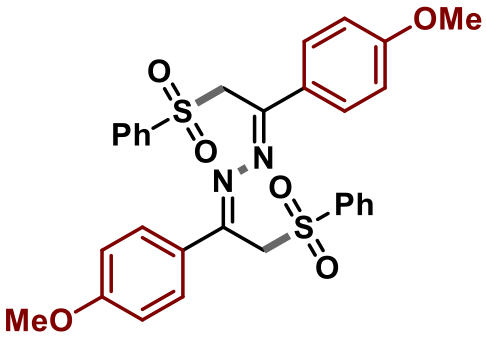
(1Z,2Z)-1,2-bis(2-(phenylsulfonyl)-1-(p-tolyl)ethylidene)hydrazine (3ba). Bright orange solid. 223 mg (yield 82%). R_f = 0.55 ($CHCl_3$:EA 50:1), mp = 245.0-246.0°C. ^{1}H NMR (DMSO-d6), δ: 2.39 (s, 6H), 5.08 (s, 4H), 7.25 (d, *J* = 8.2 Hz, 4H), 7.39-7.44 (m, 4H), 7.55-7.60 (m, 2H), 7.63-7.70 (m, 8H). ^{13}C NMR (DMSO-d6), δ: 21.0, 53.9, 127.7, 128.1, 128.8, 129.1, 132.5, 134.0, 139.6, 141.0, 155.3. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{30}H_{28}N_2NaO_4S_2]^+$: 567.1383. Found: 567.1387.



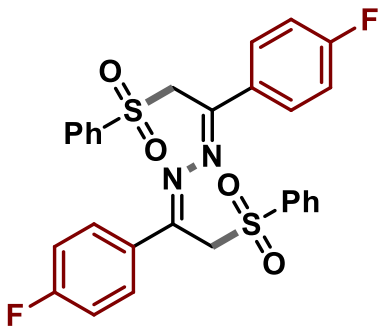
(1Z,2Z)-1,2-bis(1-(4-isopropylphenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3ca). Bright orange solid. 279 mg (yield 93%). R_f = 0.73 ($CHCl_3$:EA 50:1), mp = 226.0-228.0°C. ^{1}H NMR (DMSO-d6), δ: 1.28 (d, *J* = 6.9 Hz, 12H), 2.98 (m, 2H), 5.08 (s, 4H), 7.28 (d, *J* = 8.3 Hz, 4H), 7.39-7.44 (m, 4H), 7.54-7.59 (m, 2H), 7.68-7.73 (m, 8H). ^{13}C NMR, (DMSO-d6) δ: 23.5, 33.3, 54.1,126.1, 127.6, 128.0, 128.9, 132.8, 133.7, 139.6, 151.5, 155.1. HRMS (ESI) m/z ($M+K^+$) calculated for $[C_{34}H_{36}N_2KO_4S_2]^+$: 639.1748. Found: 639.1736.



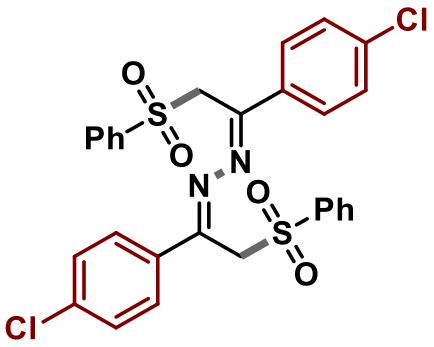
(1Z,2Z)-1,2-bis(1-(4-(tert-butyl)phenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3da). Bright orange solid. 195 mg (yield 62%). R_f = 0.35 ($CHCl_3$:EA 50:1), mp = 229.0-230.0°C. ^{1}H NMR (DMSO-d6), δ: 1.36 (s, 18H), 5.09 (s, 4H), 7.38-7.44 (m, 8H), 7.54-7.58 (m, 2H), 7.67-7.73 (m, 8H). ^{13}C NMR (DMSO-d6), δ: 30.9, 34.6, 54.1, 125.0, 127.7, 127.9, 129.0, 132.5, 133.9, 139.6, 153.8, 155.1. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{36}H_{40}N_2NaO_4S_2]^+$: 651.2322. Found: 651.2314.



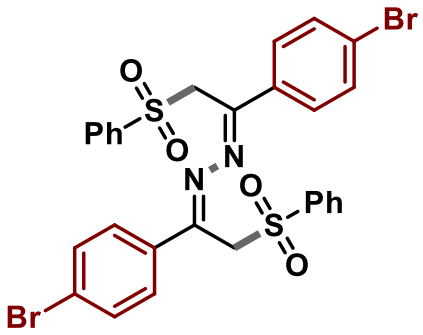
(1Z,2Z)-1,2-bis(1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3ea). Bright orange solid. 262 mg (yield 91%). R_f = 0.75 ($CHCl_3$:EA 50:1), mp = 249.0-251.0°C. ^{1}H NMR (DMSO-d6), δ: 3.86 (s, 6H), 5.08 (s, 4H), 6.97-7.00 (m, 4H), 7.39-7.44 (m, 4H), 7.54-7.60 (m, 2H), 7.63-7.66 (m, 4H), 7.74-7.77 (m, 4H). ^{13}C NMR, (DMSO-d6) δ: 53.7, 55.4, 113.7, 127.7, 127.8, 129.1, 129.9, 133.9, 139.5, 154.7, 161.6. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{30}H_{29}N_2O_6S_2]^+$: 577.1462. Found: 577.1467.



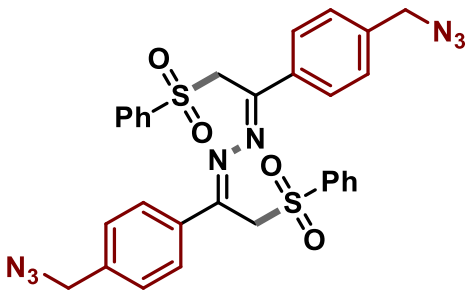
(1Z,2Z)-1,2-bis(1-(4-fluorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3fa). Bright orange solid. 221 mg (yield 80%). R_f = 0.38 ($CHCl_3$:EA 50:1), mp = 205.0-206.0°C. ^{1}H NMR (DMSO-d6), δ: 5.14 (s, 4H), 7.24-7.30 (m, 4H), 7.39-7.44 (m, 4H), 7.53-7.58 (m, 2H), 7.66-7.68 (m, 4H), 7.84-7.89 (m, 4H). ^{13}C NMR (DMSO-d6), δ: 53.9, 115.2 (d, *J* = 21.8 Hz), 127.8, 129.1, 130.6 (d, *J* = 8.8 Hz), 131.7 (d, *J* = 2.9 Hz), 134.0, 139.3, 155.0, 163.8 (d, *J* = 249.7 Hz), HRMS (ESI) m/z ($M+K^+$) calculated for $[C_{28}H_{22}F_2N_2KO_4S_2]^+$: 591.0621. Found: 591.0613.



(1Z,2Z)-1,2-bis(1-(4-chlorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3ga). Bright orange solid. 263 mg (yield 90%). R_f = 0.46 ($CHCl_3$:EA 50:1), mp = 247.0-249.0°C. ^{1}H NMR (DMSO-d6), δ: 5.10 (s, 4H), 7.41-7.51 (m, 8H), 7.56-7.61 (m, 2H), 7.68-7.71 (m, 4H), 7.80-7.83 (m, 4H). ^{13}C NMR, (DMSO-d6) δ: 53.9, 127.7, 128.2, 129.1, 129.9, 133.9, 134.0, 135.9, 139.2, 155.2. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{28}H_{23}{}^{35}Cl_2N_2O_4S_2]^+$: 585.0471. Found: 585.0476.

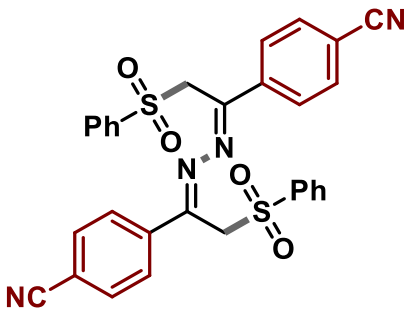


(1Z,2Z)-1,2-bis(1-(4-bromophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3ha). Bright orange solid. 277 mg (yield 82%). R_f = 0.71 ($CHCl_3$:EA 50:1), mp = 265.0-267.0°C. ^{1}H NMR (DMSO-d6), δ: 5.11 (s, 4H), 7.40-7.45 (m, 4H), 7.52-7.60 (m, 2H), 7.63-7.67 (m, 8H), 7.72-7.75 (m, 4H). ^{13}C NMR, (DMSO-d6) δ: 53.8, 125.0, 127.8, 129.2, 130.2, 131.2, 134.1, 134.3, 139.2, 155.4. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{28}H_{22}{}^{79}Br_2N_2NaO_4S_2]^+$: 694.9280. Found: 694.9270.

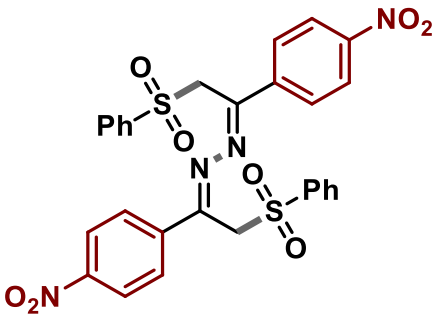


(1Z,2Z)-1,2-bis(1-(4-(azidomethyl)phenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3ia). Bright orange solid. 279 mg (yield 89%). R_f = 0.60 ($CHCl_3$:EA 50:1), mp = 183.0-

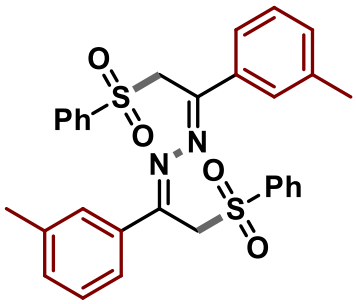
185.0°C. ^{1}H NMR (DMSO-d6), δ: 4.56 (s, 4H), 5.14 (s, 4H), 7.37-7.45 (m, 8H), 7.52-7.57 (m, 2H), 7.67-7.69 (m, 4H), 7.82-7.85 (m, 4H). ^{13}C NMR, (DMSO-d6) δ: 53.2, 54.0, 127.7, 128.1, 128.5, 129.1, 134.0, 134.9, 138.6, 139.5, 155.4. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{30}H_{27}N_8O_4S_2]^+$: 627.1591. Found: 627.1587.



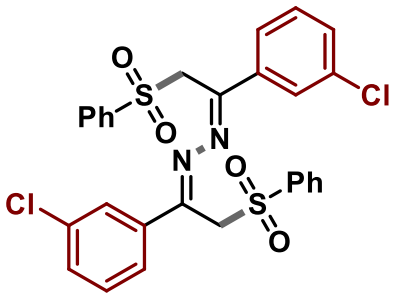
4,4'-((1Z,1'Z)-hydrazine-1,2-diylidenebis(2-(phenylsulfonyl)ethan-1-yl-1-ylidene)) dibenzonitrile (3ja). Bright orange solid. 221 mg (yield 78%). R_f = 0.38 ($CHCl_3$:EA 30:1), mp = 162.0-163.0°C. ^{1}H NMR (DMSO-d6), δ: 5.19 (s, 4H), 7.39-7.44 (m, 4H), 7.53-7.58 (m, 2H), 7.66-7.69 (m, 4H), 7.91 (d, *J* = 8.4 Hz, 4H), 7.99 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR, (DMSO-d6), δ: 54.0, 113.2, 118.5, 127.9, 127.9, 129.0, 129.2, 132.1, 134.2, 139.1, 155.5. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{30}H_{22}N_4NaO_4S_2]^+$: 589.0975. Found: 589.0975.



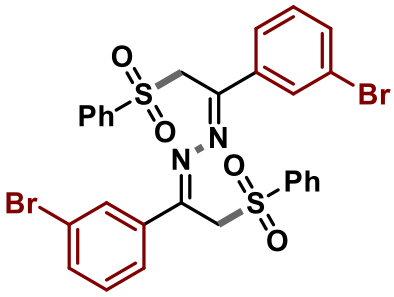
(1Z,2Z)-1,2-bis(1-(4-nitrophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3ka). Bright orange solid. 215 mg (yield 71%). R_f = 0.49 ($CHCl_3$:EA 30:1), mp = 181.0-182.0°C. ^{1}H NMR (DMSO-d6), δ: 5.22 (s, 4H), 7.39-7.44 (m, 4H), 7.52-7.57 (m, 2H), 7.67-7.69 (m, 4H), 8.09 (d, *J* = 9.0 Hz, 4H), 8.28 (d, *J* = 9.0 Hz, 4H). ^{13}C NMR, (DMSO-d6) δ: 54.2, 123.2, 127.9, 129.3, 129.7, 134.3, 140.0, 140.7, 148.7, 155.4. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{28}H_{23}N_4O_8S_2]^+$: 607.0952. Found: 607.0942.



(1Z,2Z)-1,2-bis(2-(phenylsulfonyl)-1-(m-tolyl)ethylidene)hydrazine (3la). Bright orange solid. 261 mg (yield 96%). R_f = 0.43 ($CHCl_3$:EA 50:1), mp = 225.0-227.0°C. ^{1}H NMR (DMSO-d6), δ: 2.36 (s, 6H), 5.10 (s, 4H), 7.31-7.32 (m, 4H), 7.41-7.46 (m, 4H), 7.56-7.63 (m, 6H), 7.70-7.73 (m, 4H). ^{13}C NMR, (DMSO-d6) δ: 21.0, 54.2, 125.3, 127.6, 128.1, 128.4, 129.0, 131.6, 133.9, 135.1, 137.3, 139.7, 155.4. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{30}H_{28}N_2NaO_4S_2]^+$: 567.1383. Found: 567.1389.

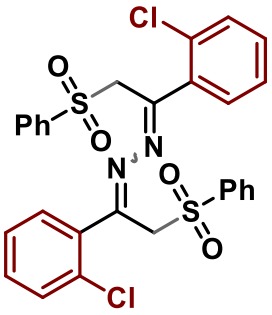


(1Z,2Z)-1,2-bis(1-(3-chlorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3ma). Bright orange solid. 234 mg (yield 80%). R_f = 0.61 ($CHCl_3$:EA 50:1), mp = 237.0-239.0°C. ^{1}H NMR (DMSO-d6), δ: 5.14 (s, 4H), 7.43-7.49 (m, 6H), 7.55-7.59 (m, 4H), 7.71-7.74 (m, 4H), 7.77-7.80 (m, 2H), 7.84-7.85 (m, 2H). ^{13}C NMR, (DMSO-d6), δ: 54.1, 126.9, 127.7, 127.7, 129.1, 130.0, 130.8, 133.2, 134.0, 137.1, 139.3, 155.1. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{28}H_{22}{}^{35}Cl_2N_2NaO_4S_2]^+$: 607.0290. Found: 607.0286.

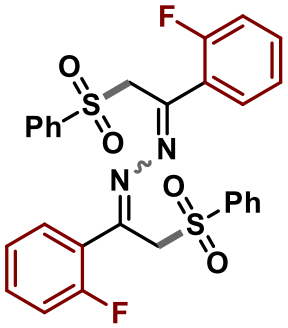


(1Z,2Z)-1,2-bis(1-(3-bromophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (3na). Bright orange solid. 287 mg (yield 85%). R_f = 0.50 ($CHCl_3$:EA 50:1), mp = 233.0-235.0°C. ^{1}H NMR (DMSO-d6), δ: 5.16 (s, 4H), 7.38-7.48 (m, 6H), 7.55-7.60 (m, 2H),

7.70-7.73 (m, 6H), 7.82-7.84 (m, 2H), 8.00 (s, 2H). ^{13}C NMR ($CDCl_3$), δ: 54.1, 121.7, 127.2, 127.7, 129.1, 130.2, 130.5, 133.7, 134.0, 137.3, 139.3, 155.1. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{28}H_{22}{}^{79}Br_2N_2NaO_4S_2]^+$: 694.9280. Found: 694.9278.

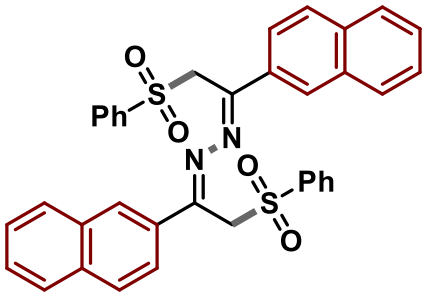


(1Z,2Z)-1,2-bis(1-(2-chlorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (major) (3oa). Mixture of diastereomeres ZZ : ZE+EE (2.8:1). Bright orange solid. 217 mg (yield 74%). R_f = 0.31 ($CHCl_3$:EA 50:1). ^{1}H NMR (DMSO-d6), δ: *ZZ-isomer (major)* : 5.08 (s, 4H), 7.23-7.98 (m, 18H); *ZE- and EE-isomers (minor)*: 4.79 (s, 4H, ZE-or EE-isomer), 4.85 (s, 4H, ZE-or EE-isomer), 7.23-7.98 (m, 18H).^{13}C NMR (DMSO-d6), δ: 55.78, 56.56, 62.33, 126.39, 126.78, 126.95, 127.39, 127.51, 127.62, 127.92, 129.00, 129.10, 129.31, 129.67, 130.10, 130.20, 130.26, 130.71, 130.94, 131.05, 131.25, 131.43, 133.92, 134.09, 153.21, 154.04, 154.56. HRMS (ESI) m/z ($M+Na^+$) calculated for $[C_{28}H_{22}{}^{35}Cl_2N_2NaO_4S_2]^+$: 607.0290. Found: 607.0280.

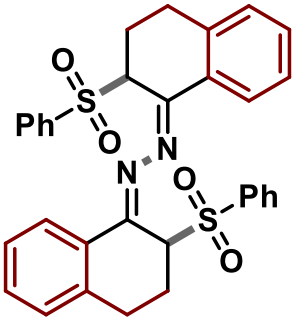


(1Z,2Z)-1,2-bis(1-(2-fluorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine (major) (3pa). Mixture of diastereomeres ZZ : ZE+EE (4.1:1). Bright orange solid. 116 mg (yield 42%). R_f = 0.47 ($CHCl_3$:EA 50:1), mp = 192.0-194.0°C. ^{1}H NMR (DMSO-d6), δ: *ZZ-isomer (major)*: 4.97 (s, 4H), 7.03-7.86 (m, 18H); *ZE- and EE-isomers (minor)*: 4.63 (s, 4H, ZE-or EE-isomer), 4.76 (s, 4H, ZE-or EE-isomer), 7.03-7.86 (m, 18H).^{13}C NMR (DMSO-d6), δ: 55.5, 55.5, 56.0, 56.1, 62.8, 115.1, 115.4, 115.8, 116.1, 116.4, 123.5, 123.7, 123.8, 124.3, 124.3, 124.4, 124.4, 127.6, 127.7, 127.9, 129.0, 129.1, 129.3, 129.6, 129.6, 130.3, 130.3, 130.7, 130.8, 132.2, 132.2, 132.2, 132.3, 132.3, 132.4,

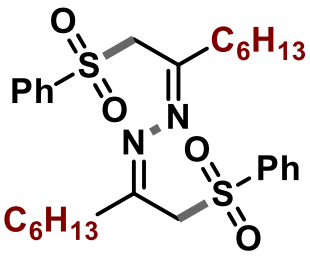
132.7, 132.8, 134.0, 134.1, 134.2, 138.8, 139.1, 150.7, 151.5, 151.5, 153.0, 153.0, 158.1, 158.3, 161.7. HRMS (ESI) m/z ($M+NH_4^+$) calculated for $[C_{28}H_{26}F_2N_3O_4S_2]^+$: 570.1327. Found: 570.1327.



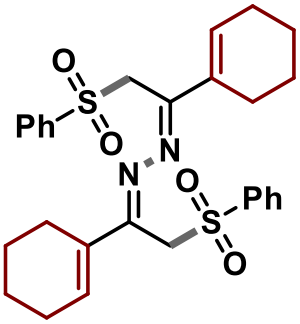
(1Z,2Z)-1,2-bis(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethylidene)hydrazine (3qa). Bright orange solid. 265 mg (yield 86%). R_f = 0.74 ($CHCl_3$:EA 50:1), mp = 246.0-248.0°C. ^{1}H NMR (DMSO-d6), δ: 5.30 (s, 4H), 7.36-7.41 (m, 4H), 7.48-7.53 (m, 2H), 7.61-7.65 (m, 4H), 7.74-7.76 (m, 4H), 7.96-8.00 (m, 8H), 8.40 (s, 2H). ^{13}C NMR (DMSO-d6), δ: 54.0, 124.2, 126.6, 127.5, 127.7, 127.7, 128.9, 129.0, 129.6, 129.6, 132.3, 132.6, 133.9, 134.0, 139.5, 155.5. HRMS (ESI) m/z ($M+K^+$) calculated for $[C_{36}H_{28}KN_2O_4S_2]^+$: 655.1122. Found: 655.1116



1,2-bis((S,Z)-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine (3ra). Bright orange solid. 145 mg (yield 51%). R_f = 0.39 ($CHCl_3$:EA 50:1), mp = 246.0-247.0°C. ^{1}H NMR ($CDCl_3$), δ: 2.07 – 2.20 (m, 2H), 2.84 (dd, *J* = 16.6, 6.0 Hz, 4H), 3.57 – 3.69 (m, 2H), 5.40 (dd, *J* = 5.4, 1.8 Hz, 2H), 7.13 – 7.20 (m, 8H), 7.27 – 7.32 (m, 2H), 7.35 – 7.40 (m, 2H), 7.64 – 7.67 (m, 6H).^{13}C NMR ($CDCl_3$), δ: 23.2, 25.5, 59.3, 126.1, 126.6, 128.7, 128.7, 129.2, 130.9, 131.2, 133.3, 139.7, 139.9, 156.3. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{32}H_{29}N_2O_4S_2]^+$: 569.1563. Found: 569.1563.

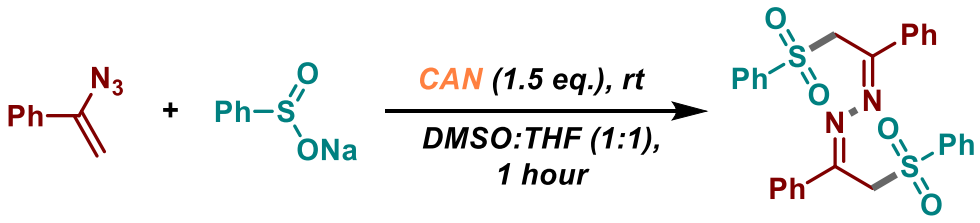


(1Z,2Z)-1,2-bis(1-(phenylsulfonyl)octan-2-ylidene)hydrazine (3sa). Colorless solid. 83 mg (yield 31%). R_f = 0.78 ($CHCl_3$:EA 50:1), mp = 106.0-107.0°C. ^1H NMR ($CDCl_3$), δ: 0.88-0.91 (m, 6H), 1.22-1.35 (m, 16H), 2.40 (t, *J* = 7.4 Hz, 4H), 4.22 (s, 4H), 7.48-7.53 (m, 4H), 7.60-7.62 (m, 2H), 7.81-7.84 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 14.2, 22.7, 25.6, 29.1, 31.8, 37.2, 56.8, 128.2, 129.2, 133.9, 140.0, 158.6. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{28}H_{41}N_2O_4S_2]^+$: 533.2502. Found: 533.2504.



(1Z,2Z)-1,2-bis(1-(cyclohex-1-en-1-yl)-2-(phenylsulfonyl)ethylidene)hydrazine (3ta). Pale yellow solid. 197 mg (yield 75%). R_f = 0.6 ($CHCl_3$:EA 50:1), mp = 170.0-171.0°C. ^1H NMR ($CDCl_3$), δ: 1.59-1.62 (m, 8H), 2.15-2.21 (m, 8H), 4.59 (s, 4H), 6.44 (d, *J* = 4.0 Hz, 2H), 7.43-7.48 (m, 4H), 7.55-7.60 (m, 2H), 7.79-7.81 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 21.9, 22.3, 25.0, 26.7, 53.6, 128.4, 128.9, 133.7, 135.8, 137.3, 140.2, 154.9. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{28}H_{33}N_2O_4S_2]^+$: 525.1876. Found: 525.1866.

Procedure for scaled synthesis of sulfonylated azine 3aa (Table 2)



1a, 7.5 mmol
1088 mg

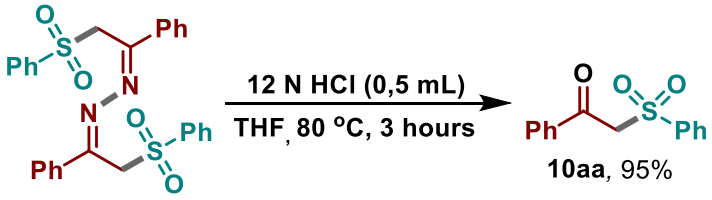
2a, 5 mmol
820 mg

3aa, 70%
904 mg

A 100-mL round bottom flask was equipped with a magnetic stir bar. Vinyl azide **1** (1088 mg, 7.5 mmol) and sodium sulfinate **2** (821 mg, 5 mmol) were dissolved in 50 mL of THF−DMSO (1:1). After that, cerium (IV) ammonium nitrate (4,11 g, 7.5 mmol) were added in one portion at room temperature under magnetic stirring. When reaction was completed, the reaction mixture was diluted with water (100 mL) and extracted with DCM (4×30 mL). Combined organic layer was washed with water (30 mL) and brine (30mL), dried over Na_2SO_4 and concentrated under reduced pressure. The desired products **3aa**

was isolated by chromatography on SiO_2 with elution using $CHCl_3$-EA in a gradient of the latter from 2 to 5 vol% to give title compound in yield 70%.

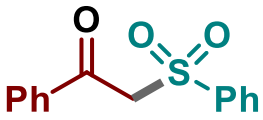
Procedure for the synthesis of β-ketosulfone 10aa from ketazine 3aa



3aa, 0.5 mmol

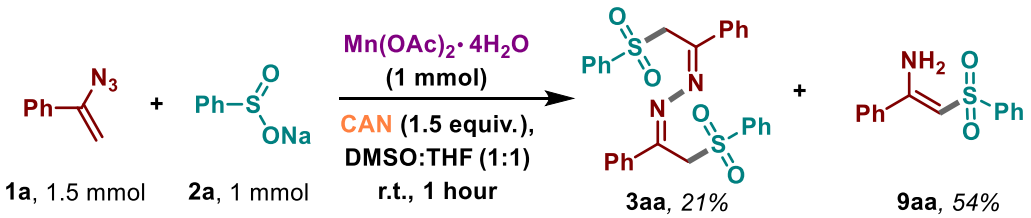
10aa, 95%

A 20-mL sealed tube was equipped with a magnetic stir bar. (1Z,2Z)-1,2-bis(1-phenyl-2-(phenylsulfonyl)ethylidene)hydrazine **3aa** (258 mg, 0.5 mmol) and 12 N hydrochloric acid (0.5 mL) were dissolved in 5 mL of THF. With all reagents added the sealed tube was equipped with silicone rubber septa and then the tube was placed in an oil bath at an ambient temperature of 80 °C and was stirred for 3 hours. After completition of reaction the mixture was diluted with water (50 mL) and extracted with DCM (3×10 mL). The organic layer was separated and washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was characterized without any additional purification.



1-phenyl-2-(phenylsulfonyl)ethan-1-one (10aa).[19] Colorless solid. 247 mg (yield 95%). R_f = 0.51 (PE:EA = 2:1), mp = 92.0-93.0°C. ^{1}H NMR ($CDCl_3$), δ: 4.74 (s, 4H), 7.44-7.67 (m, 6H), 7.88-7.94 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 63.5, 128.7, 129.0, 129.3, 129.4, 134.3, 134.5, 135.8, 138.9, 188.1.

Procedure for the experiment with $Mn(OAc)_2{\cdot}4H_2O$ addition (Scheme 5, A)

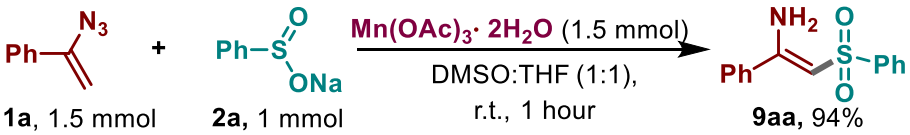


1a, 1.5 mmol **2a**, 1 mmol **3aa**, *21%* **9aa**, *54%*

A 100-mL round bottom flask was equipped with a magnetic stir bar. (1-Azidovinyl)benzene **1a** (218 mg, 1.5 mmol), sodium benzenesulfinate **2a** (164 mg, 1 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (245 mg, 1 mmol) were dissolved in 10 mL of THF−DMSO (1:1). After that, cerium (IV) ammonium nitrate (822 mg, 1.5 mmol) were added in one

portion at room temperature under magnetic stirring. When the reaction was completed, the reaction mixture was diluted with water (50 mL) and extracted with DCM (4×10 mL). Combined organic layer was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The yield of the desired products **3aa** and **9aa** was determined by ^{1}H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard.

Procedure for the experiment with $Mn(OAc)_3{\cdot}2H_2O$ (Scheme 5, B)

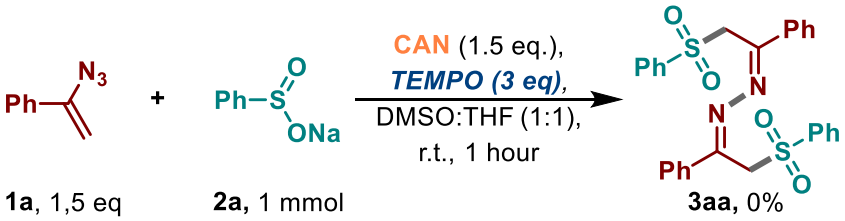


1a, 1.5 mmol **2a,** 1 mmol **9aa,** 94%

A 100-mL round bottom flask was equipped with a magnetic stir bar. (1-Azidovinyl)benzene **1a** (218 mg, 1.5 mmol), sodium benzenesulfinate **2a** (164 mg, 1 mmol) and $Mn(OAc)_2{\cdot}4H_2O$ (245 mg, 1 mmol) were dissolved in 10 mL of THF−DMSO (1:1). After that $Mn(OAc)_3{\cdot}2H_2O$ (402 mg, 1.5 mmol) were added in one portion at room temperature under magnetic stirring. When the reaction was completed, the reaction mixture was diluted with water (50 mL) and extracted with DCM (4×10 mL). Combined organic layer was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The yield of product **9aa** was determined by ^{1}H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard.

Radical trapping experiments

Procedure for radical trapping experiment with addition of TEMPO (Scheme 2)

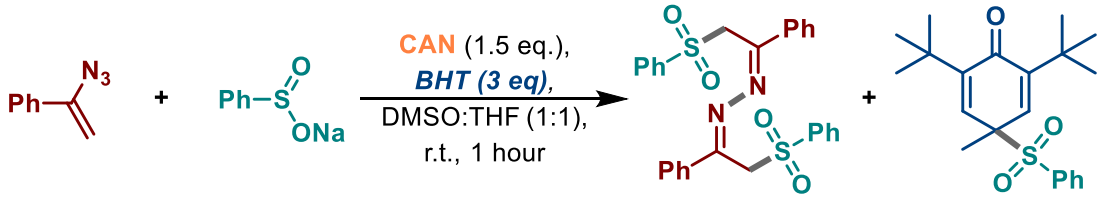


1a, 1,5 eq **2a,** 1 mmol **3aa,** 0%

A 100-mL round bottom flask was equipped with a magnetic stir bar. (1-Azidovinyl)benzene **1a** (218 mg, 1.5 mmol), sodium benzenesulfinate **2a** (164 mg, 1 mmol) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (469 mg, 3 mmol) were dissolved in 10 mL of THF−DMSO (1:1). After that, cerium (IV) ammonium nitrate (822 mg, 1.5 mmol) were added in one portion at room temperature under magnetic stirring. When the reaction was completed, the reaction mixture was diluted with water (50 mL) and extracted with DCM (4×10 mL). Combined organic layer was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure.

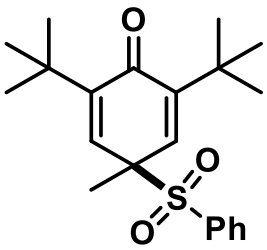
The yield of the desired product **3aa** was determined by ^{1}H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard.

Procedure for radical trapping experiment with addition of BHT (Scheme 2)



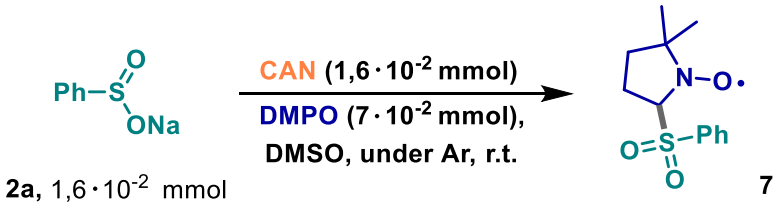
1a, 1,5 eq **2a,** 1 mmol **3aa,** 66% **6**, 14 mg

A 100-mL round bottom flask was equipped with a magnetic stir bar. (1-Azidovinyl)benzene **1a** (218 mg, 1.5 mmol), sodium benzenesulfinate **2a** (164 mg, 1 mmol) and 2,6-Di-tert-butyl-4-methylphenol (BHT) (469 mg, 3 mmol) were dissolved in 10 mL of THF−DMSO (1:1). After that, cerium (IV) ammonium nitrate (822 mg, 1.5 mmol) were added in one portion at room temperature under magnetic stirring. When reaction was completed, the reaction mixture was diluted with water (50 mL) and extracted with DCM (4×10 mL). Combined organic layer was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The yield of the desired product **3aa** was determined by ^{1}H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard. After that, the remaining reaction mixture was purified by chromatography on SiO_2 with elution using PE-EA in a gradient of the latter from 2 to 50 vol% to give adduct **6** (14 mg).



2,6-di-tert-butyl-4-methyl-4-(phenylsulfonyl)cyclohexa-2,5-dien-1-one (6).[20] Colorless solid. 14 mg (yield 4%). R_f = 0.71 (PE:EA 5:1), mp = 170.0-171.0°C. ^{1}H NMR ($CDCl_3$), δ: 1.10 (s, 18H), 1.83 (s, 3H), 6.65 (s, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$), δ: 18.6, 29.1, 35.4, 66.0, 128.4, 130.5, 133.8, 134.4, 135.7, 151.5, 183.8. HRMS (ESI) m/z ($M+H^+$) calculated for $[C_{21}H_{29}O_3S]^+$: 361.1832. Found: 361.1835.

EPR-spectra of spin-adducts of sulfonyl radicals with DMPO



2a, 1,6·10^{-2} mmol **7**

EPR spectrum was recorded under Ar atmosphere on Adani Spinscan X instrument (X-Band, ca. 9.4 GHz) at 30–32 °C with modulation amplitude of 100 μT, center field – 336 mT, sweep width – 7 mT, sweep time – 60 s, MW power 2.8 mW, one scan per spectrum. All solutions were prepared using dried DMSO stored under molecular sieves. DMPO (5,5-dimethyl-1-pyrroline N-oxide, 8 mg, 7×10^{-2} mmol) was added into glass vial equipped with rubber septum. After that, 0.01M solution of sodium benzenesulfinate (1.6 mL) was added using 2 mL syringe, which was preliminary back-filled with argon. This solution was purged with argon for 3 minutes and then 0.01M solution of cerium (IV) ammonium nitrate (1.6 mL) was added using 2 mL syringe. Right after that resultant solution was transferred into a capillary tube (internal diameter was ca. 1.2 mm) preliminary purged with argon, placed into spectrometer cavity, and the spectrum was recorded 2 min after mixing of reagents. Experimental spectrum was successfully fitted and simulated using EasySpin 6.0.0 software[21] applying following parameters (g_{iso}=2.00572, a_N= 1.27 mT, a_H= 1.40 mT) (Figure S1).[22, 23]

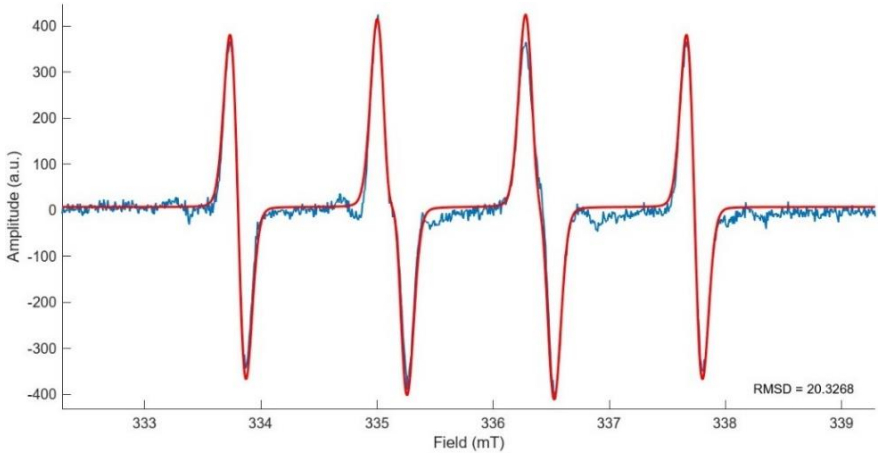
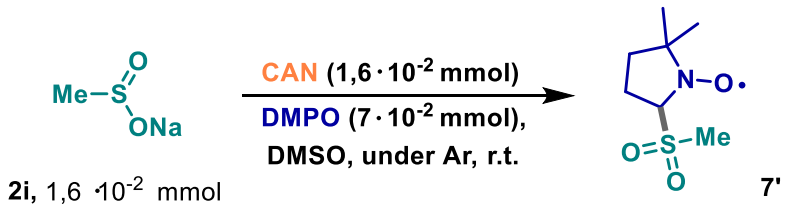


Figure S1. Experimental spectrum of spin-adduct **7** (blue line) and simulated spectrum of **7** (red line).

In addition, g-factor and hyperfine splitting constants for spin-adduct **7** were calculated (g_{iso}=2.00564, a_N= 0.99 mT, a_H= 1.97 mT). EPR calculations were performed on the level of theory PBE0-D3(BJ)/ZORA-def2-QZVPP/CPCM(DMSO)//B3LYP/def2-QZVP/CPCM(DMSO) with zeroth order regular approximation in ORCA 5.0.3 program package.



2i, 1,6 ·10^{-2} mmol **7'**

EPR spectrum was recorded under Ar atmosphere on Adani Spinscan X instrument (X-Band, ca. 9.4 GHz) at 30–32 °C with modulation amplitude of 100 μT, center field – 336 mT, sweep width – 7 mT, sweep time – 60 s, MW power 2.8 mW, one scan per spectrum. All solutions were prepared using dried DMSO stored under molecular sieves. DMPO (5,5-dimethyl-1-pyrroline N-oxide, 8 mg, 7×10^{-2} mmol) was added into glass vial equipped with rubber septum. After that, 0.01M solution of sodium methanesulfinate (1.6 mL) was added using 2 mL syringe, which was preliminary back-filled with argon. This solution was purged with argon for 3 minutes and then 0.01M solution of cerium (IV) ammonium nitrate (1.6 mL) was added using 2 mL syringe. Right after that resultant solution was transferred into a capillary tube (internal diameter was ca. 1.2 mm) preliminary purged with argon, placed into spectrometer cavity, and the spectrum was recorded 2 min after mixing of reagents. Experimental spectrum was successfully fitted and simulated using EasySpin 6.0.0 software[21] applying following parameters (g_{iso}=2.00566, a_N= 1.30 mT, a_H= 1.48 mT) (Figure S2).[22, 23]

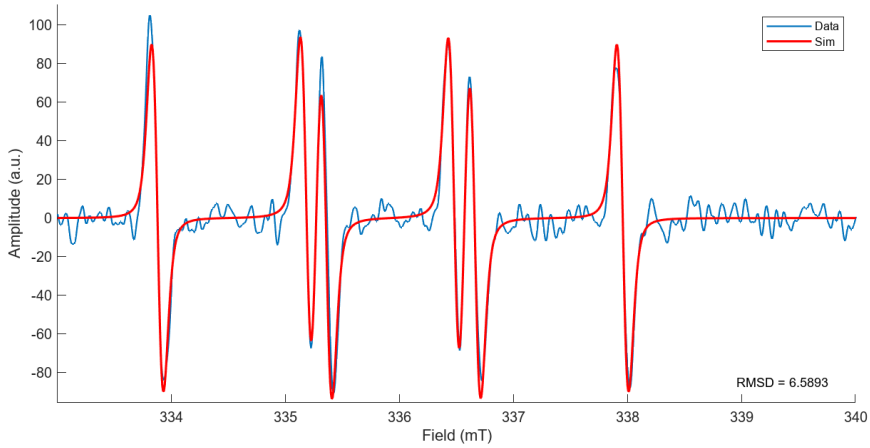
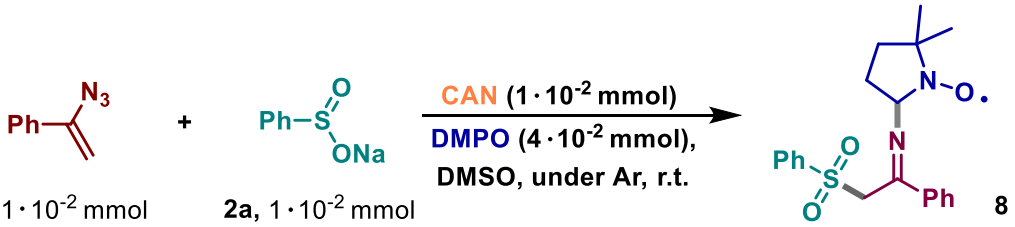


Figure S2. Experimental spectrum of spin-adduct **7'** (blue line) and simulated spectrum of **7'** (red line).

In addition, g-factor and hyperfine splitting constants for spin-adduct **7'** were calculated (g_{iso}=2.00582, a_N= 1.00 mT, a_H= 1.28 mT). EPR calculations were performed on the level of theory PBE0-D3(BJ)/ZORA-def2-QZVPP/CPCM(DMSO)//B3LYP/def2-QZVP/CPCM(DMSO) with zeroth order regular approximation in ORCA 5.0.3 program package.

EPR-spectra of spin-adducts of iminyl radicals with DMPO.



1a, $1 \cdot 10^{-2}$ mmol **2a**, $1 \cdot 10^{-2}$ mmol

EPR spectrum was recorded under Ar atmosphere on Adani Spinscan X instrument (X-Band, ca. 9.4 GHz) at 30–32 °C with modulation amplitude of 100 μT, center field – 336 mT, sweep width – 7 mT, sweep time – 60 s, MW power 2.8 mW, one scan per spectrum. For detection of spin-adduct **8**, DMPO (5,5-dimethyl-1-pyrroline N-oxide, 5 mg, 4×10^{-2} mmol) was added into glass vial equipped with rubber septum. After that, 0.01M solution of sodium benzenesulfinate **2a** (1 mL) and 0.01M solution of (1-azidovinyl)benzene **1a** (1 mL) was added using 2 mL syringe, which was preliminary back-filled with argon. This solution was purged with argon for 3 minutes and then 0.01M solution of cerium (IV) ammonium nitrate (1 mL) was added using 2 mL syringe. Right after that resultant solution was transferred into a capillary tube (internal diameter was ca. 1.2 mm) preliminary purged with argon, placed into spectrometer cavity, and the spectrum was recorded 2 min after mixing of reagents. Experimental spectrum was successfully fitted and simulated using EasySpin 6.0.0 software applying following parameters (g_{iso}=2.00583, a_N^1= 0.27 mT, a_N^2= 1.39 mT, a_H= 1.57 mT) (Figure S3).

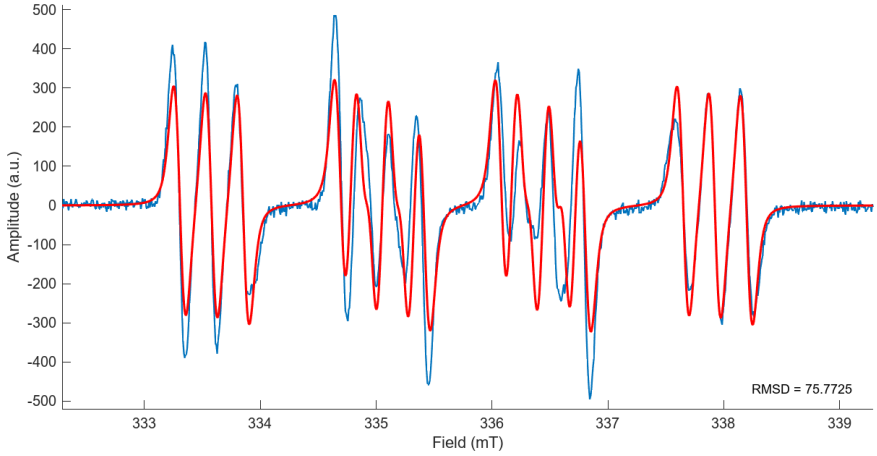
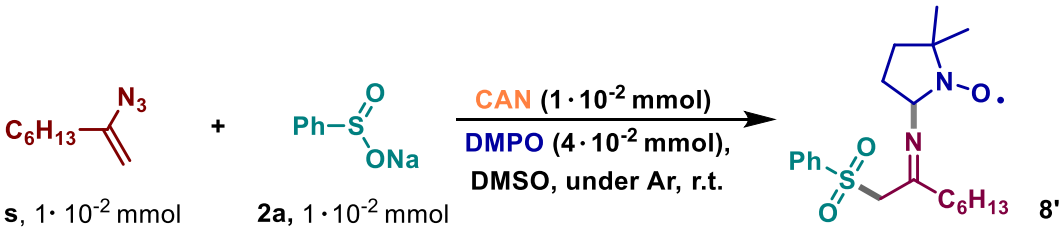


Figure S3. Experimental spectrum of spin-adduct **8** (blue line) and simulated spectrum of **8** (red line).

In addition, g-factor and hyperfine splitting constants for spin-adduct **8** were calculated (g_{iso}=2.00564, a_N^1= 0.17 mT, a_N^2= 1.19 mT, a_H= 2.02 mT). EPR calculations were performed on the level of theory PBE0-D3(BJ)/ZORA-def2-

QZVPP/CPCM(DMSO)//B3LYP/def2-QZVP/CPCM(DMSO) with zeroth order regular approximation in ORCA 5.0.3 program package.



EPR spectrum was recorded under Ar atmosphere on Adani Spinscan X instrument (X-Band, ca. 9.4 GHz) at 30–32 °C with modulation amplitude of 100 μT, center field – 336 mT, sweep width – 7 mT, sweep time – 60 s, MW power 2.8 mW, one scan per spectrum. For detection of spin-adduct **8'**, DMPO (5,5-Dimethyl-1-pyrroline N-oxide, 5 mg, 4×10^{-2} mmol) was added into glass vial equipped with teflon rubber septum. After that, 0.01M solution of sodium benzenesulfinate **2a** (1 mL) and 0.01M solution of 2-azidooct-1-ene **1s** (1 mL) was added using 2 mL syringe, which was preliminary back-filled with argon. This solution was purged with argon for 3 minutes and then 0.01M solution of cerium (IV) ammonium nitrate (1 mL) was added using 2 mL syringe. Right after that resultant solution was transferred into a capillary tube (internal diameter was ca. 1.2 mm) preliminary purged with argon, placed into spectrometer cavity, and the spectrum was recorded 2 min after mixing of reagents. Experimental spectrum was successfully simulated using EasySpin 6.0.0 software[21] applying following parameters (g_{iso}=2.00572, a_N^1= 0.32 mT, a_N^2= 1.42 mT, a_H= 1.47 mT) (Figure S4).

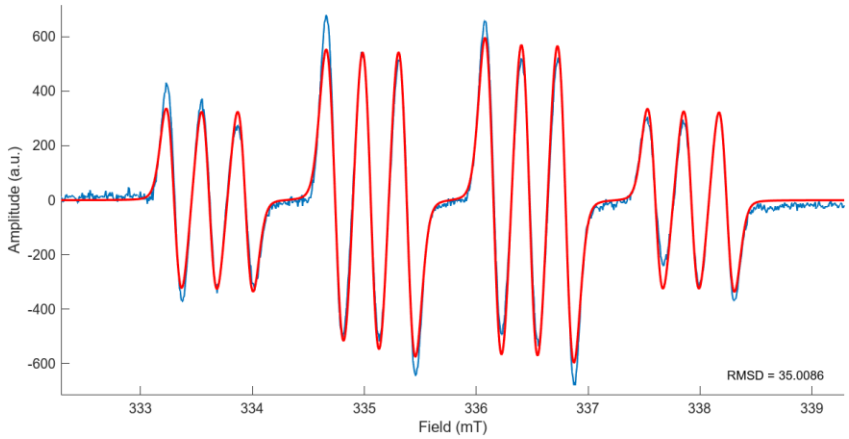
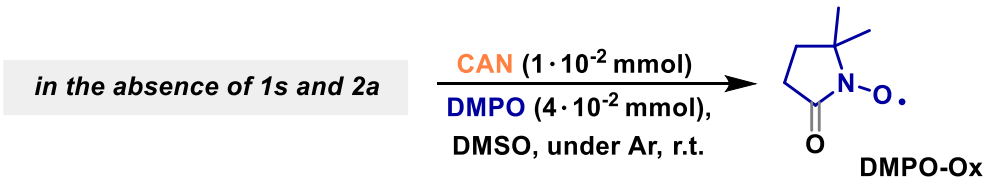


Figure S3. Experimental spectrum of spin-adduct **8'** (blue line) and simulated spectrum of **8'** (red line).

In addition, g-factor and hyperfine splitting constants for spin-adduct **8'** were calculated (g_{iso}=2.00569, a_N^1= 0.16 mT, a_N^2= 1.12 mT, a_H= 2.05 mT). EPR calculations were performed on the level of theory PBE0-D3(BJ)/ZORA-def2-

QZVPP/CPCM(DMSO)//B3LYP/def2-QZVP/CPCM(DMSO) with zeroth order regular approximation in ORCA 5.0.3 program package.

Excluding the formation of analogous EPR-spectra when cerium (IV) ammonium nitrate was used with DMPO we carried out control experiments confirming the source of resulting signals.



EPR spectrum was recorded under Ar atmosphere on Adani Spinscan X instrument (X-Band, ca. 9.4 GHz) at 30–32 °C with modulation amplitude of 100 μT, center field – 336 mT, sweep width – 7 mT, sweep time – 60 s, MW power 2.8 mW, one scan per spectrum. DMPO (5,5-Dimethyl-1-pyrroline N-oxide, 5 mg, 4×10^{-2} mmol) was added into glass vial equipped with teflon rubber septum and dissolved in DMSO (1mL). This solution was purged with argon for 3 minutes and then 0.01M solution of cerium (IV) ammonium nitrate (1 mL) was added using 2 mL syringe. Right after that resultant solution was transferred into a capillary tube (internal diameter was ca. 1.2 mm) preliminary purged with argon, placed into spectrometer cavity, and the spectrum was recorded 2 min after mixing of reagents. Experimental spectrum was successfully simulated using EasySpin 6.0.0 software[21] applying following parameters (g_{iso}= 2.00691, a_N= 0.70 mT, a_H^1= 0.36 mT, a_H^2= 0.34 mT) (Figure S5).

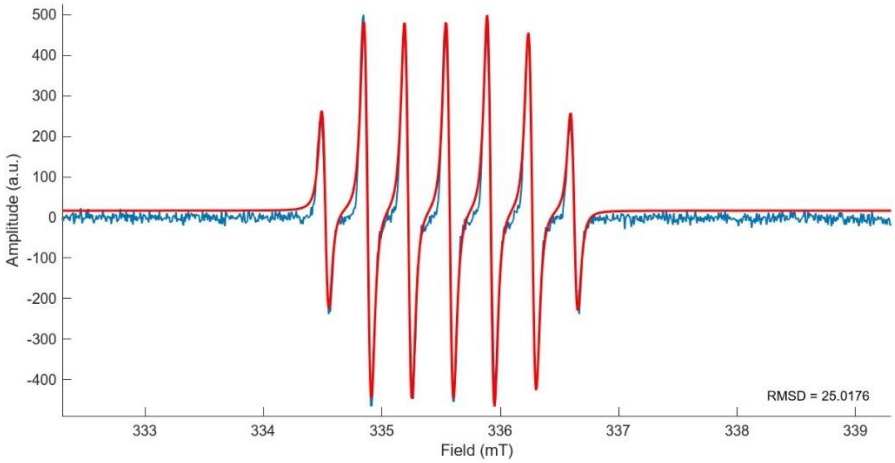
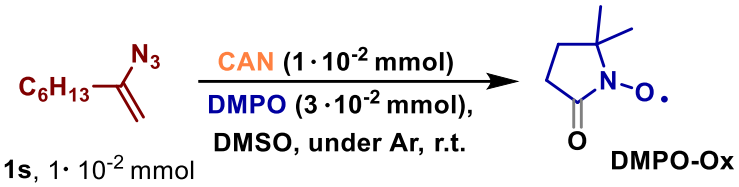


Figure S5. Experimental spectrum of **DMPO-Ox** (blue line) and simulated spectrum of **DMPO-Ox** (red line)



EPR spectrum was recorded under Ar atmosphere on Adani Spinscan X instrument (X-Band, ca. 9.4 GHz) at 30–32 °C with modulation amplitude of 100 μT, center field – 336 mT, sweep width – 7 mT, sweep time – 60 s, MW power 2.8 mW, one scan per spectrum. DMPO (5,5-Dimethyl-1-pyrroline N-oxide, 3.4 mg, 3×10^{-2} mmol) was added into glass vial equipped with teflon rubber septum. After that, 0.01M solution of solution of 2-azidooct-1-ene **1s** (1 mL) was added using 2 mL syringe, which was preliminary back-filled with argon. This solution was purged with argon for 3 minutes and then 0.01M solution of cerium (IV) ammonium nitrate (1 mL) was added using 2 mL syringe. Right after that resultant solution was transferred into a capillary tube (internal diameter was ca. 1.2 mm) preliminary purged with argon, placed into spectrometer cavity, and the spectrum was recorded 2 min after mixing of reagents. Experimental spectrum was successfully fitted and simulated using EasySpin 6.0.0 software[21] applying following parameters (g_{iso}=2.00671, a_N= 0.70 mT, a_H^1= 0.37 mT, a_H^2= 0.36 mT) (Figure S6).

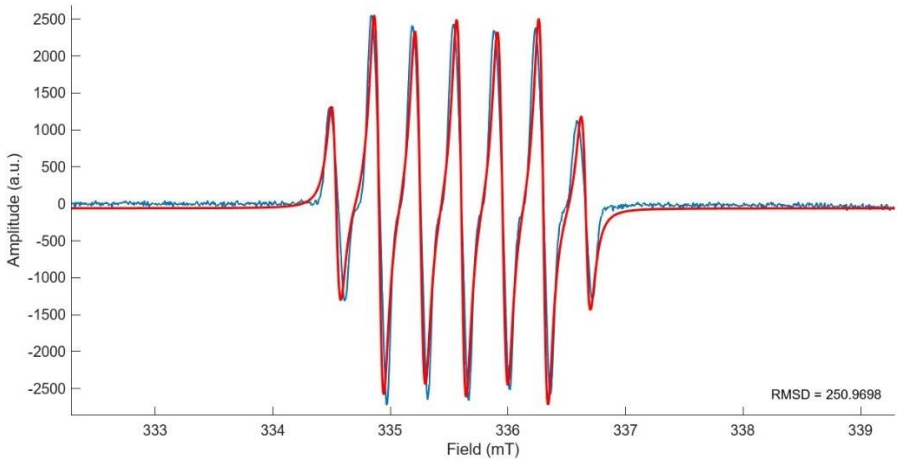


Figure S6. Experimental spectrum of **DMPO-Ox** (blue line) and simulated spectrum of **DMPO-Ox** (red line)

In addition, g-factor and hyperfine splitting constants for **DMPO-Ox** were calculated (g_{iso}=2.00661, a_N= 0.53 mT, a_H^1= 0.34 mT, a_H^2= 0.44 mT). The observed EPR spectra of the radical **DMPO-Ox** were also consistent with the literature data[24]. EPR calculations were performed on the level of theory PBE0-D3(BJ)/ZORA-def2-QZVPP/CPCM(DMSO)//B3LYP/def2-QZVP/CPCM(DMSO) with zeroth order regular approximation in ORCA 5.0.3 program package.

As a result, in absence of sulfinate-anions signals detecting the formation of DMPO oxidation product **DMPO-Ox** were observed. Therefore, there were no signals similar to spin-adducts **7**, **8** or **8'** in absence of sulfonyl radical source.

X-ray crystallographic data and refinement details

X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K_a-radiation (0.71073 Å). The intensity data were integrated by the SAINT program and corrected for absorption and decay using SADABS. The structure was solved by direct methods using SHELXT and refined on F^2 using SHELXL-2018. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The SHELXTL program suite was used for molecular graphics.

Sample preparation: compound **3aa** was dissolved in dichloromethane and crystallized. CCDC 2429110 contains supplementary crystallographic data for **3aa**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

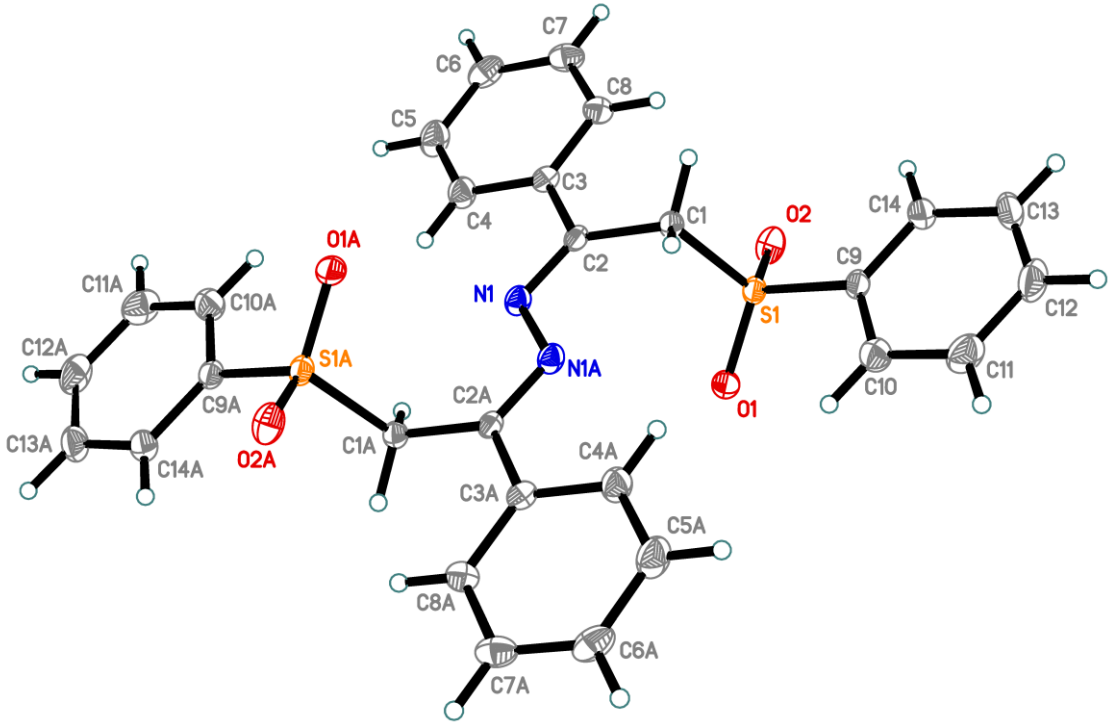


Figure S7. Molecular structure of **3aa** presented in thermal ellipsoids (P = 50%)

Table S1. Crystal data and structure refinement for **3aa.**

Identification code	**3aa**	
Empirical formula	C28 H24 N2 O4 S2	
Formula weight	516.61	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 5.3963(2) Å	α = 90°.
	b = 17.4674(7) Å	β = 99.1140(12)°.
	c = 13.4272(5) Å	γ = 90°.
Volume	1249.66(8) $Å^3$	
Z	2	
Density (calculated)	1.373 g/cm^3	
Absorption coefficient	0.251 mm^{-1}	
F(000)	540	
Crystal size	0.53 x 0.035 x 0.035 mm^3	
Theta range for data collection	2.332 to 30.000°.	
Index ranges	-7<=h<=7, -24<=k<=24, -18<=l<=18	
Reflections collected	40667	
Independent reflections	3652 [R(int) = 0.0965]	
Observed reflections	2961	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6952 and 0.6240	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3652 / 0 / 163	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.0910	
R indices (all data)	R1 = 0.0587, wR2 = 0.1015	
Largest diff. peak and hole	0.376 and -0.457 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	8934(1)	6500(1)	6554(1)	16(1)
O(1)	11517(2)	6415(1)	6423(1)	24(1)
O(2)	7630(2)	7193(1)	6215(1)	23(1)
N(1)	9227(2)	5177(1)	4604(1)	16(1)
C(1)	7197(3)	5700(1)	5981(1)	15(1)
C(2)	7512(3)	5610(1)	4887(1)	14(1)
C(3)	5789(3)	6002(1)	4080(1)	16(1)
C(4)	6115(3)	5909(1)	3070(1)	21(1)
C(5)	4453(3)	6246(1)	2301(1)	27(1)
C(6)	2446(3)	6676(1)	2520(1)	26(1)
C(7)	2126(3)	6777(1)	3514(1)	24(1)
C(8)	3794(3)	6448(1)	4294(1)	19(1)
C(9)	8799(3)	6376(1)	7849(1)	16(1)
C(10)	10664(3)	5950(1)	8430(1)	23(1)
C(11)	10621(4)	5881(1)	9459(1)	30(1)
C(12)	8751(4)	6237(1)	9884(1)	30(1)
C(13)	6898(3)	6660(1)	9298(1)	26(1)
C(14)	6900(3)	6732(1)	8266(1)	20(1)

Table S3. Bond lengths [Å] and angles [°] for **3aa**.

S(1)-O(2)	1.4382(12)
S(1)-O(1)	1.4394(12)
S(1)-C(9)	1.7659(15)
S(1)-C(1)	1.7867(15)
N(1)-C(2)	1.2981(19)
N(1)-N(1)#1	1.388(2)
C(1)-C(2)	1.514(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.478(2)
C(3)-C(8)	1.395(2)
C(3)-C(4)	1.405(2)
C(4)-C(5)	1.387(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.387(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.384(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.392(2)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-C(10)	1.388(2)
C(9)-C(14)	1.389(2)
C(10)-C(11)	1.390(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.383(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.383(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.391(2)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
O(2)-S(1)-O(1)	118.86(8)
O(2)-S(1)-C(9)	108.62(7)
O(1)-S(1)-C(9)	107.41(7)
O(2)-S(1)-C(1)	109.00(7)
O(1)-S(1)-C(1)	108.65(7)

C(9)-S(1)-C(1)	103.17(7)
C(2)-N(1)-N(1)#1	113.97(15)
C(2)-C(1)-S(1)	111.50(10)
C(2)-C(1)-H(1A)	109.3
S(1)-C(1)-H(1A)	109.3
C(2)-C(1)-H(1B)	109.3
S(1)-C(1)-H(1B)	109.3
H(1A)-C(1)-H(1B)	108.0
N(1)-C(2)-C(3)	116.78(13)
N(1)-C(2)-C(1)	122.60(13)
C(3)-C(2)-C(1)	120.59(13)
C(8)-C(3)-C(4)	118.76(14)
C(8)-C(3)-C(2)	121.62(14)
C(4)-C(3)-C(2)	119.59(14)
C(5)-C(4)-C(3)	120.32(16)
C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	120.44(16)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(7)-C(6)-C(5)	119.61(15)
C(7)-C(6)-H(6)	120.2
C(5)-C(6)-H(6)	120.2
C(6)-C(7)-C(8)	120.51(16)
C(6)-C(7)-H(7)	119.7
C(8)-C(7)-H(7)	119.7
C(7)-C(8)-C(3)	120.33(15)
C(7)-C(8)-H(8)	119.8
C(3)-C(8)-H(8)	119.8
C(10)-C(9)-C(14)	121.93(15)
C(10)-C(9)-S(1)	118.65(12)
C(14)-C(9)-S(1)	119.37(12)
C(9)-C(10)-C(11)	118.68(16)
C(9)-C(10)-H(10)	120.7
C(11)-C(10)-H(10)	120.7
C(12)-C(11)-C(10)	119.92(17)
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-H(11)	120.0
C(13)-C(12)-C(11)	120.93(16)
C(13)-C(12)-H(12)	119.5

C(11)-C(12)-H(12)	119.5
C(12)-C(13)-C(14)	120.04(16)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
C(9)-C(14)-C(13)	118.49(16)
C(9)-C(14)-H(14)	120.8
C(13)-C(14)-H(14)	120.8

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	18(1)	18(1)	13(1)	-3(1)	3(1)	-4(1)
O(1)	17(1)	34(1)	21(1)	-8(1)	7(1)	-8(1)
O(2)	33(1)	16(1)	19(1)	0(1)	1(1)	-2(1)
N(1)	19(1)	17(1)	13(1)	0(1)	-1(1)	2(1)
C(1)	16(1)	17(1)	14(1)	-2(1)	3(1)	-2(1)
C(2)	14(1)	15(1)	13(1)	-2(1)	0(1)	-2(1)
C(3)	15(1)	16(1)	16(1)	1(1)	1(1)	-2(1)
C(4)	23(1)	23(1)	16(1)	0(1)	1(1)	4(1)
C(5)	32(1)	30(1)	16(1)	1(1)	-2(1)	4(1)
C(6)	24(1)	23(1)	25(1)	5(1)	-8(1)	1(1)
C(7)	18(1)	22(1)	31(1)	4(1)	0(1)	3(1)
C(8)	17(1)	20(1)	20(1)	1(1)	3(1)	1(1)
C(9)	18(1)	18(1)	13(1)	-3(1)	3(1)	-2(1)
C(10)	23(1)	26(1)	20(1)	-1(1)	2(1)	3(1)
C(11)	29(1)	38(1)	20(1)	5(1)	-3(1)	0(1)
C(12)	36(1)	39(1)	14(1)	-2(1)	4(1)	-9(1)
C(13)	29(1)	30(1)	21(1)	-8(1)	10(1)	-4(1)
C(14)	20(1)	21(1)	19(1)	-4(1)	5(1)	-1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for **3aa**.

	x	y	z	U(eq)
H(1A)	7777	5228	6355	18
H(1B)	5396	5771	6024	18
H(4)	7480	5614	2912	25
H(5)	4689	6182	1620	32
H(6)	1299	6901	1991	31
H(7)	758	7074	3666	28
H(8)	3573	6528	4974	23
H(10)	11944	5710	8131	28
H(11)	11875	5590	9870	36
H(12)	8738	6191	10588	36
H(13)	5624	6900	9600	31
H(14)	5630	7018	7856	24

Table S6. Torsion angles [°] for **3aa**.

O(2)-S(1)-C(1)-C(2)	75.91(12)
O(1)-S(1)-C(1)-C(2)	-55.01(12)
C(9)-S(1)-C(1)-C(2)	-168.79(11)
N(1)#1-N(1)-C(2)-C(3)	-179.65(15)
N(1)#1-N(1)-C(2)-C(1)	-1.6(2)
S(1)-C(1)-C(2)-N(1)	92.51(16)
S(1)-C(1)-C(2)-C(3)	-89.52(15)
N(1)-C(2)-C(3)-C(8)	176.50(14)
C(1)-C(2)-C(3)-C(8)	-1.6(2)
N(1)-C(2)-C(3)-C(4)	-1.8(2)
C(1)-C(2)-C(3)-C(4)	-179.87(14)
C(8)-C(3)-C(4)-C(5)	-1.0(2)
C(2)-C(3)-C(4)-C(5)	177.30(16)
C(3)-C(4)-C(5)-C(6)	-0.2(3)
C(4)-C(5)-C(6)-C(7)	0.9(3)
C(5)-C(6)-C(7)-C(8)	-0.3(3)
C(6)-C(7)-C(8)-C(3)	-1.0(3)
C(4)-C(3)-C(8)-C(7)	1.6(2)
C(2)-C(3)-C(8)-C(7)	-176.67(15)
O(2)-S(1)-C(9)-C(10)	-154.61(13)
O(1)-S(1)-C(9)-C(10)	-24.86(15)
C(1)-S(1)-C(9)-C(10)	89.81(14)
O(2)-S(1)-C(9)-C(14)	22.84(15)
O(1)-S(1)-C(9)-C(14)	152.59(13)
C(1)-S(1)-C(9)-C(14)	-92.73(14)
C(14)-C(9)-C(10)-C(11)	-0.2(3)
S(1)-C(9)-C(10)-C(11)	177.18(14)
C(9)-C(10)-C(11)-C(12)	-0.3(3)
C(10)-C(11)-C(12)-C(13)	0.5(3)
C(11)-C(12)-C(13)-C(14)	-0.1(3)
C(10)-C(9)-C(14)-C(13)	0.6(2)
S(1)-C(9)-C(14)-C(13)	-176.81(13)
C(12)-C(13)-C(14)-C(9)	-0.4(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1

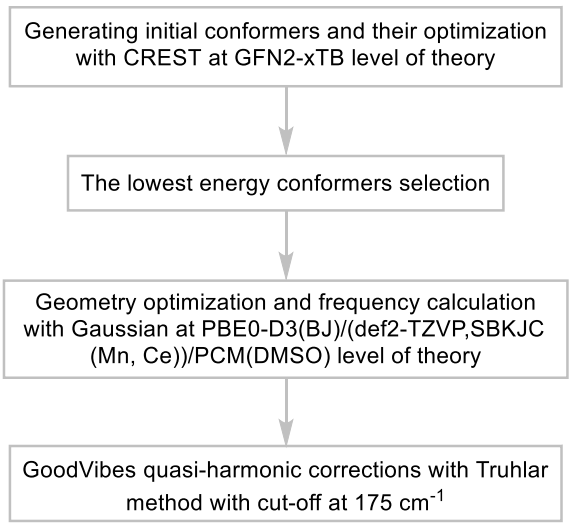
Computation details

Routine quantum chemical calculations

The initial geometries of all structures were generated using the CREST program package[25] at the GFN2-xTB level of theory[26], solvation by DMSO were accounted with generalized Born model with surface area contributions (GBSA)[27]. Geometry optimizations and vibrational frequency calculations (excluding those related to EPR) were conducted using Gaussian 16 Rev. A.03[28], applying density functional theory (DFT) with the PBE0 hybrid functional[29] and Grimme's dispersion corrections (D3(BJ))[30]. The PBE0 functional has demonstrated robust performance across various applications in computational chemistry, as evidenced by studies[31-34]. Consequently, it was selected for use in this investigation. For metal atoms, the SBKJC basis set with effective core potentials (ECPs) was employed to incorporate scalar relativistic effects[35-37], while the def2-TZVP basis set was used for non-metal atoms[38]. Solvent effects were accounted for using the polarizable continuum model (PCM)[39], with DMSO as the chosen solvent. This computational setup corresponds to the PBE0-D3(BJ)/(def2-TZVP, SBKJC(Ce, Mn))/PCM(DMSO) level of theory. For all non-transition-state structures, all elements of the Hessian matrix were found to be positive. Spin density visualizations were generated using the IQmol software[40].

Quasi-harmonic corrections to Gibbs free energies were applied via Truhlar's method, utilizing a frequency cutoff of 175 cm^{-1}, as implemented in the GoodVibes program package[41]. To address convergence difficulties encountered in metal-containing complexes, the SCF convergence process was refined using the quadratic convergence

algorithm (**scf=xqc**). The stability of the wavefunctions was checked using **stable=opt** keyword. The complete workflow is summarized in Scheme S1.



Scheme S1. The workflow of routine quantum chemical calculations.

Transition states were calculated the same way; Hessian matrix contained one imaginary mode, which corresponded to transition from reactants to products by reaction coordinate.

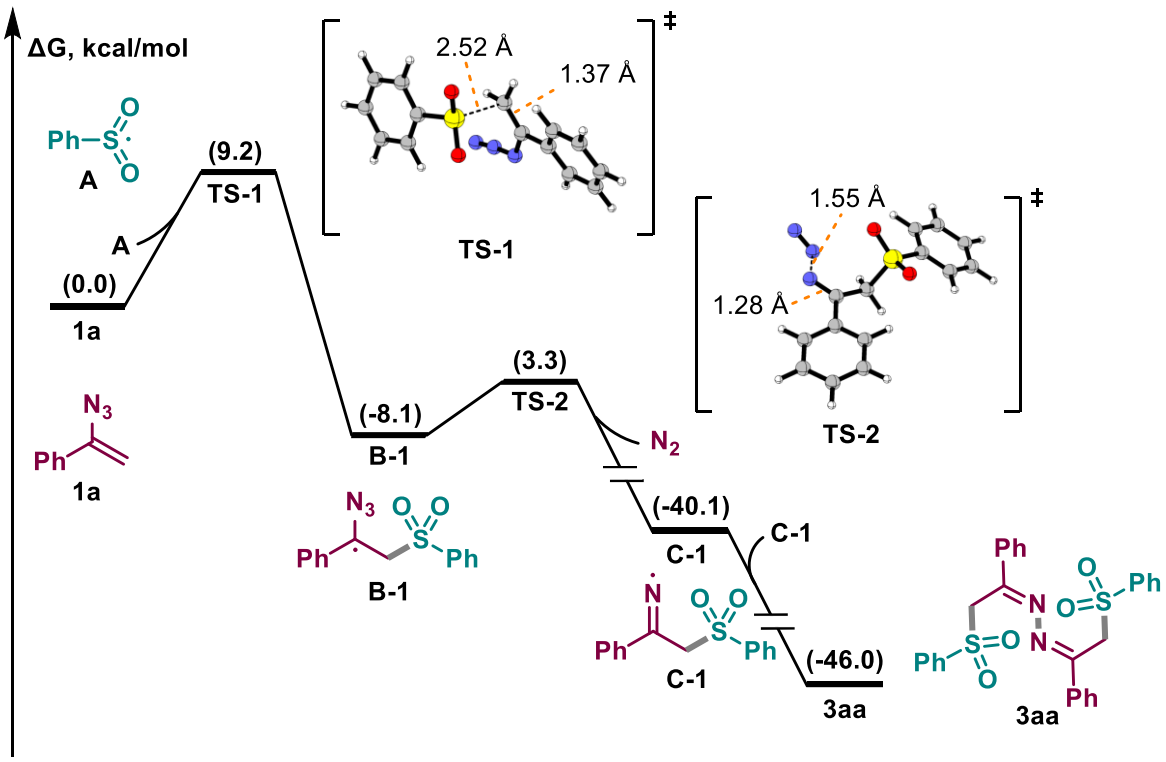
Rate constants were computed from activation energies according to Eyring-Polanyi equation:

$$k = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right),$$

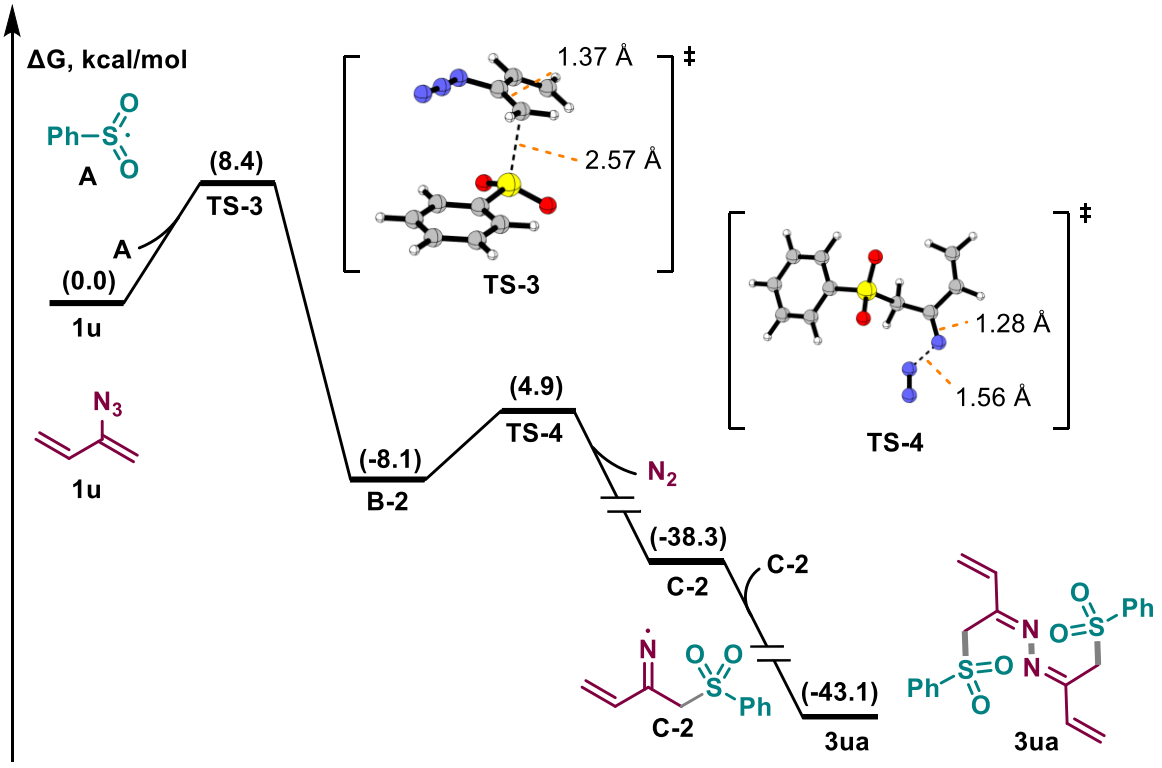
where k is the rate constant, κ is the transmission coefficient (were assumed to be equal 1), k_B is the Boltzmann constant, T is the temperature, h is the Planck constant, $\Delta G^{\ddagger}$ is the Gibbs energy of activation and R is the gas constant.

Activation barriers were explicitly calculated from the free energies of the reacting molecules. While the transition states for radical coupling could not be identified, it was assumed that the associated activation barrier is below 5 kcal/mol, suggesting that the process is primarily diffusion controlled.

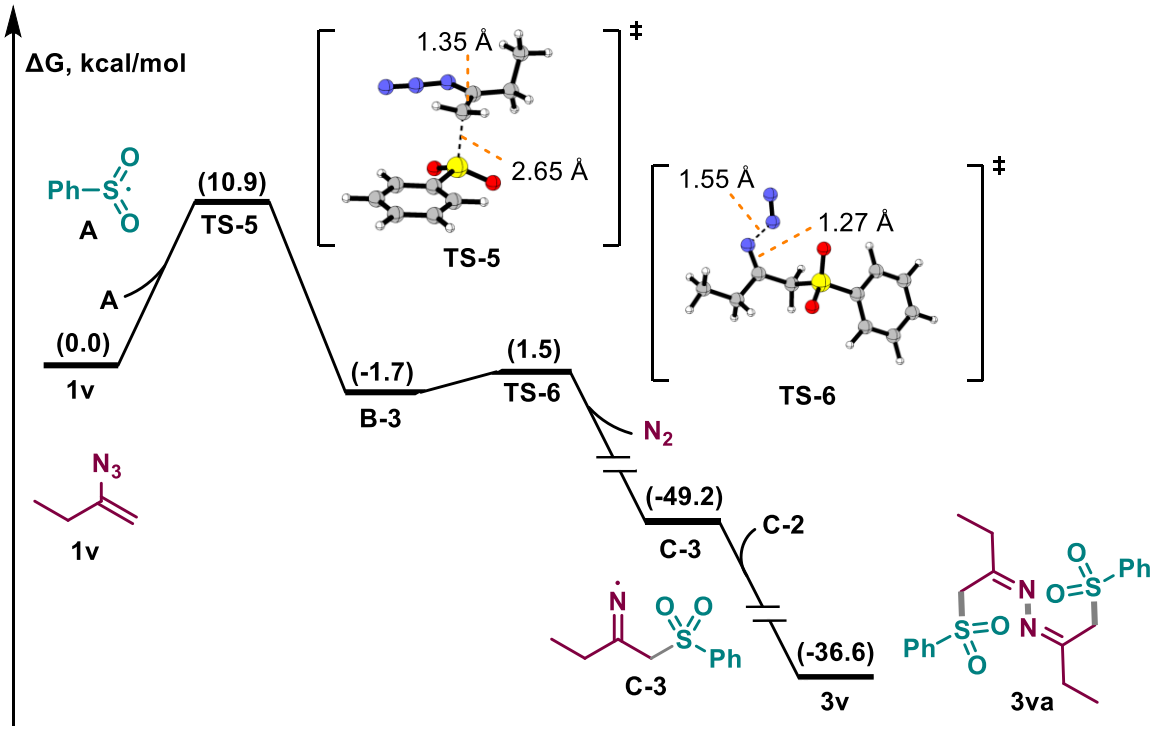
Potential energy surfaces for the formation of ketazines **3aa**, **3ua** and **3va** are represented below in Schemes S2-S4.



Scheme S2. Formation potential energy surface (PES) of ketazine **3aa**



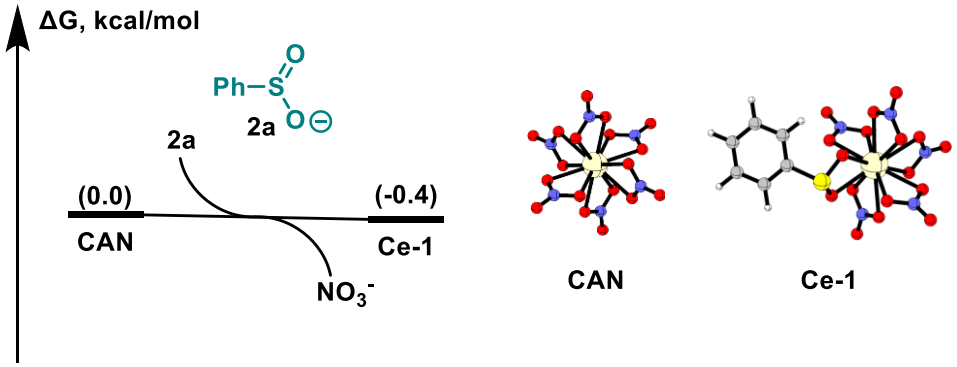
Scheme S3. Formation PES of the ketazine **3ua**



Scheme S4. Formation PES of the ketazine **3va**

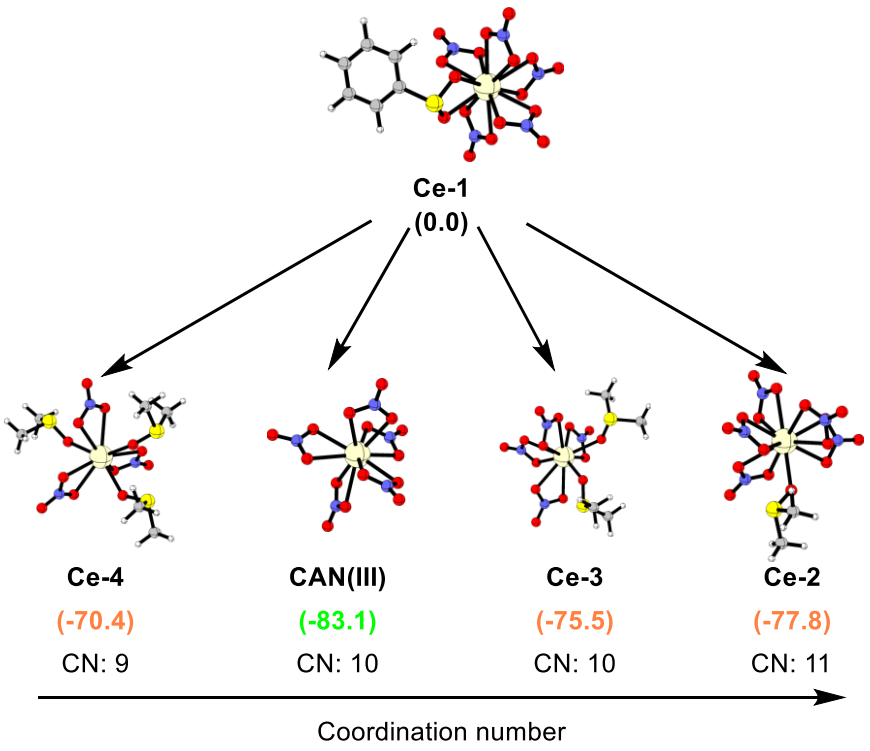
Metal complexes models

It is hypothesized that the initial step in the formation of the benzenesulfinate radical involves the substitution of the nitrate anion within the coordination sphere of cerium ammonium nitrate by the benzenesulfinate anion. This step is characterized by a slight energetic favorability as can be seen in Scheme S5.



Scheme S5. Energy profile of formation substituted CAN by benzenesulfinate anion.

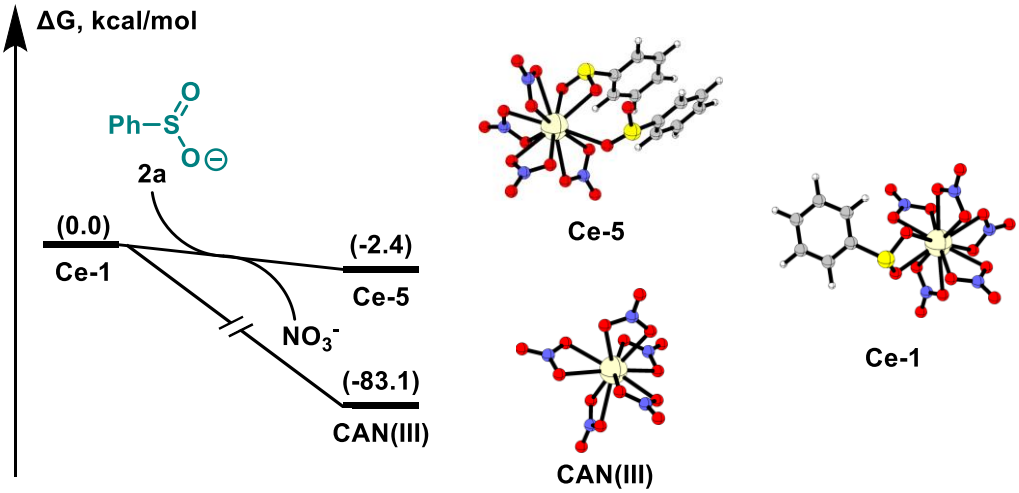
Cerium in the +3 oxidation state is reported in the literature to exhibit coordination numbers ranging from 4 to 12.[42] To identify the most stable reaction product, additional computational investigations were performed. The primary objectives were to: (a) determine the predominant decomposition product of **Ce-1**, and (b) analyze the dependence of Gibbs free energy (ΔG) on variations in coordination number to elucidate underlying trends.



Scheme S6. Potential pathways for the transformation of the **Ce-1** complex.

The computational analysis reveals that the optimal decomposition product of **Ce-1** is cerium (III) ammonium nitrate (**CAN(III)**). Additionally, the results demonstrate a clear trend wherein a reduction in coordination number corresponds to a decrease in the change in Gibbs free energy (Scheme S6).

The theoretical analysis indicates that the substitution of a nitrate ligand in **Ce-1** with a benzenesulfinate anion (**2a**) is feasible; however, it is thermodynamically less favorable compared to the decomposition of **Ce-1** to **CAN(III)** (Scheme S7).

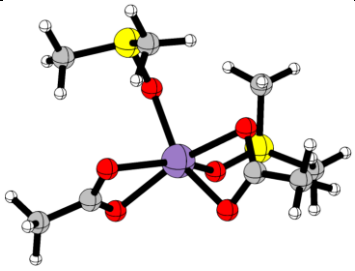
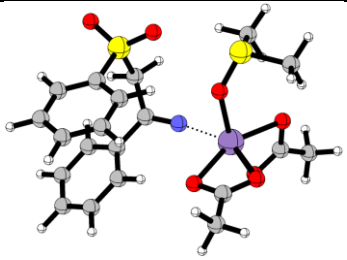
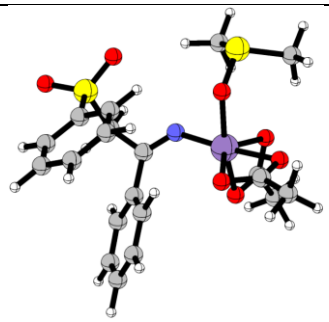


Scheme S7. Comparison of the substitution of the nitrate anion by a benzenesulfinate anion (**2a**) against the simple decomposition of **Ce-1**.

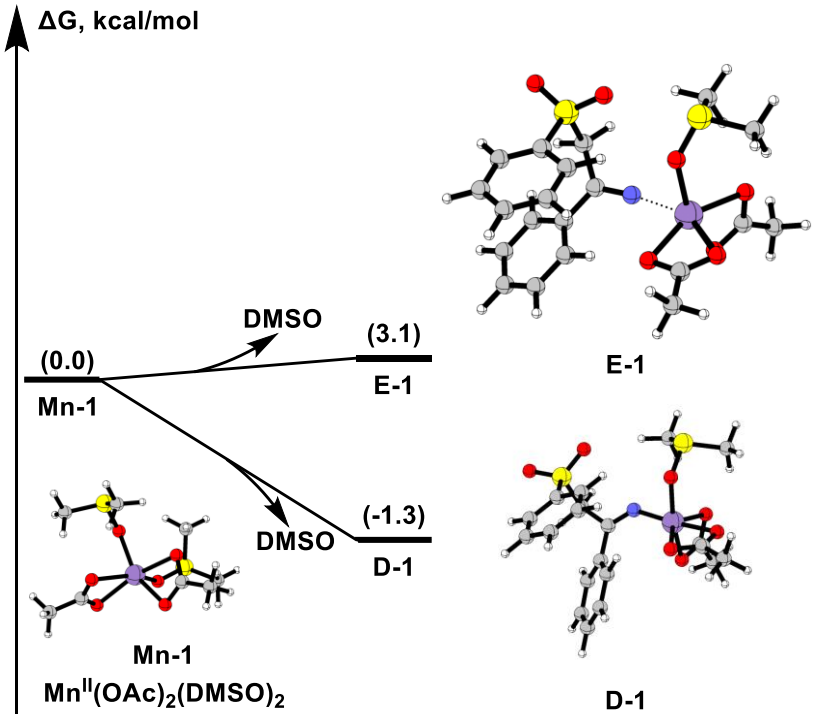
Based on the computational data presented above, it is inferred that **Ce-1** predominantly decomposes into **CAN(III)**, while the formation of other products, including **Ce-2**, **Ce-3**, **Ce-4**, and **Ce-5**, is thermodynamically less favorable.

For all manganese containing structures, both low spin and high spin electronic states were evaluated, with the results indicating that the high spin state is energetically more favorable (Table S7).

Table S7. Comparative analysis of the calculated energies for low-spin and high-spin states in manganese complexes **Mn-1**, **E-1** and **D-1**.

Structure	Low spin electron configuration, a.u.	High spin electron configuration, a.u.	ΔG(low-high), kcal/mol
 **Mn-1**	Doublet, d^5 G_{QH} = -1666.3622024	Sextet, d^5 G_{QH} = -1666.457325	-59.7
 **E-1**	Triplet, d^5 G_{QH} = -2256.647407	Septet, d^5 G_{QH} = -2256.690775	-27.2
 **D-1**	Singlet, d^4 G_{QH} = -2256.618320	Quintet, d^4 G_{QH} = -2256.697736	-49.8

The conversion of **Mn-1** and **C-1** into **E-1** and **D-1** proceeds through the following thermodynamic reactions (Scheme S8).

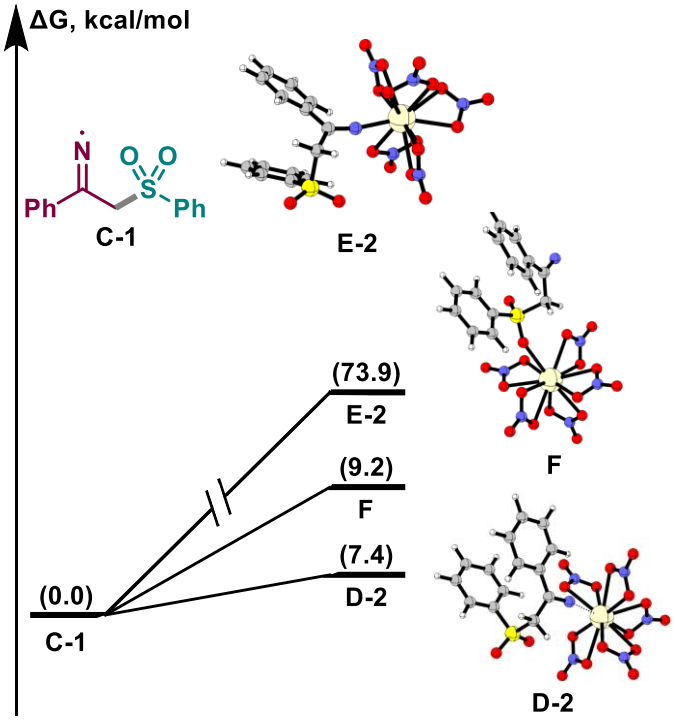


Scheme S8. Analysis of the coordination of the iminyl radical **C-1** with **Mn-1**.

The oxidation states of all metal containing structures were analyzed using the localized orbital bonding analysis (LOBA) method, as implemented in the MultiWFN program package.[43, 44] The results confirmed that the assigned oxidation states of the metal atoms align well with chemical intuition.

Coordination of iminyl radical (C-1) by cerium (III)

To evaluate potential pathways for the stabilization of the iminyl radical **C-1**, changes in Gibbs free energies were compared for the metalloradical species **F-1** and **E-2**, as well as the unbound radical **C-1**.



Scheme S9. Prospective complexes of cerium(III) and cerium(IV) with the **C-1** iminyl radical.

From the calculations and experimental data, it was concluded that cerium does not exhibit the ability to coordinate with the generated iminyl radicals (Scheme S9).

Relative stability of sulfonyl radicals

Additional quantum chemical computations were performed to investigate the stability trends of selected sulfonyl radicals (Scheme S10).

Scheme S10. Sulfonyl radicals that were analyzed for their stability.

As a metric for assessing the stability of the radical species, we selected the radical stabilization energy (RSE_z) [45] (eq. 1), along with previously described approach[46].

$$RSE_z = 0.5 * (D[CH_3— CH_3] - D[R— R]_{calc}), \quad \text{(eq. 1)}$$

where $D[CH_3— CH_3]$ is bond dissociation enthalpy (BDE) which we have taken from experimental data, which equals to 88.6 kcal/mol and $D[R— R]_{calc}$ is a hypothetical "strain-free" BDE value was derived by applying Pauling's electronegativity equation to BDEs of CH_3—R and Cl—R, where both reference systems were selected to minimize steric contributions.

$$D[CH_3— R] = 0.5 * (D[CH_3— CH_3] + D[R— R]_{calc}) + 23 * (\chi[CH_3] - \chi[R])^2, \text{ (eq. 2)}$$

$$D[Cl— R] = 0.5 * (D[Cl— Cl] + D[R— R]_{calc}) + 23 * (\chi[Cl] - \chi[R])^2. \text{ (eq. 3)}$$

By utilizing established parameters ($\chi[CH_3]$ = 2.520, $\chi[Cl]$ = 3.176, $D[CH_3— CH_3]$ = 88.6 kcal/mol, $D[Cl— Cl]$ = 57.2 kcal/mol) in conjunction with computed $D[CH_3— R]$ and $D[Cl— R]$ values by chemical equations presented below (eq. 4 and eq. 5, respectively), the system of equations can be solved simultaneously to determine two key unknowns: the electronegativity of studied radical species ($\chi[R]$) and its "strain-free" BDE $D[R— R]_{calc}$.

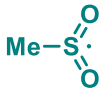
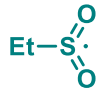
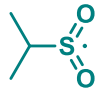
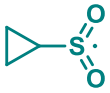
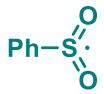
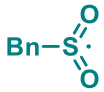
$$CH_3— R = \bullet CH_3 + \bullet R \; \Delta_r H \equiv D[CH_3— R], \quad \text{(eq. 4)}$$

$$Cl— R = \bullet Cl + \bullet R \; \Delta_r H \equiv D[Cl— R]. \quad \text{(eq. 5)}$$

The initial molecular geometries were constructed following the standardized computational methodology outlined in Scheme S1. To obtain higher-accuracy electronic energies, single-point calculations were conducted on the optimized DFT

geometries at the DLPNO-CCSD(T)/aug-cc-pVTZ/CPCM(DMSO)[47-50] level of theory using ORCA 6.0.0, [51] employing the following computational settings: ! TightSCF TightPNO AutoAux.

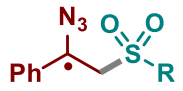
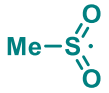
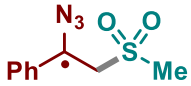
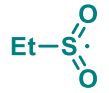
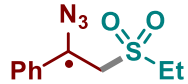
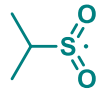
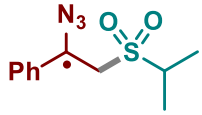
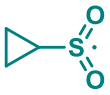
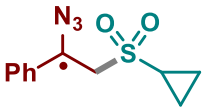
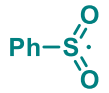
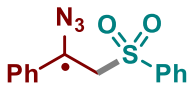
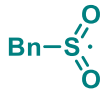
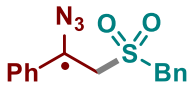
Table S8. Bond dissociation enthalpies of R—R, R—CH_3 and R—Cl bonds, electronegativities of sulfur centered radicals and RSEs (kcal/mol) at DLPNO-CCSD(T)/aug-cc-pVTZ/CPCM(DMSO)//PBE0-D3(BJ)/def2-TZVP/CPCM(DMSO) level of theory.

Radicals	$D[R-CH_3], \frac{kcal}{mol}$	$D[R-Cl], \frac{kcal}{mol}$	$D[R-R]_{calc}, \frac{kcal}{mol}$	$\chi(R)$	$RSE_z, \frac{kcal}{mol}$
	71.5	60.9	53.2	2.679	17.7
	70.9	61.4	52.5	2.643	18.05
	70.2	61.5	51.4	2.616	18.6
	75.1	64.7	60.5	2.672	14.05
	72.2	61	54.3	2.699	17.15
	71.6	61.1	53.5	2.676	17.55

The computational results quantifying radical stability are summarized in Table S8. Analysis of the RSEz values reveals that the relatively low yields observed for the methylsulfonyl radical system originate not from inherent thermodynamic instability, but rather from alternative factors.

To elucidate the radical addition pathway involving various sulfonyl radicals with (1-azidovinyl)benzene **1a**, we conducted additional thermodynamic calculations of Gibbs free energy changes for relevant species (Table S9).

Table S9. Changes in Gibbs free energy for sulfonyl species calculated at PBE0-D3(BJ)/def2-TZVP/CPCM(DMSO) level of theory.

R		$\Delta_r G, \frac{kcal}{mol}$
		−9.33
		-8.28
		-7.02
		-9.44
		-8.14
		-7.15

The computational results are consistent with experimental findings, which demonstrate that stability of sulfonyl radicals is not crucial factor affecting on the yields of ketazines **3**.

EPR calculations

For EPR calculations, initial molecular geometries were generated using the CREST program. These geometries were subsequently optimized at the B3LYP/def2-QZVP/CPCM(DMSO) level of theory in Gaussian 16 Rev. A.03. The optimized structures were then employed in ORCA 5.0.3[51] to compute hyperfine splitting constants and the g-tensor at the PBE0-D3(BJ)/ZORA-def2-QZVPP/CPCM(DMSO) level of theory, incorporating the zeroth-order regular approximation (ZORA)[52] and the !DEFGRID3 keyword. Wavefunction stability was verified using the **stable=opt** keyword in Gaussian. This computational setup provided the best balance of accuracy and computational efficiency.

References

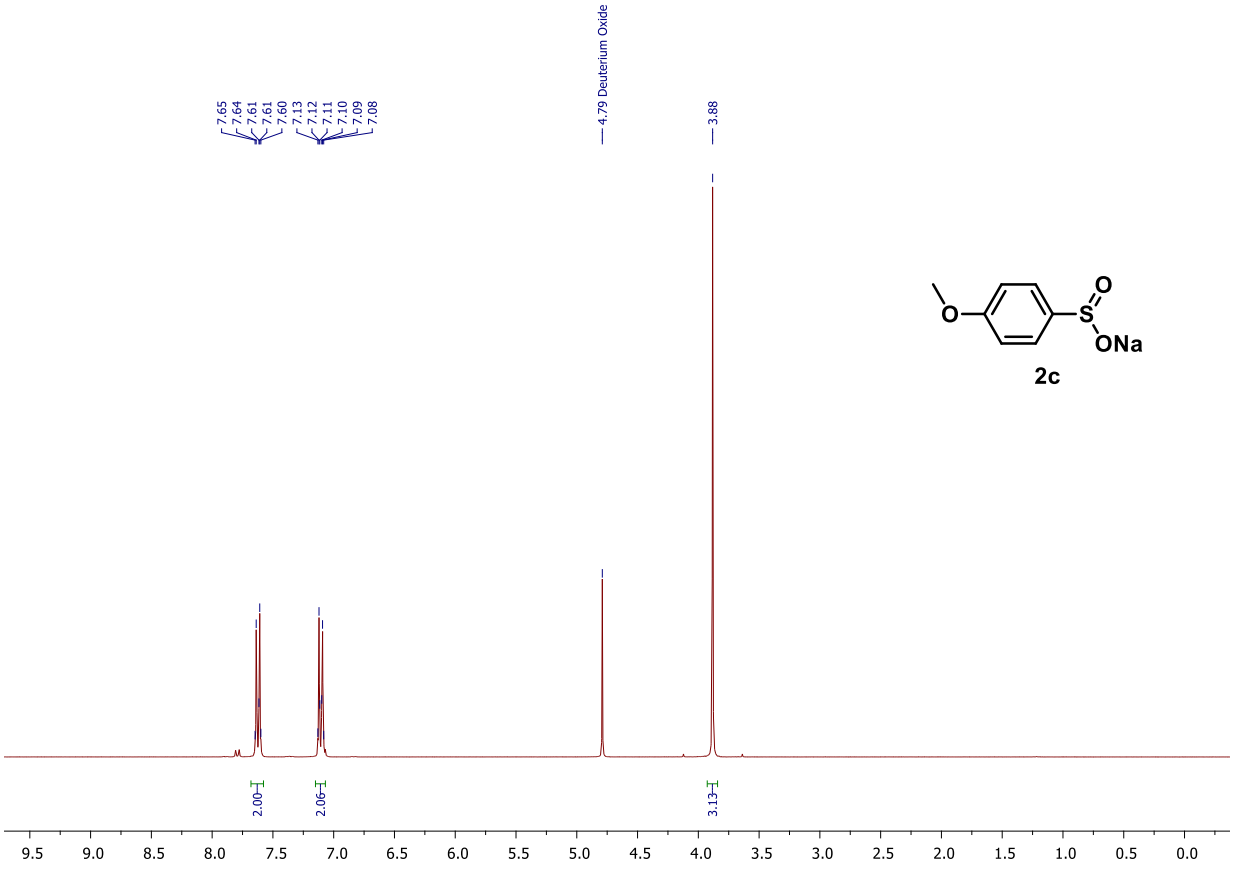
1. A. U. Meyer, S. Jäger, D. Prasad Hari and B. König, *Adv. Synth. Catal.*, 2015, **357**, 2050-2054.
2. M.-S. Liu, H.-W. Du, H. Meng, Y. Xie and W. Shu, Unified metal-free intermolecular Heck-type sulfonylation, cyanation, amination, amidation of alkenes by thianthrenation, *Nat. Commun.*, 2024, **15**, 529.
3. H.-M. Huang, P. Bellotti, P. M. Pflüger, J. L. Schwarz, B. Heidrich and F. Glorius, Three-Component, Interrupted Radical Heck/Allylic Substitution Cascade Involving Unactivated Alkyl Bromides, *J. Am. Chem. Soc.*, 2020, **142**, 10173-10183.
4. G. Bogonda, D. V. Patil, H. Y. Kim and K. Oh, Visible-Light-Promoted Thiyl Radical Generation from Sodium Sulfinates: A Radical-Radical Coupling to Thioesters, *Org. Lett.*, 2019, **21**, 3774-3779.
5. A. U. Meyer, K. Straková, T. Slanina and B. König, Eosin Y (EY) Photoredox-Catalyzed Sulfonylation of Alkenes: Scope and Mechanism, *Chemistry – A European Journal*, 2016, **22**, 8694-8699.
6. T. Chen, J. Lahbi, G. Broggini, A. Pradal and G. Poli, Allylsulfones through Palladium-Catalyzed Allylic C−H Sulfonylation of Terminal Alkenes, *Eur. J. Org. Chem.*, 2023, **26**, e202201493.
7. R. Dey and P. Banerjee, Lewis Acid Catalyzed Diastereoselective Cycloaddition Reactions of Donor-Acceptor Cyclopropanes and Vinyl Azides: Synthesis of Functionalized Azidocyclopentane and Tetrahydropyridine Derivatives, *Org. Lett.*, 2017, **19**, 304-307.
8. Y.-F. Wang, K. K. Toh, S. Chiba and K. Narasaka, Mn(III)-Catalyzed Synthesis of Pyrroles from Vinyl Azides and 1,3-Dicarbonyl Compounds, *Org. Lett.*, 2008, **10**, 5019-5022.
9. H. T. Zhu, C. M. Liang, T. Y. Li, L. Y. Li, R. L. Zhang, J. N. Wang, R. Q. Qi, J. M. Zhang, R. H. Yang, Y. Q. Yang, A. X. Zhou, X. Jin and N. N. Zhou, Dual Proton/Silver-Catalyzed Serial (5 + 2)-Cycloaddition and Nazarov Cyclization of (E)-2-Arylidene-3-hydroxyindanones with Conjugated Eneynes: Synthesis of Indanone-Fused Benzo[cd]azulenes, *J Org Chem*, 2023, **88**, 3409-3423.
10. S. Cao, Q. Ji, H. Li, M. Pang, H. Yuan, J. Zhang and X. Bi, AgN_3-Catalyzed Hydroazidation of Terminal Alkynes and Mechanistic Studies, *J. Am. Chem. Soc.*, 2020, **142**, 7083-7091.
11. N. S. Y. Loy, S. Kim and C.-M. Park, Synthesis of unsymmetrical pyrazines based on alpha-diazo oxime ethers, *Org. Lett.*, 2015, **17**, 395-397.
12. B. Nie, W. Wu, Q. Ren, Z. Wang, J. Zhang, Y. Zhang and H. Jiang, Access to Cycloalkeno[c]-Fused Pyridines via Pd-Catalyzed C(sp(2))-H Activation and Cyclization of N-Acetyl Hydrazones of Acylcycloalkenes with Vinyl Azides, *Org. Lett.*, 2020, **22**, 7786-7790.
13. J. Chen, X. Shen and Z. Lu, Cobalt-Catalyzed Markovnikov-Type Selective Hydroboration of Terminal Alkynes, *Angew. Chem. Int. Ed.*, 2021, **60**, 690-694.
14. O. M. Mulina, N. V. Zhironkina, S. A. Paveliev, D. V. Demchuk and A. O. Terent'ev, Electrochemically Induced Synthesis of Sulfonylated N-Unsubstituted Enamines from Vinyl Azides and Sulfonyl Hydrazides, *Org. Lett.*, 2020, **22**, 1818-1824.
15. P. Gu, Y. Su, X.-P. Wu, J. Sun, W. Liu, P. Xue and R. Li, Enantioselective Preparation of cis-β-Azidocyclopropane Esters by Cyclopropanation of Azido Alkenes Using a Chiral Dirhodium Catalyst, *Org. Lett.*, 2012, **14**, 2246-2249.
16. S. W. Wu and F. Liu, Synthesis of alpha-Fluoroketones from Vinyl Azides and Mechanism Interrogation, *Org Lett*, 2016, **18**, 3642-3645.

17. Y.-F. Wang, K. K. Toh, J.-Y. Lee and S. Chiba, Synthesis of Isoquinolines from α-Aryl Vinyl Azides and Internal Alkynes by Rh–Cu Bimetallic Cooperation, *Angew. Chem. Int. Ed.*, 2011, **50**, 5927-5931.
18. L. Xiang, Y. Niu, X. Pang, X. Yang and R. Yan, I(2)-catalyzed synthesis of substituted imidazoles from vinyl azides and benzylamines, *Chem Commun (Camb)*, 2015, **51**, 6598-6600.
19. D. Enders, A. Grossmann, H. Huang and G. Raabe, Dual Secondary Amine/N-Heterocyclic Carbene Catalysis in the Asymmetric Michael/Cross-Benzoin Cascade Reaction of β-Oxo Sulfones with Enals, *Eur. J. Org. Chem.*, 2011, **2011**, 4298-4301.
20. H.-L. Wan, Z. Guan and Y.-H. He, Electrochemically Promoted Bifunctionalization of Alkynes for the Synthesis of β-Keto Sulfones, *Asian J. Org. Chem.*, 2021, **10**, 3406-3410.
21. S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42-55.
22. M. Y. Balakirev and V. V. Khramtsov, ESR Study of Free Radical Decomposition of N,N-Bis(arylsulfonyl)hydroxylamines in Organic Solution, *J. Org. Chem.*, 1996, **61**, 7263-7269.
23. V. Cholvad, K. Szaboova, A. Staško, O. Nuyken and B. Voit, ESR parameters of 5,5-dimethylpyrrolidine 1-oxide (DMPO) spin adducts in the photochemical decomposition of azo compounds, *Magn. Reson. Chem.*, 1991, **29**, 402-404.
24. P. Astolfi, L. Greci and M. Panagiotaki, Spin trapping of nitrogen dioxide and of radicals generated from nitrous acid, *Free Radical Res.*, 2005, **39**, 137-144.
25. P. Pracht, S. Grimme, C. Bannwarth, F. Bohle, S. Ehlert, G. Feldmann, J. Gorges, M. Müller, T. Neudecker, C. Plett, S. Spicher, P. Steinbach, P. A. Wesołowski and F. Zeller, *J. Chem. Phys.*, 2024, **160**.
26. C. Bannwarth, S. Ehlert and S. Grimme, *J. Chem. Theory Comput.*, 2019, **15**, 1652-1671.
27. P. Pracht, F. Bohle and S. Grimme, Automated exploration of the low-energy chemical space with fast quantum chemical methods, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169-7192.
28. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Rev. A.03.*Journal*, 2016.
29. J. P. Perdew, M. Ernzerhof and K. Burke, Rationale for mixing exact exchange with density functional approximations, *J. Chem. Phys.*, 1996, **105**, 9982-9985.
30. S. Grimme, S. Ehrlich and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
31. N. Mardirossian and M. Head-Gordon, Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals, *Mol. Phys.*, 2017, **115**, 2315-2372.

32. Y. Hordijk, M. Dalla Tiezza, D. Rodrigues Silva and T. A. Hamlin, Radical Addition Reactions: Hierarchical *Ab Initio* Benchmark and DFT Performance Study, *ChemPhysChem*, 2025, **26**, e202400728.
33. M. M. Quintal, A. Karton, M. A. Iron, A. D. Boese and J. M. L. Martin, Benchmark study of DFT functionals for late-transition-metal reactions, *J. Phys. Chem. A*, 2006, **110**, 709-716.
34. M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew and K. A. Lyssenko, Density functional theory is straying from the path toward the exact functional, *Science*, 2017, **355**, 49-52.
35. B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson and T. L. Windus, New Basis Set Exchange: An Open, Up-to-Date Resource for the Molecular Sciences Community, *J. Chem. Inf. Model.*, 2019, **59**, 4814-4820.
36. W. J. Stevens, M. Krauss, H. Basch and P. G. Jasien, Relativistic compact effective potentials and efficient, shared-exponent basis sets for the third-, fourth-, and fifth-row atoms, *Can. J. Chem.*, 1992, **70**, 612-630.
37. T. R. Cundari and W. J. Stevens, Effective core potential methods for the lanthanides, *J. Chem. Phys.*, 1993, **98**, 5555-5565.
38. F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
39. S. Miertuš, E. Scrocco and J. Tomasi, Electrostatic interaction of a solute with a continuum. A direct utilizaion of AB initio molecular potentials for the prevision of solvent effects, *Chem. Phys.*, 1981, **55**, 117-129.
40. A. Gilbert, IQmol, http://iqmol.org/).
41. G. Luchini, J. Alegre-Requena, I. Funes-Ardoiz and R. Paton, GoodVibes: automated thermochemistry for heterogeneous computational chemistry data, *F1000Research*, 2020, **9**.
42. P. L. Roulhac and G. J. Palenik, Bond valence sums in coordination chemistry. The calculation of the oxidation state of cerium in complexes containing cerium bonded only to oxygen, *Inorg. Chem.*, 2003, **42**, 118-121.
43. A. J. W. Thom, E. J. Sundstrom and M. Head-Gordon, LOBA: a localized orbital bonding analysis to calculate oxidation states, with application to a model water oxidation catalyst, *Phys. Chem. Chem. Phys.*, 2009, **11**, 11297-11304.
44. T. Lu, A comprehensive electron wavefunction analysis toolbox for chemists, Multiwfn, *J. Chem. Phys.*, 2024, **161**.
45. N. Matsunaga, D. W. Rogers and A. A. Zavitsas, Pauling's Electronegativity Equation and a New Corollary Accurately Predict Bond Dissociation Enthalpies and Enhance Current Understanding of the Nature of the Chemical Bond, *J. Org. Chem.*, 2003, **68**, 3158-3172.
46. I. Degirmenci and M. L. Coote, Effect of Substituents on the Stability of Sulfur-Centered Radicals, *J. Phys. Chem. A*, 2016, **120**, 7398-7403.
47. G. Bistoni, C. Riplinger, Y. Minenkov, L. Cavallo, A. A. Auer and F. Neese, Treating Subvalence Correlation Effects in Domain Based Pair Natural Orbital Coupled Cluster Calculations: An Out-of-the-Box Approach, *J. Chem. Theory Comput.*, 2017, **13**, 3220-3227.
48. M. Saitow, U. Becker, C. Riplinger, E. F. Valeev and F. Neese, A new near-linear scaling, efficient and accurate, open-shell domain-based local pair natural orbital coupled cluster singles and doubles theory, *J. Chem. Phys.*, 2017, **146**.
49. G. L. Stoychev, A. A. Auer and F. Neese, Automatic Generation of Auxiliary Basis Sets, *J. Chem. Theory Comput.*, 2017, **13**, 554-562.

50. M. Garcia-Ratés, U. Becker and F. Neese, Implicit solvation in domain based pair natural orbital coupled cluster (DLPNO-CCSD) theory, *J. Comput. Chem.*, 2021, **42**, 1959-1973.
51. F. Neese, Software update: The ORCA program system—Version 5.0, *WIREs Comput. Mol. Sci.*, 2022, **12**, e1606.
52. C. van Wüllen, Molecular density functional calculations in the regular relativistic approximation: Method, application to coinage metal diatomics, hydrides, fluorides and chlorides, and comparison with first-order relativistic calculations, *J. Chem. Phys.*, 1998, **109**, 392-399.

NMR spectra of the synthesized compounds



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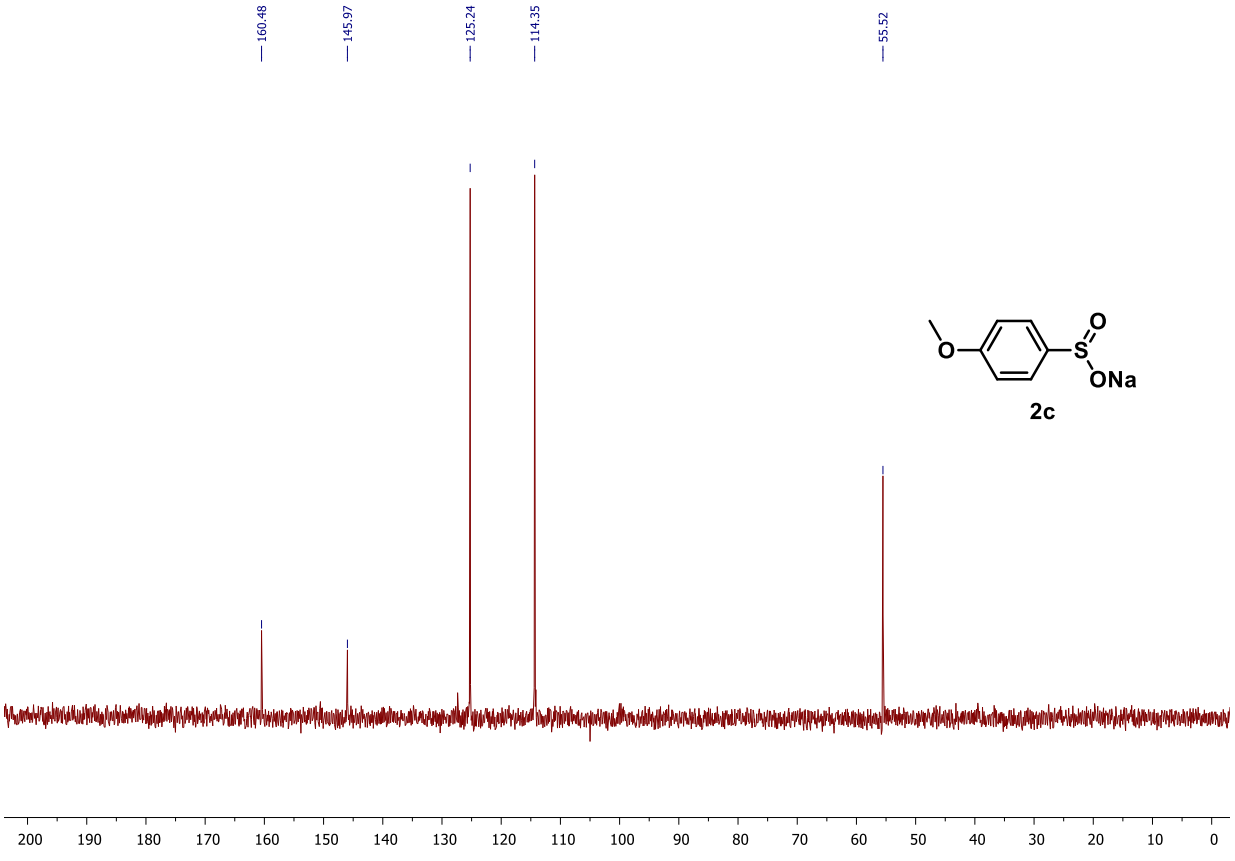

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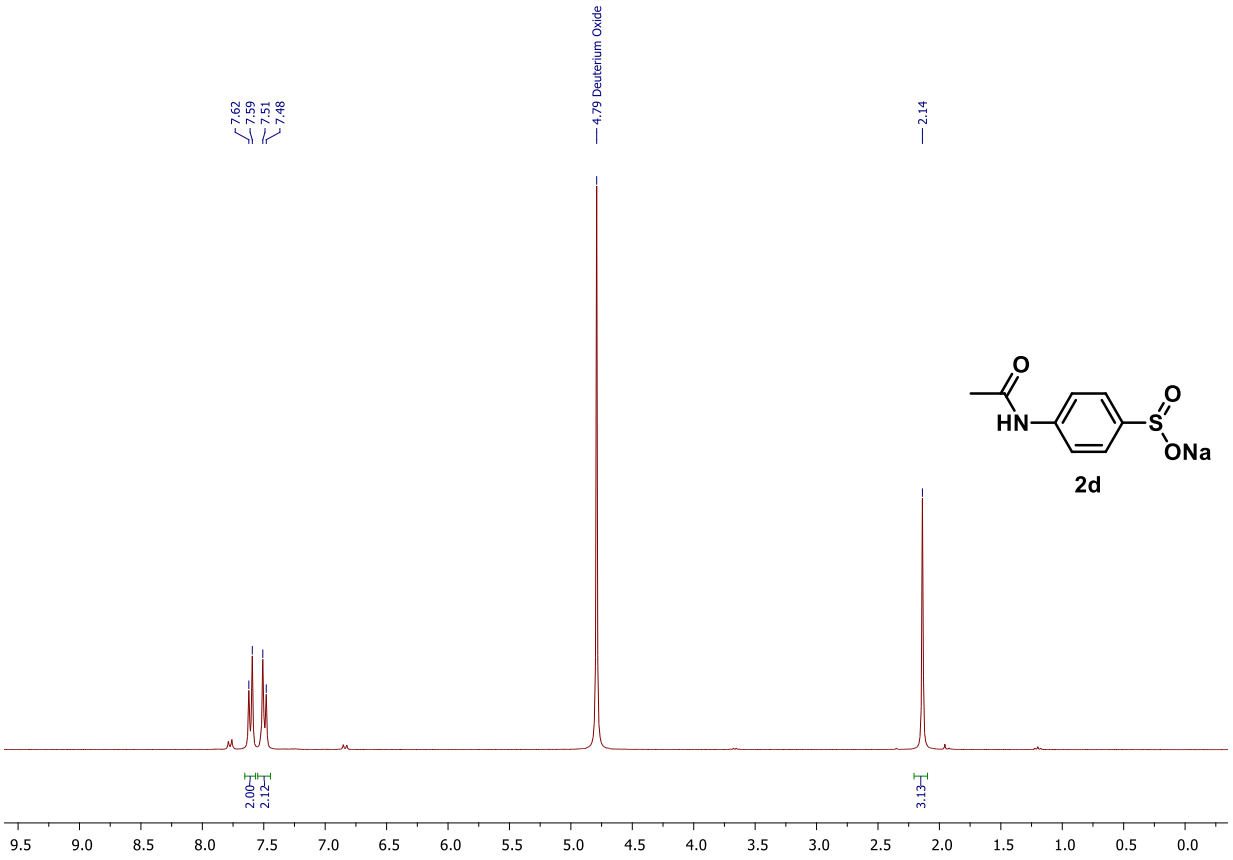
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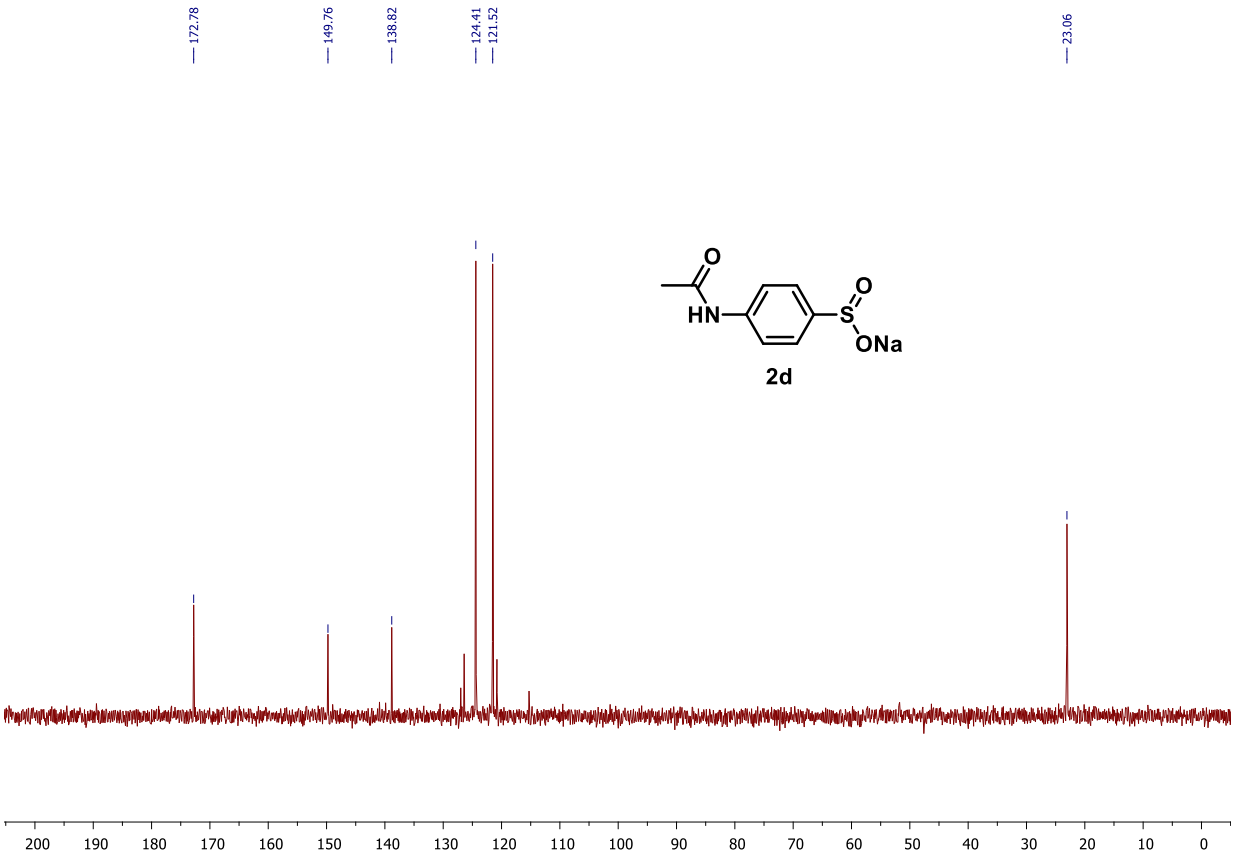
ONa
2d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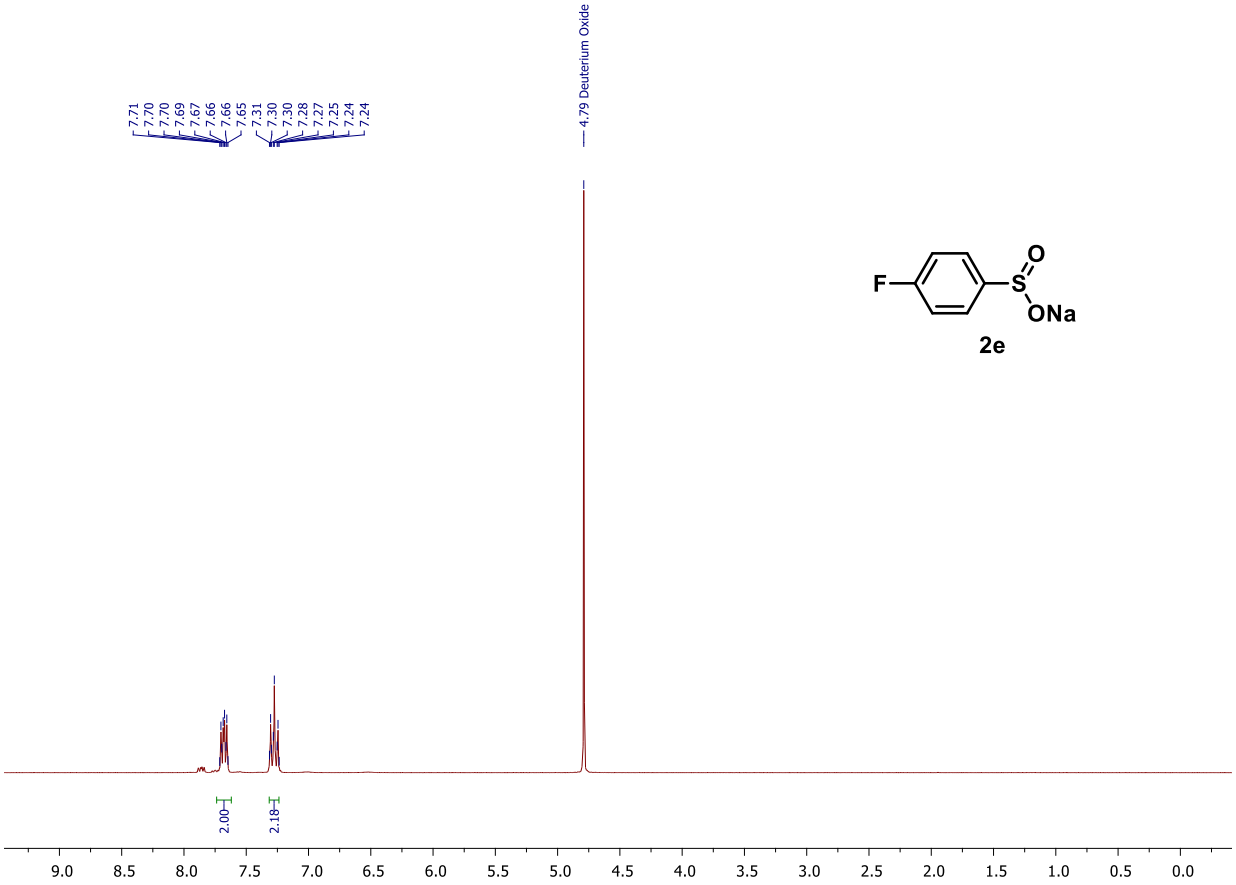
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F
S
O
ONa
2e
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9.0
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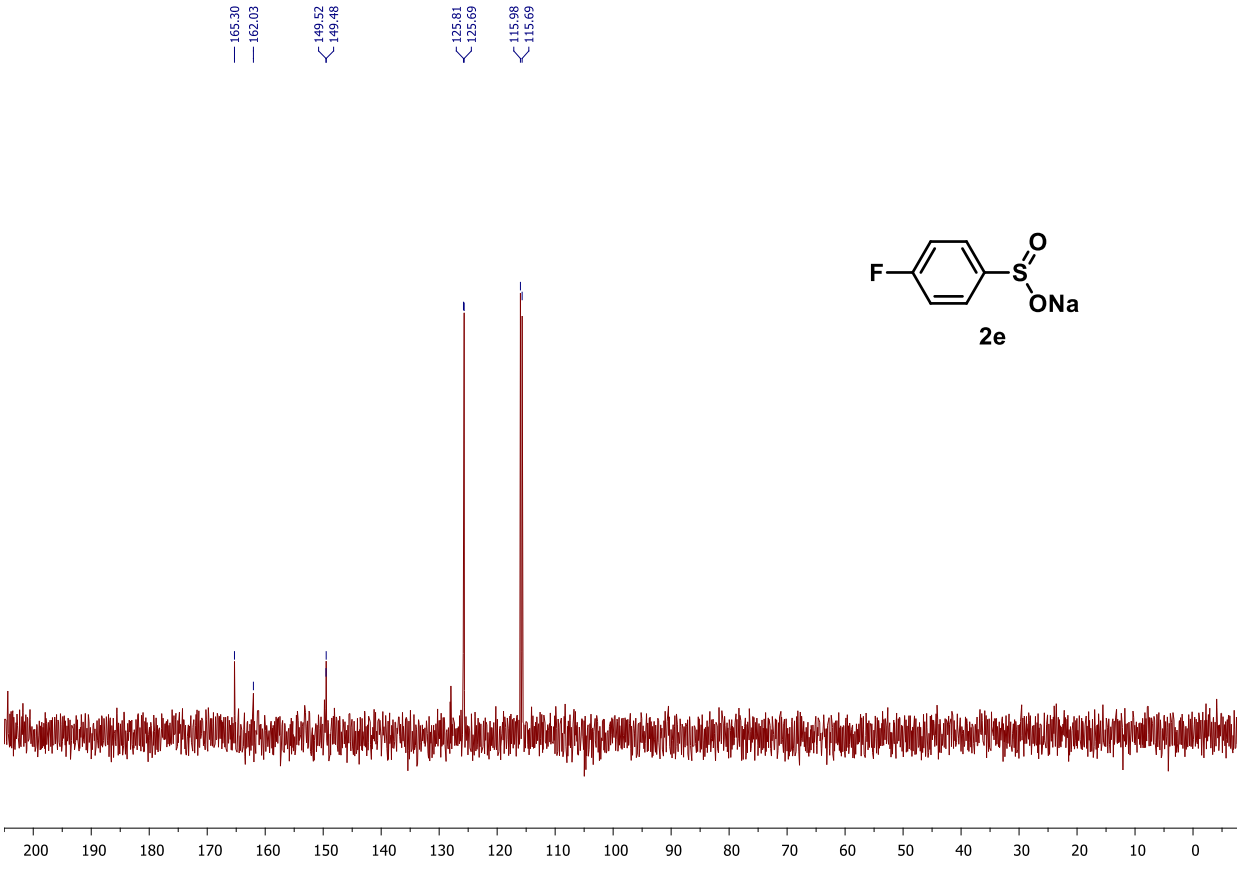
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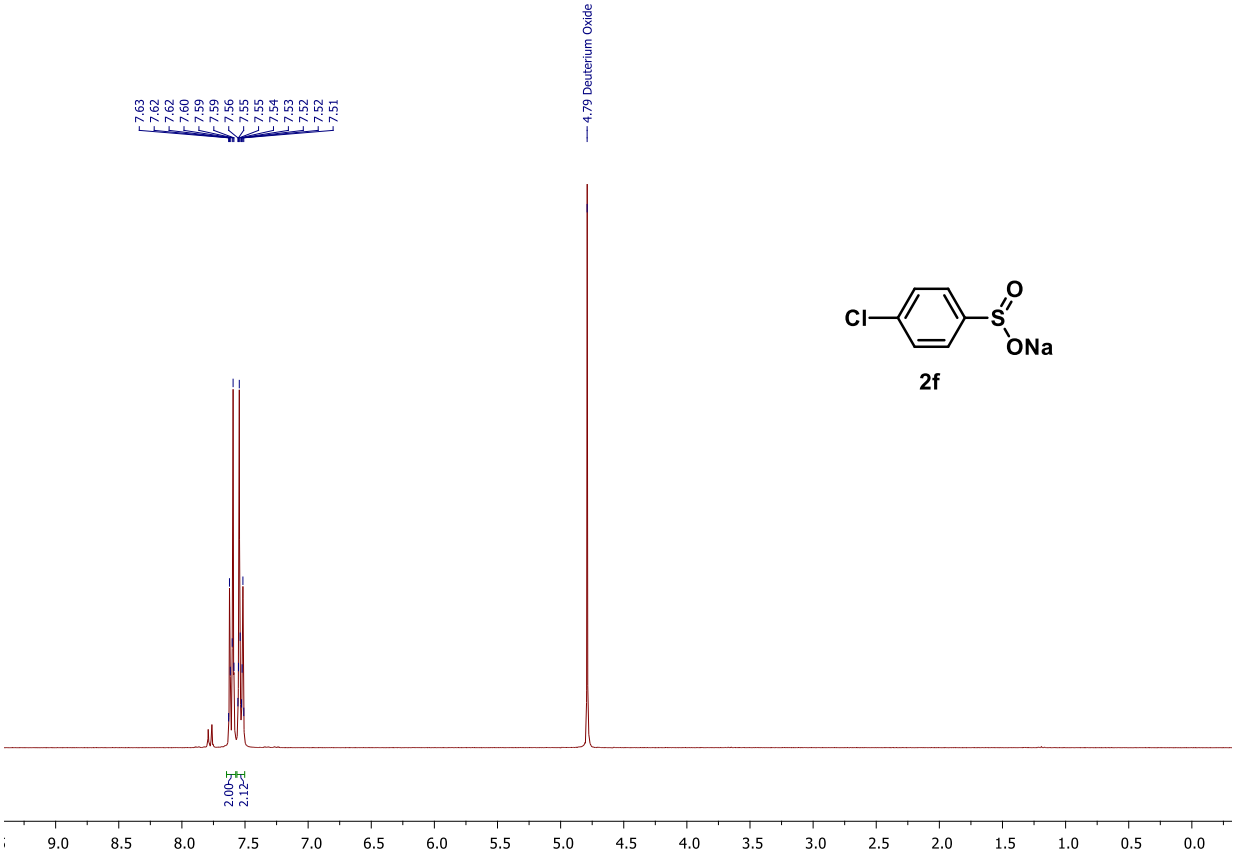
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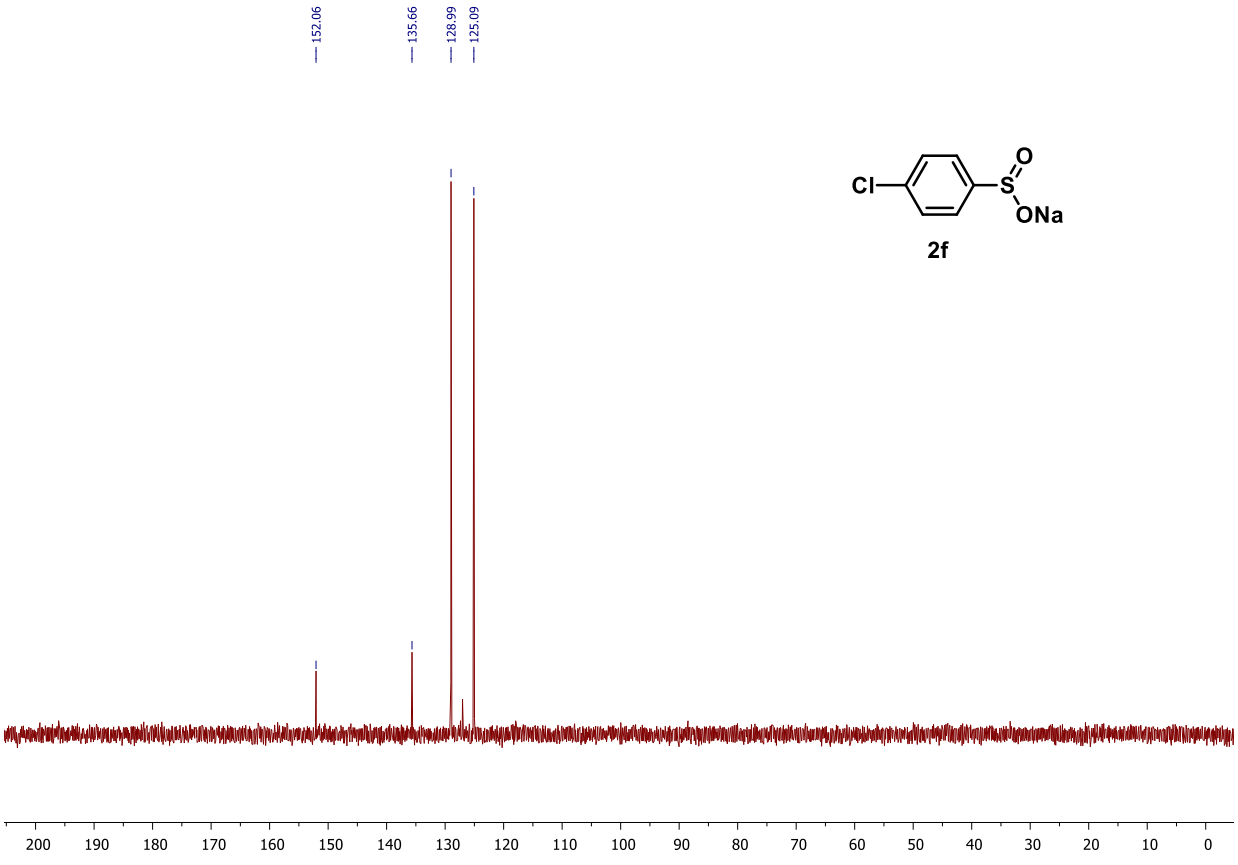
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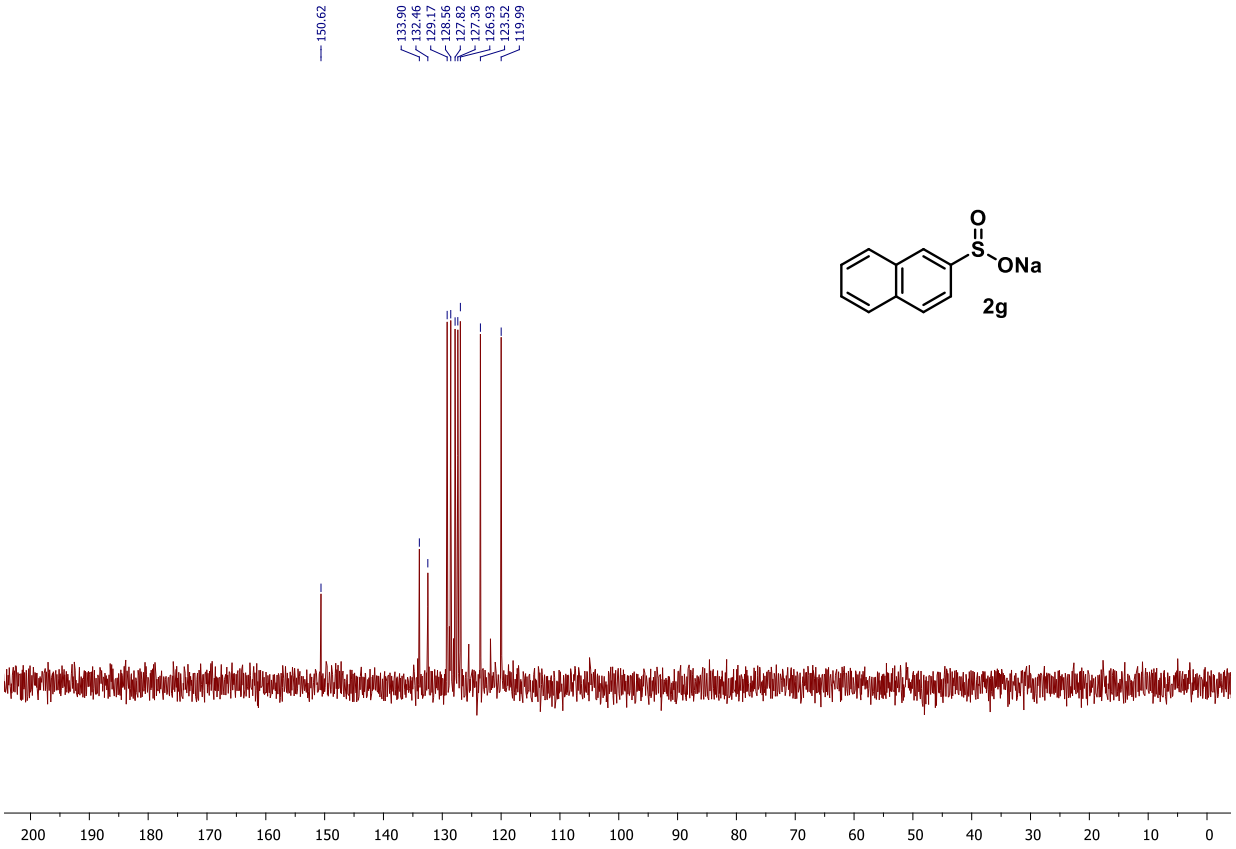
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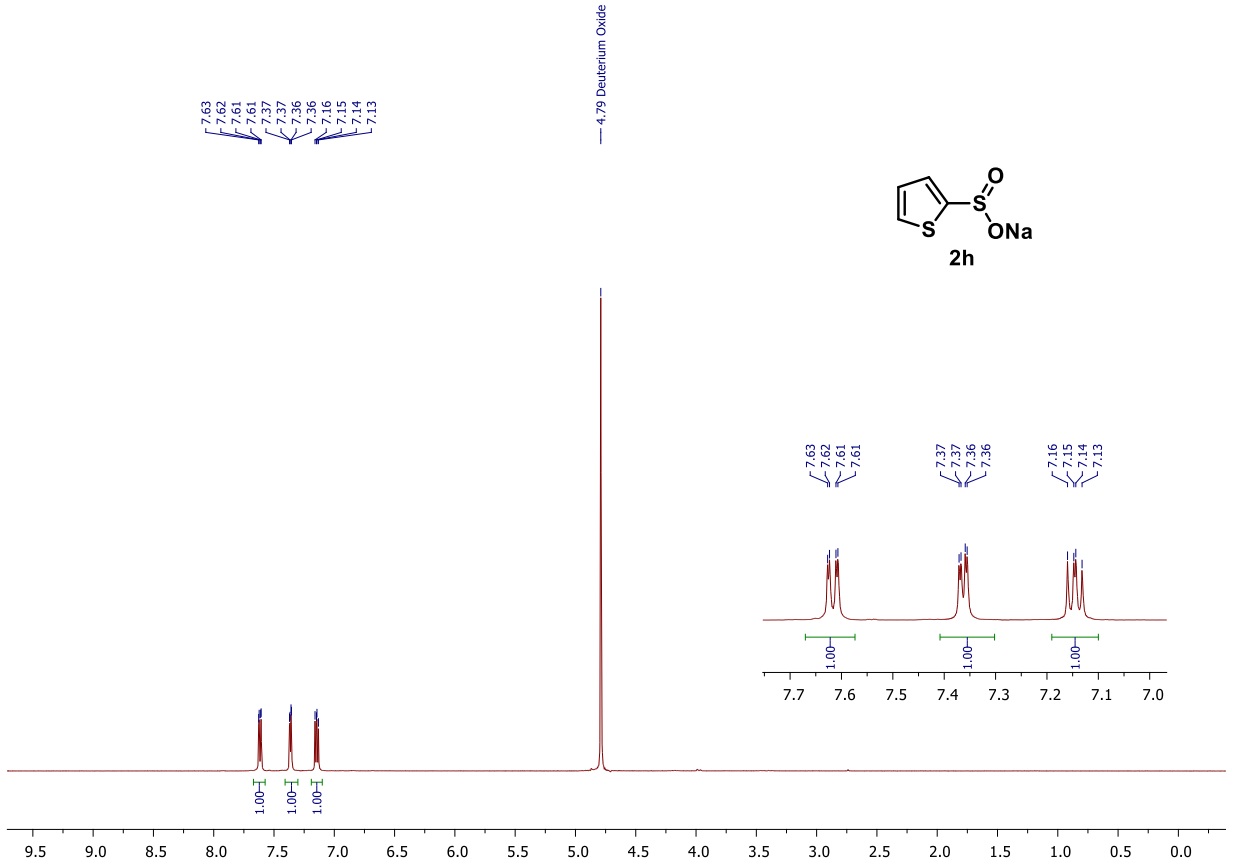
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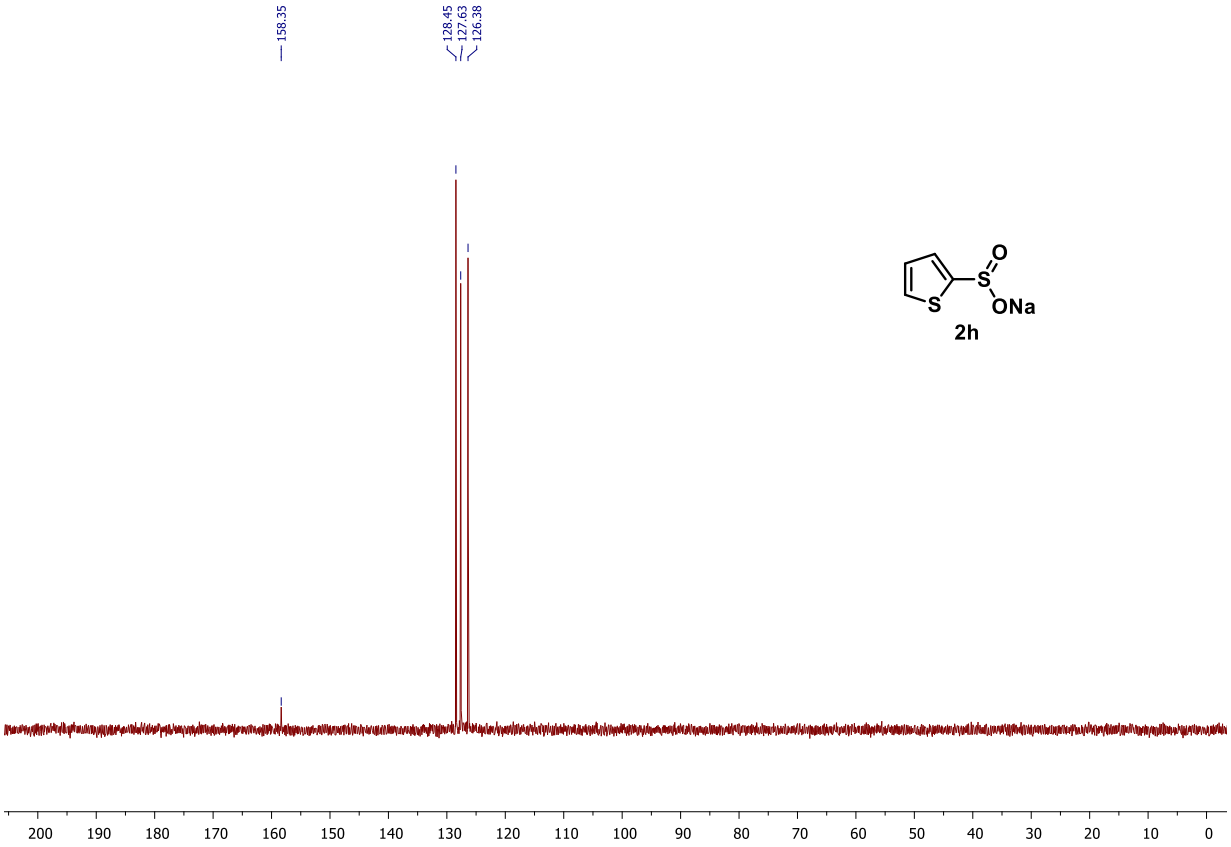
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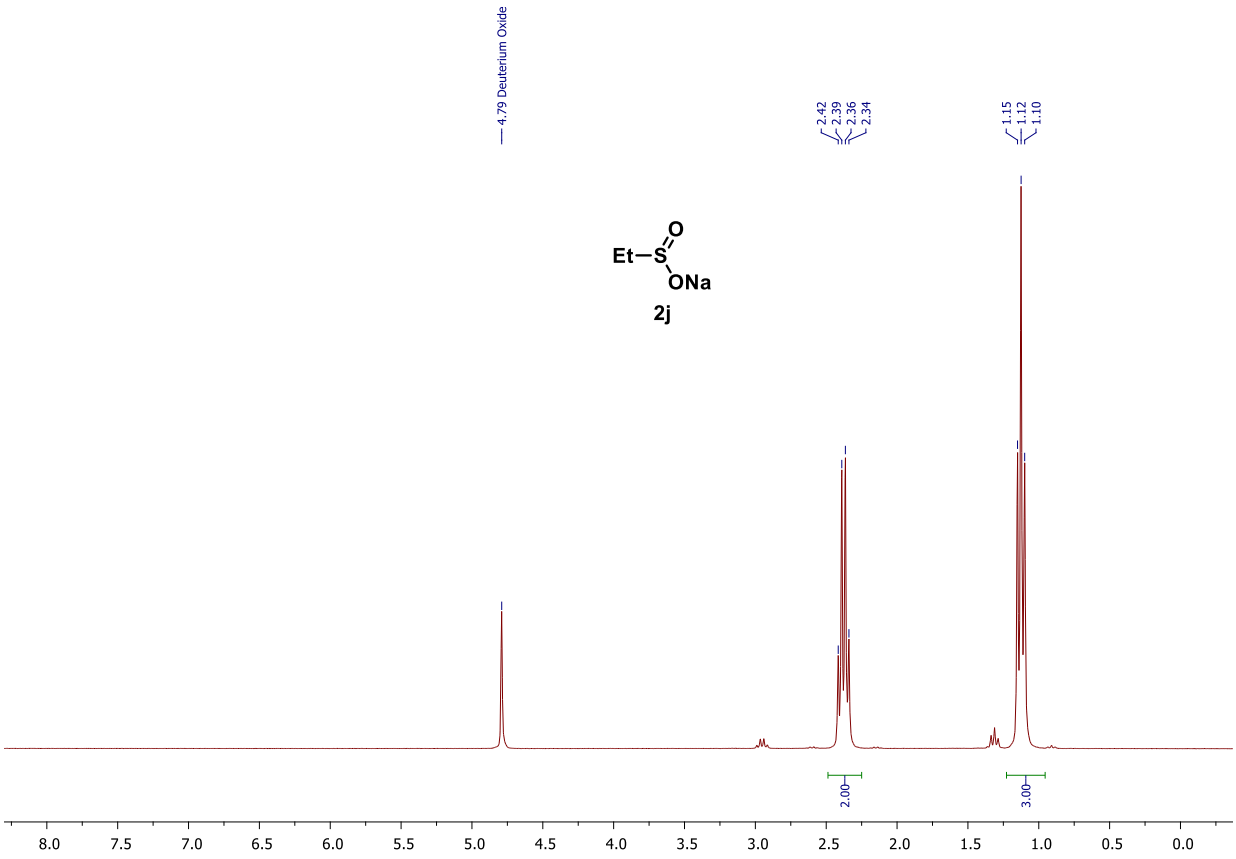
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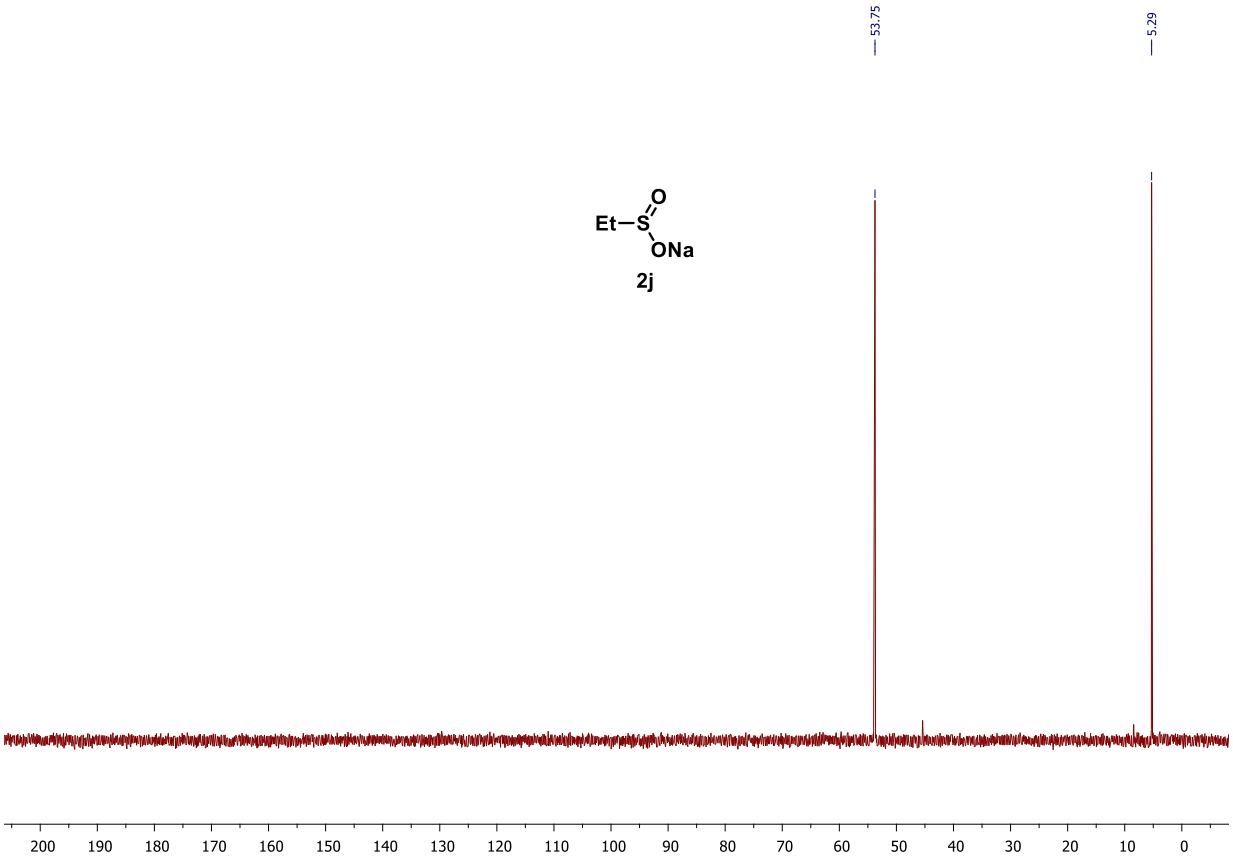
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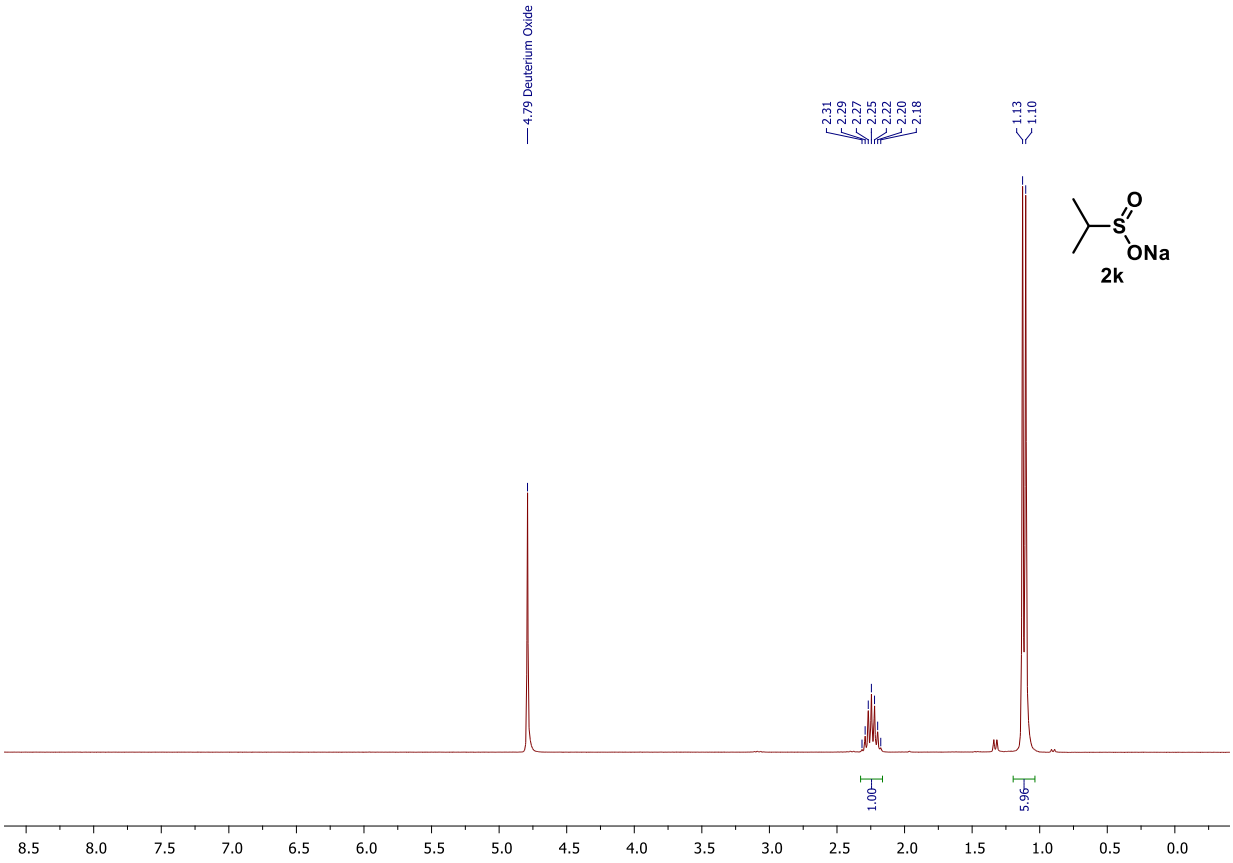
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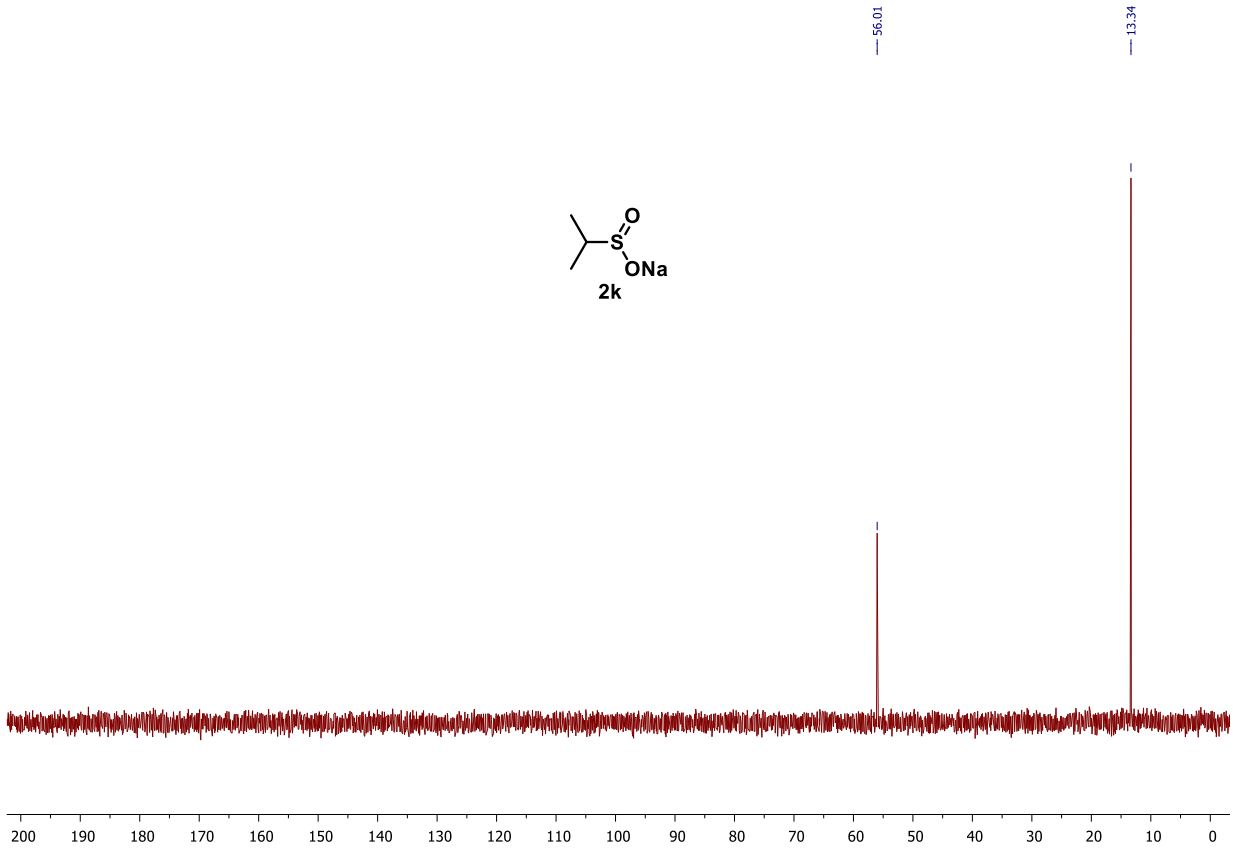
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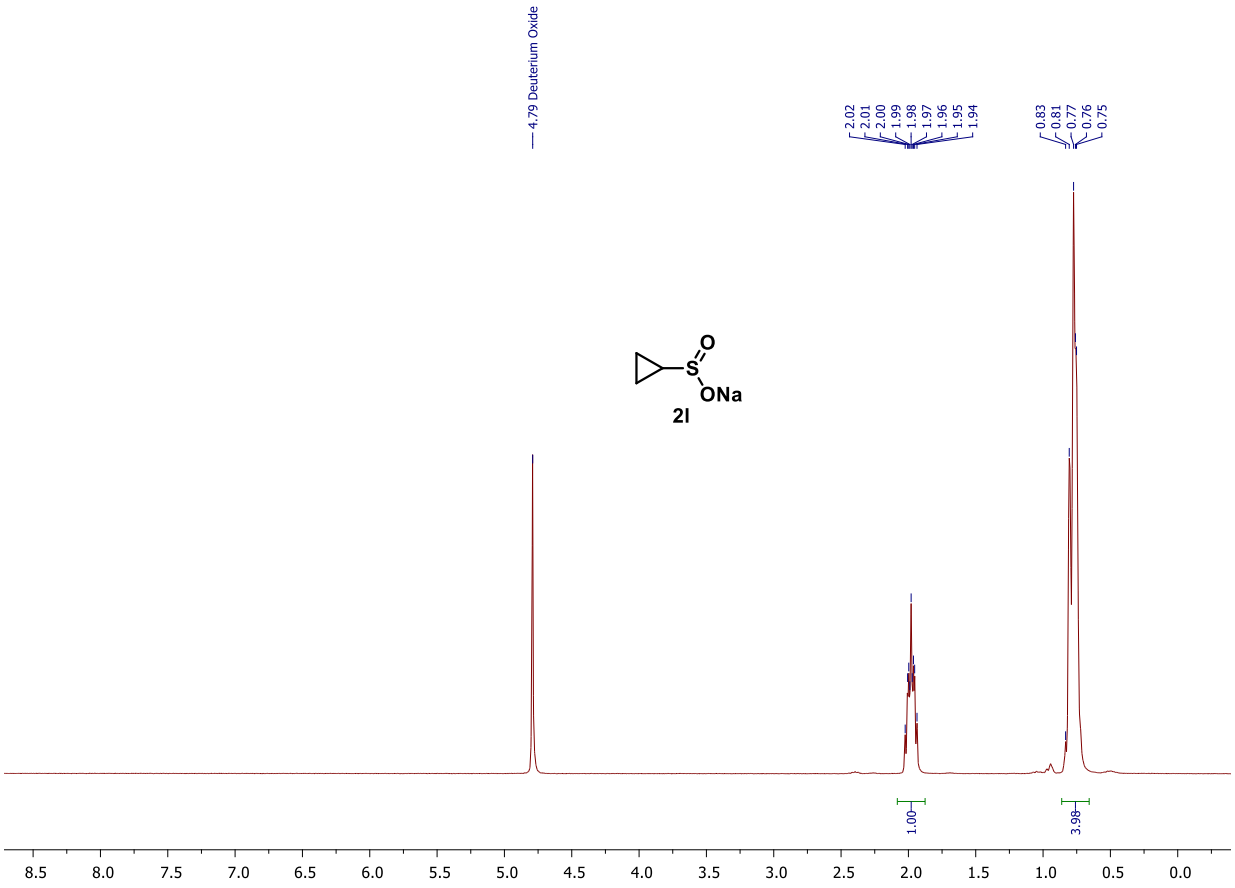
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2l
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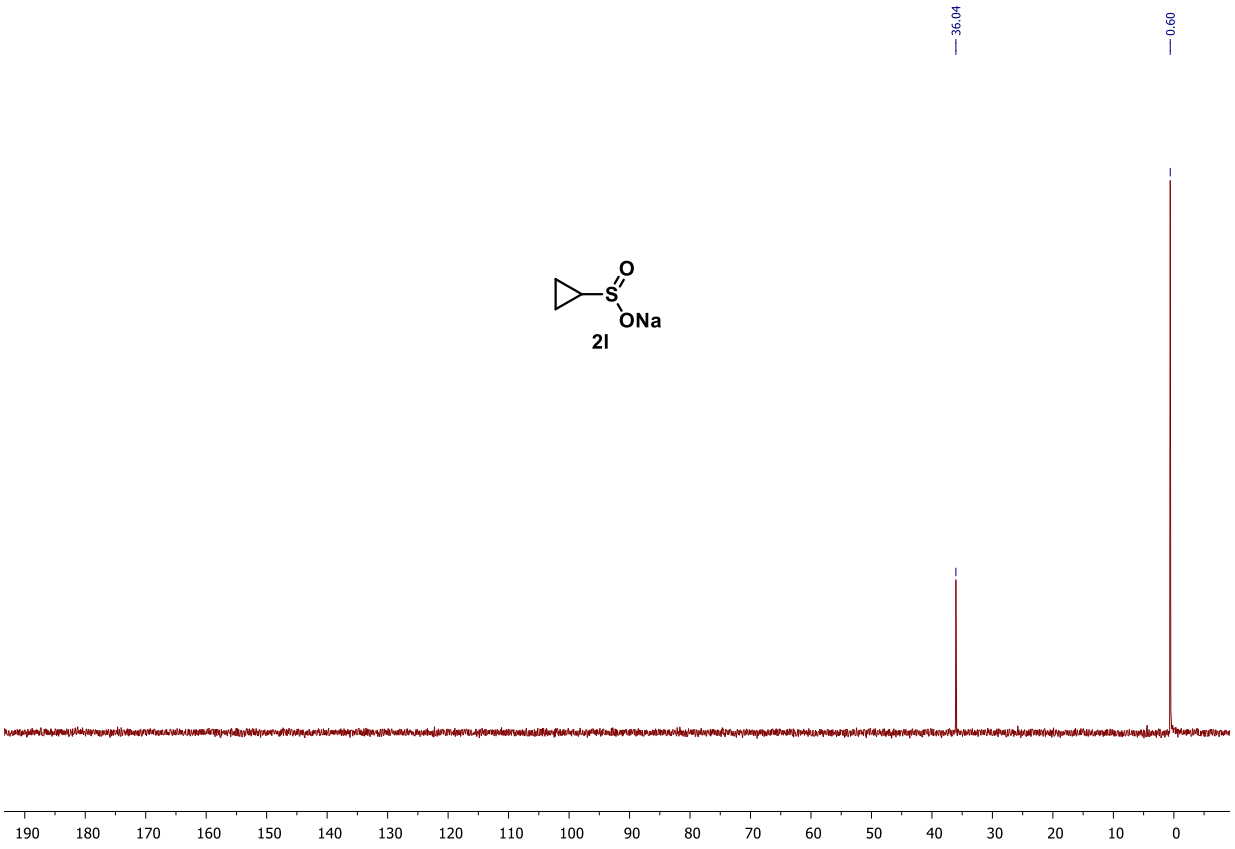
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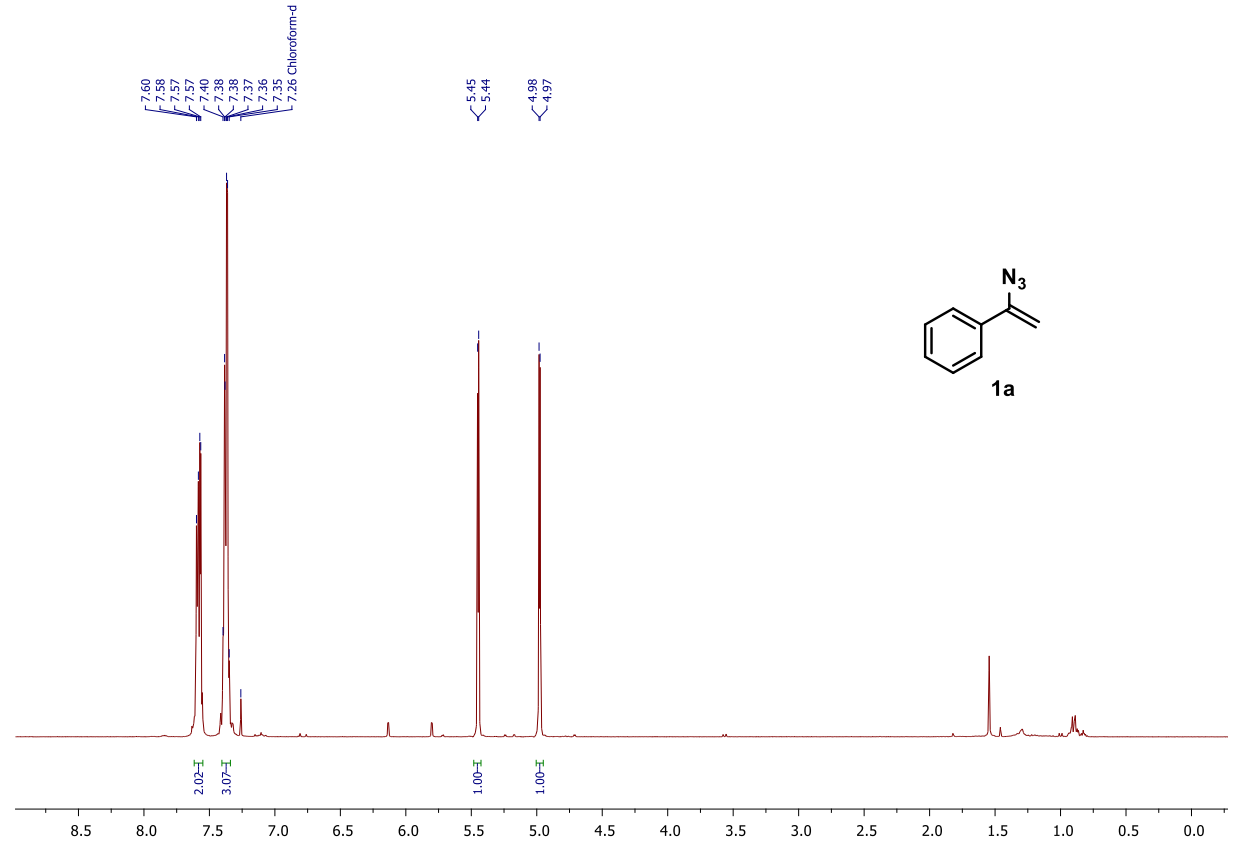
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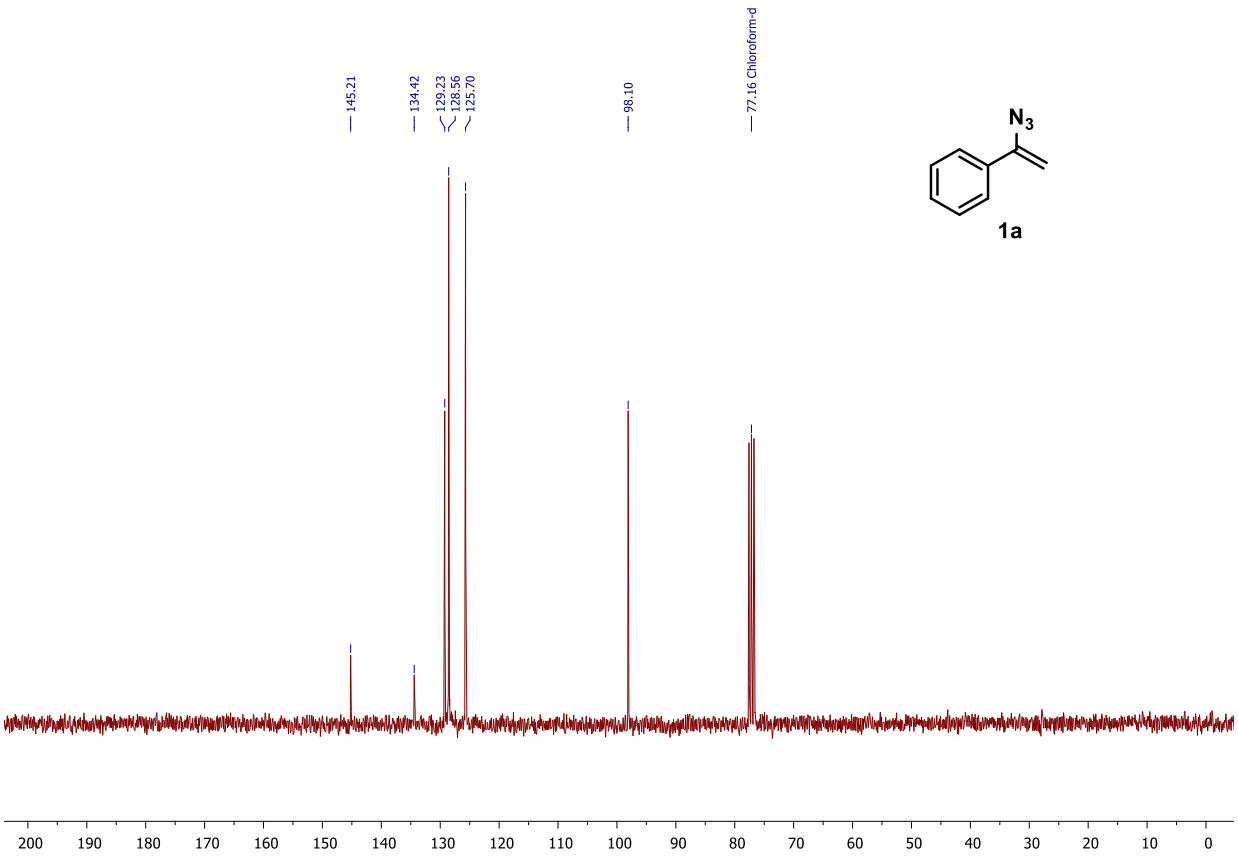
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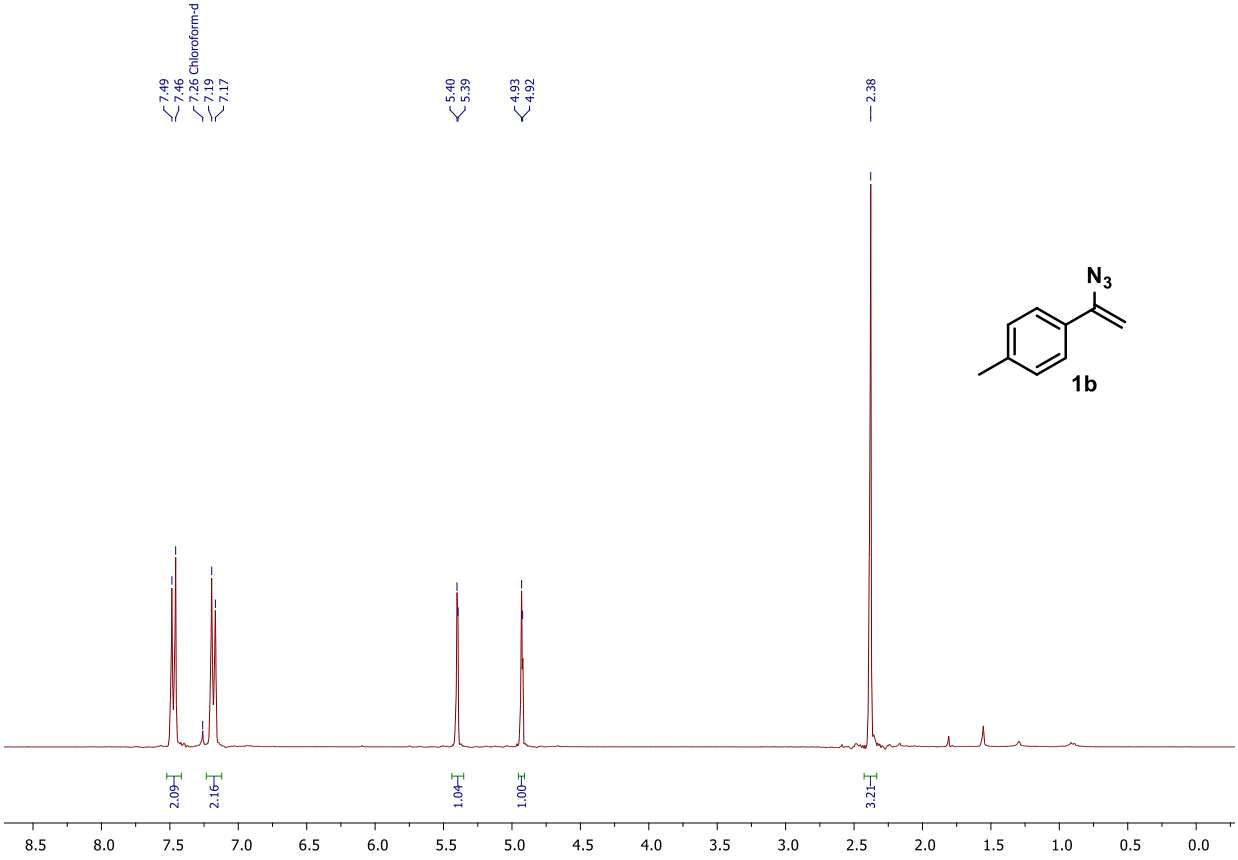
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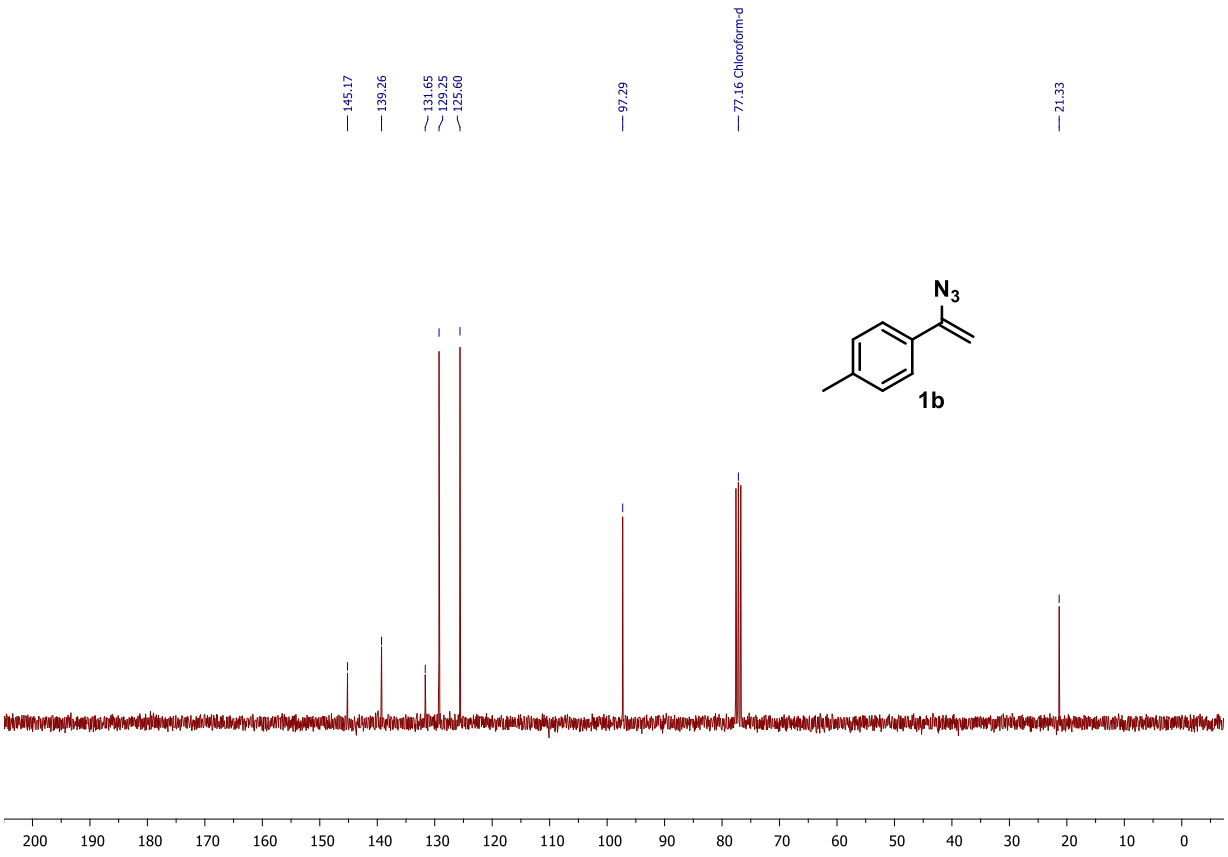
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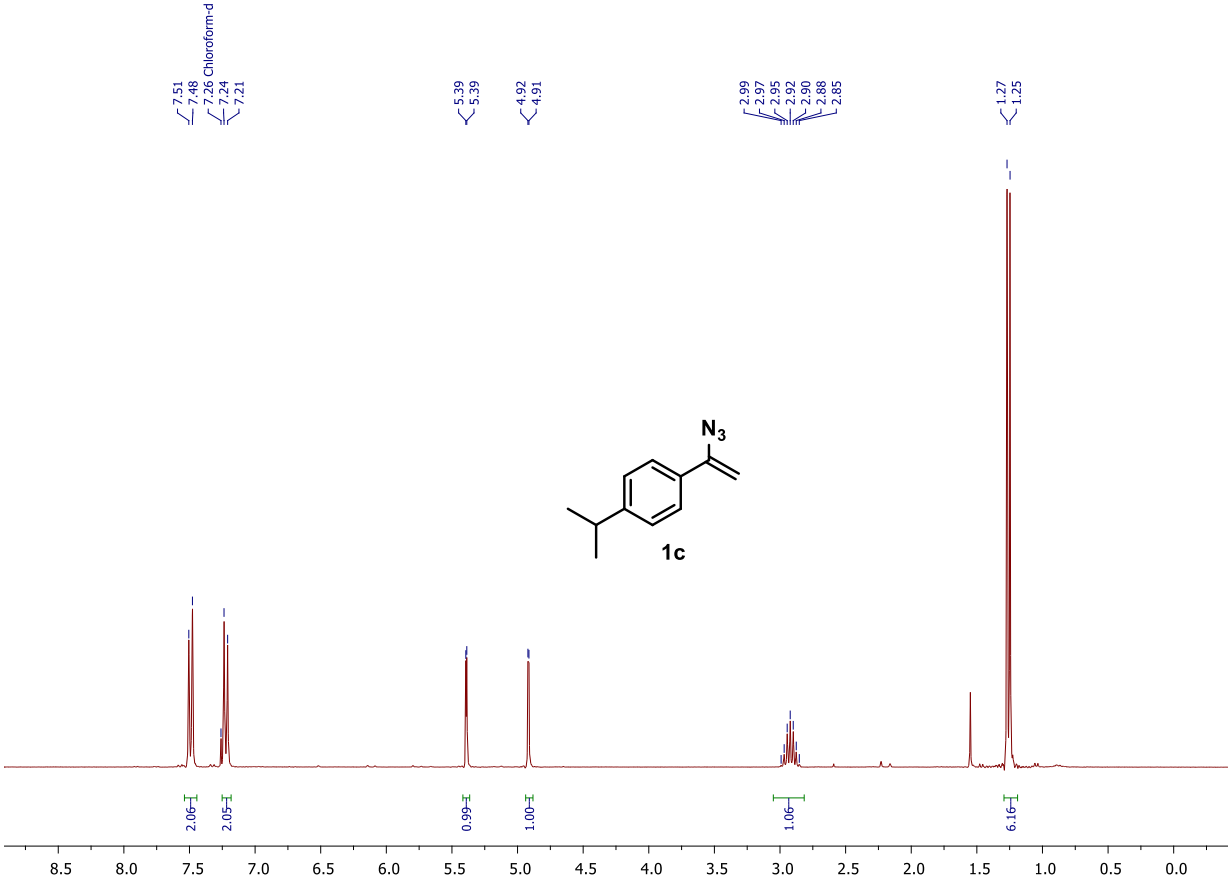
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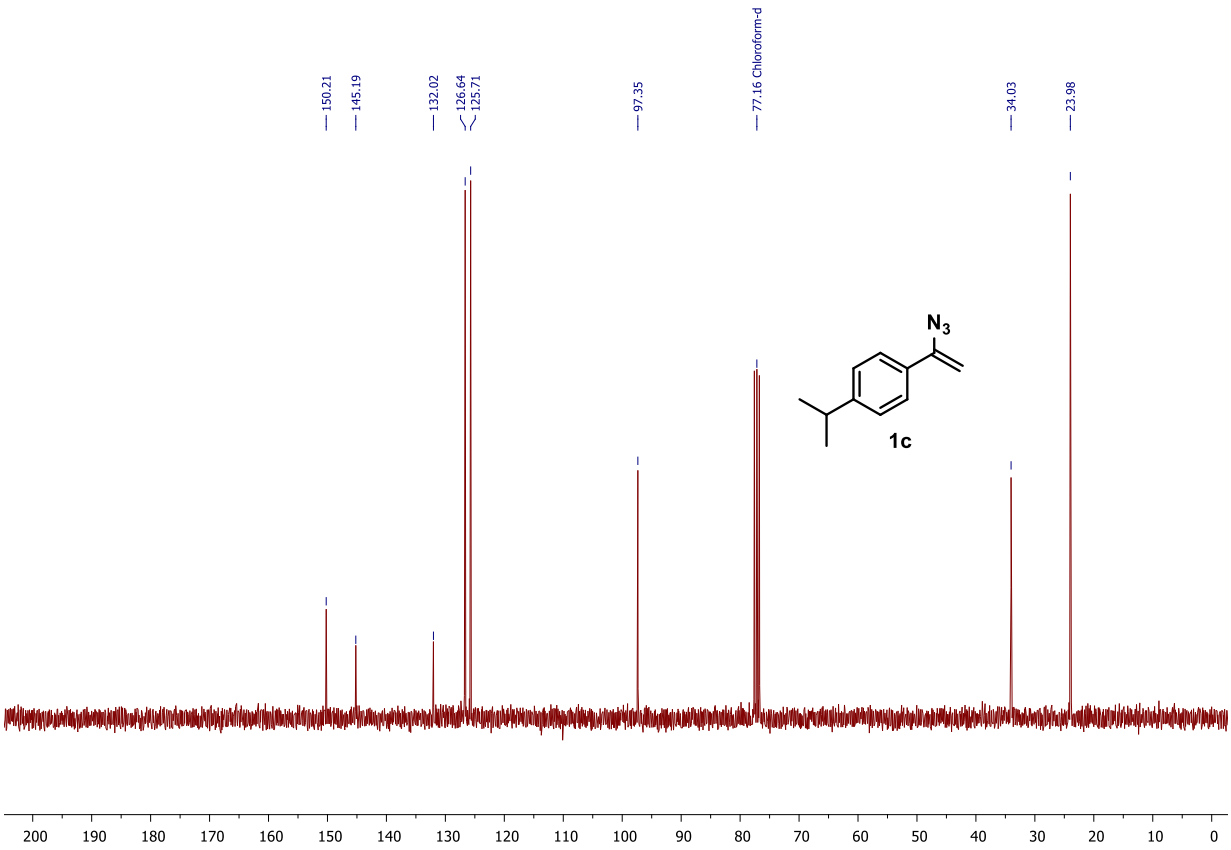
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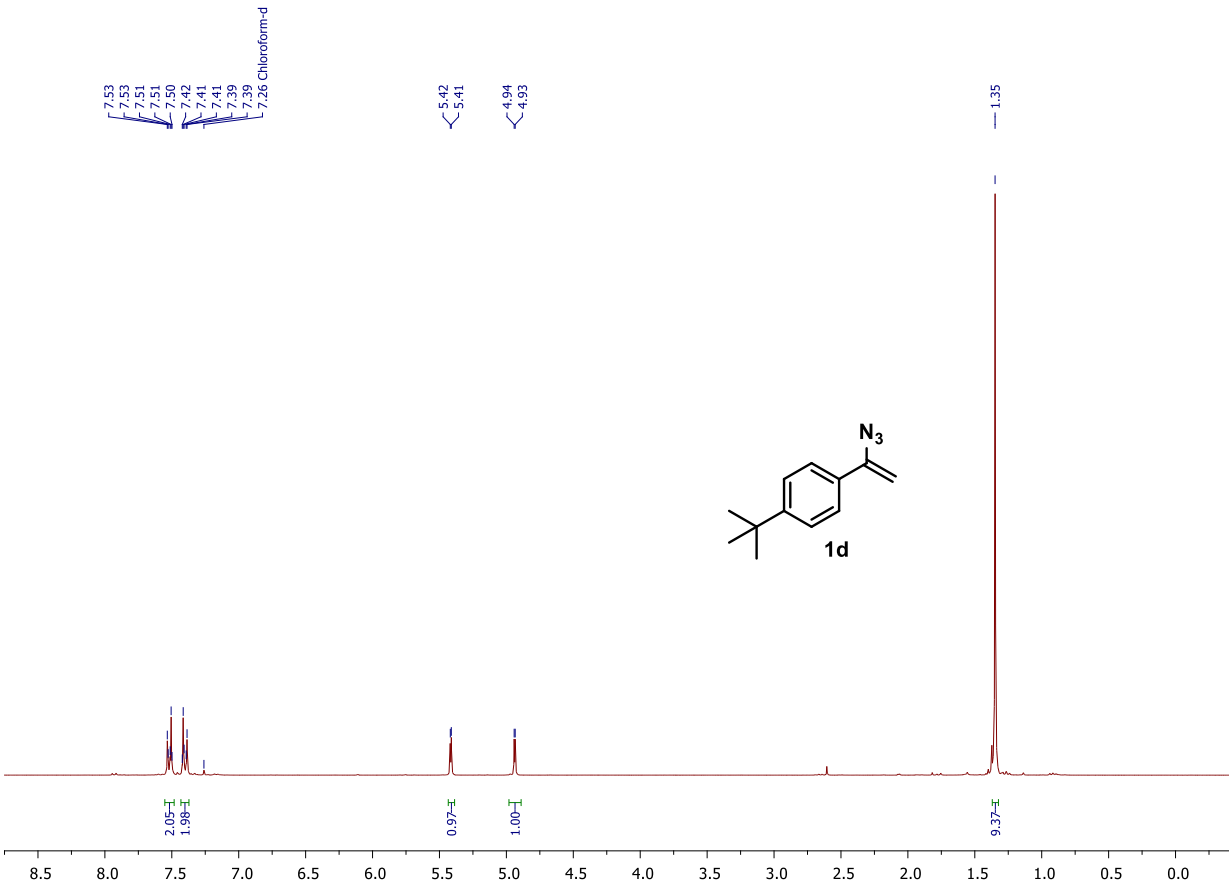
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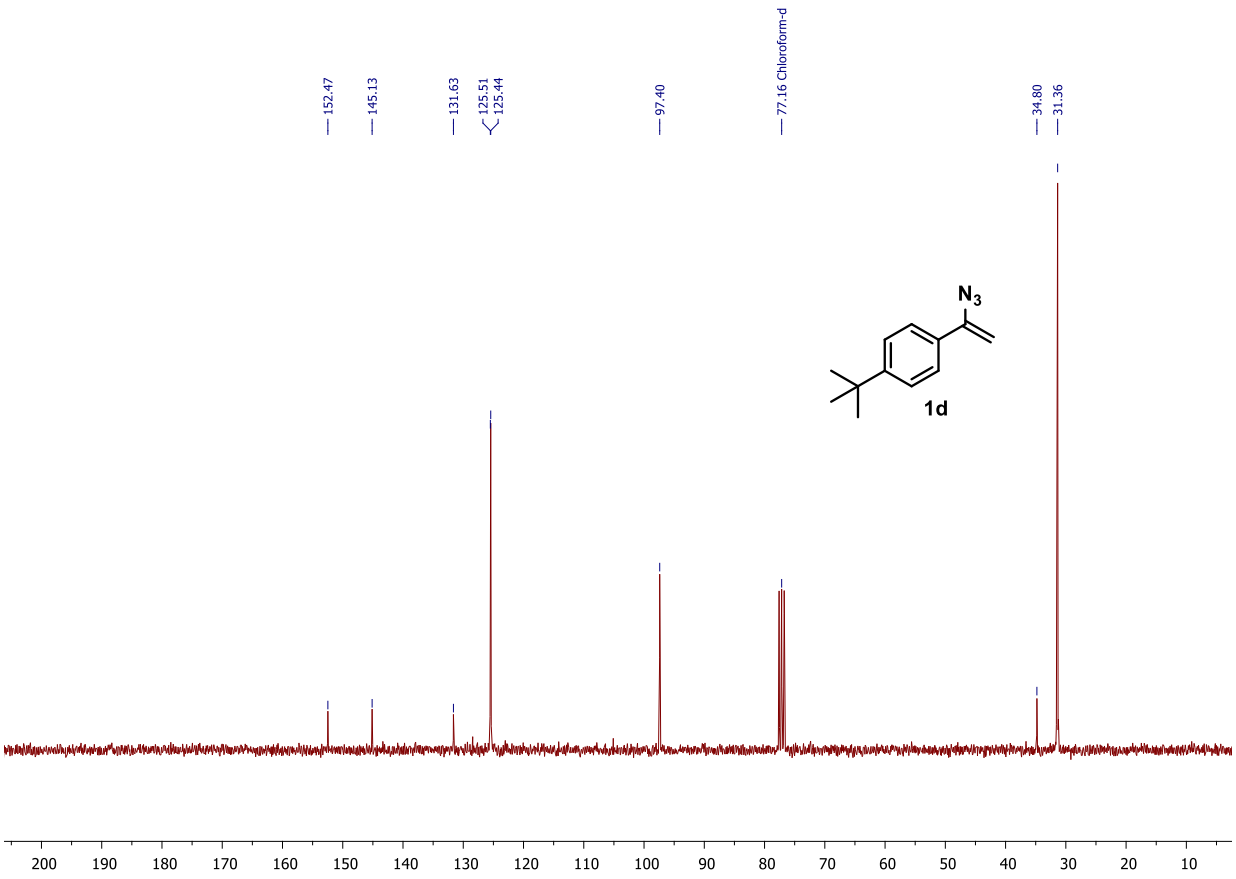
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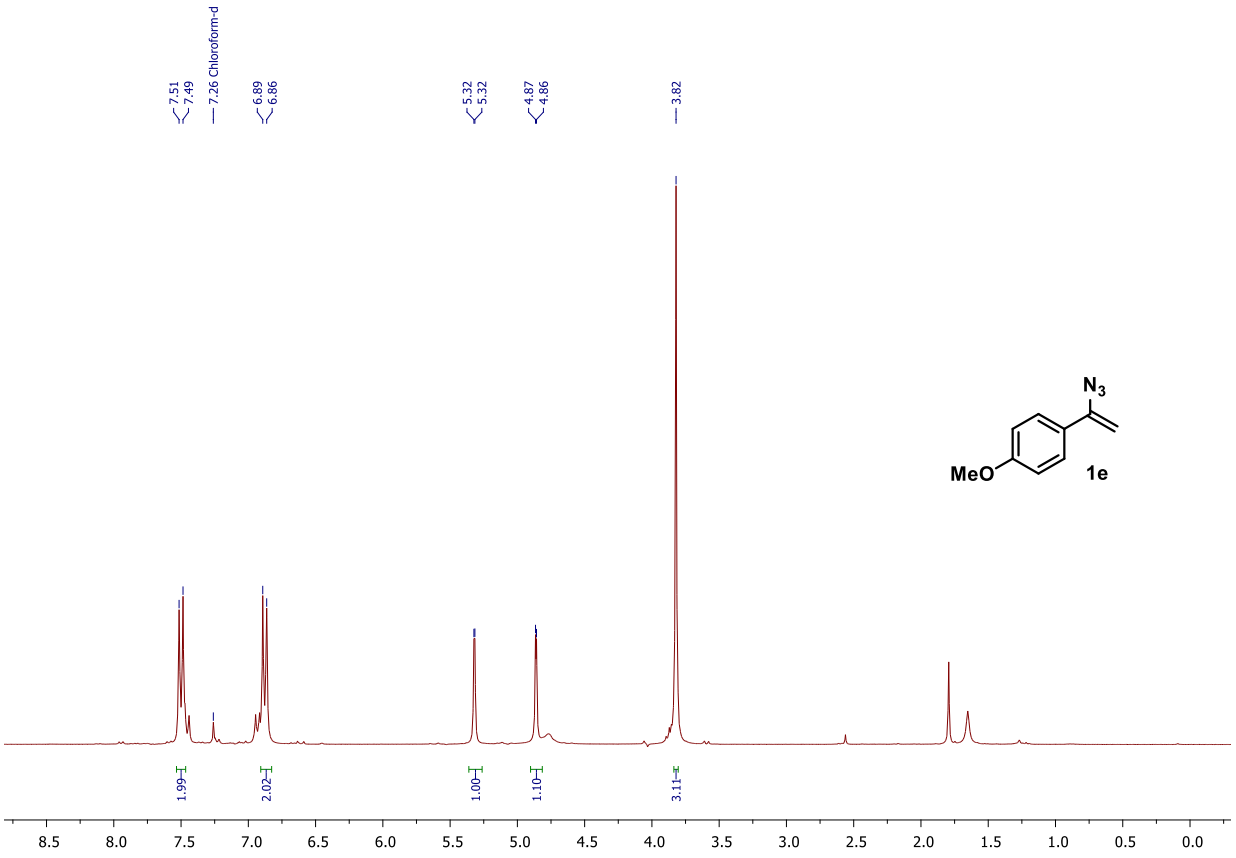
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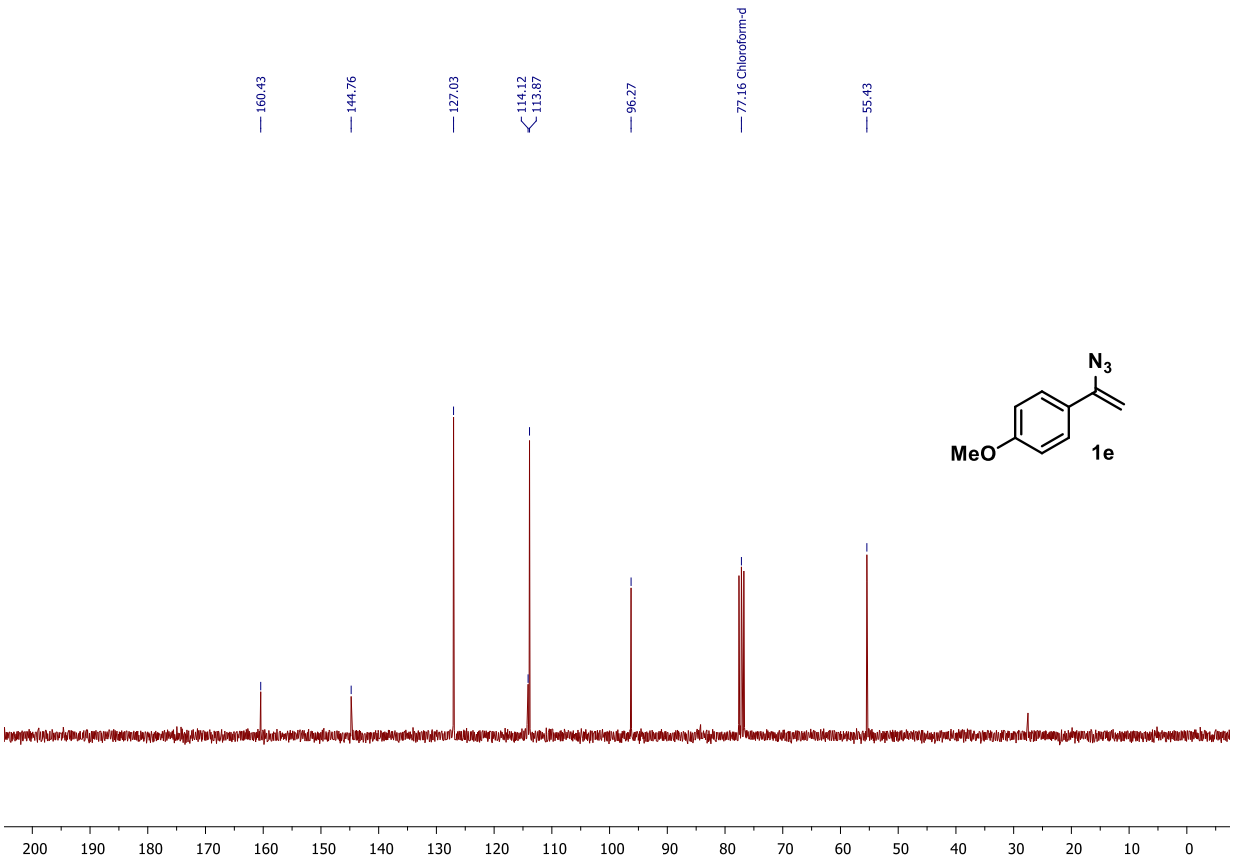
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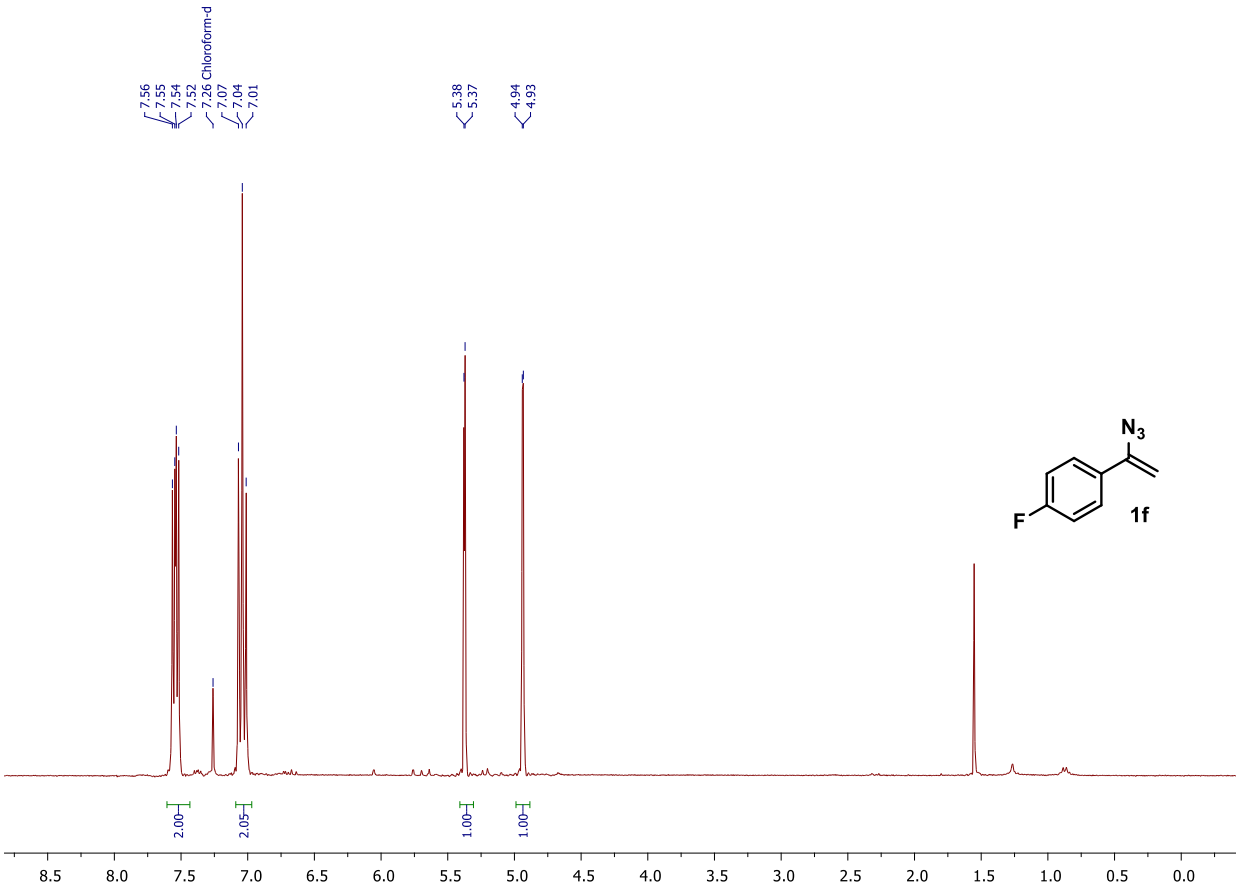
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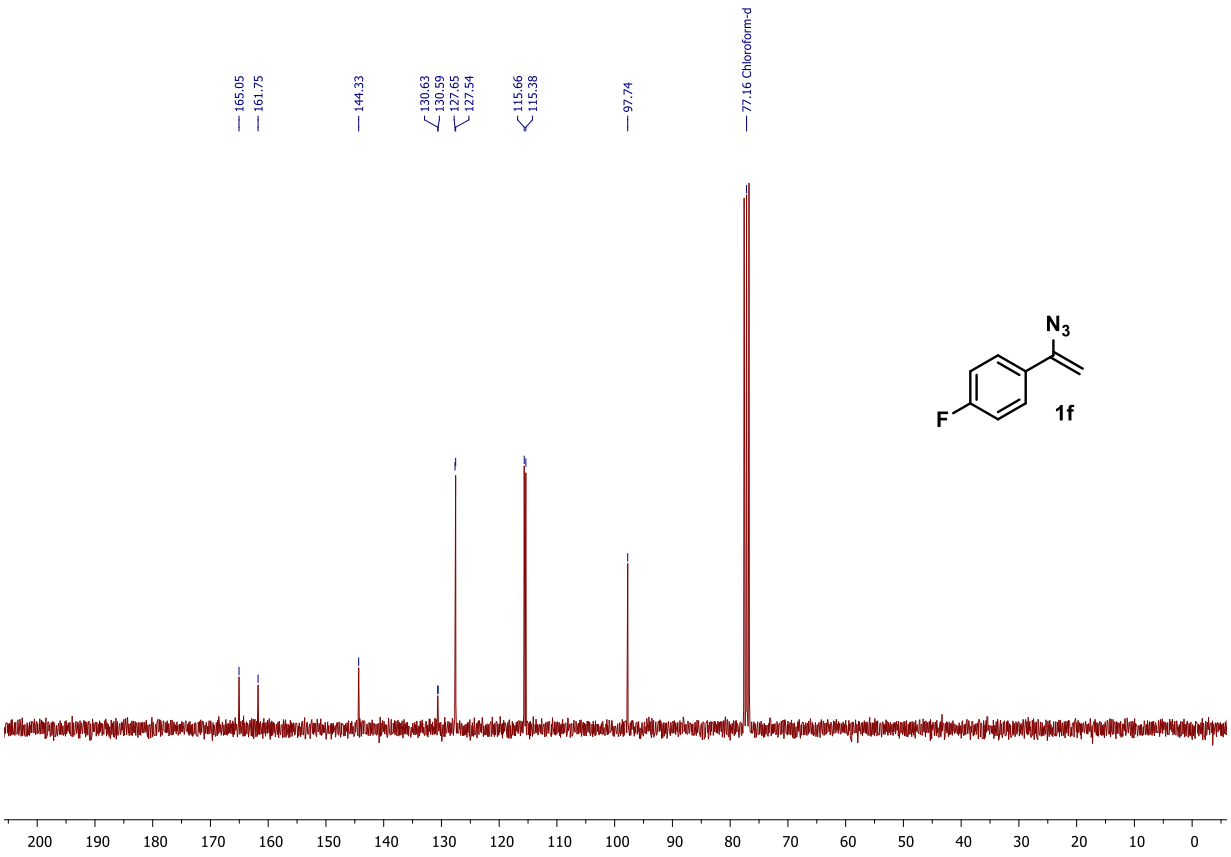
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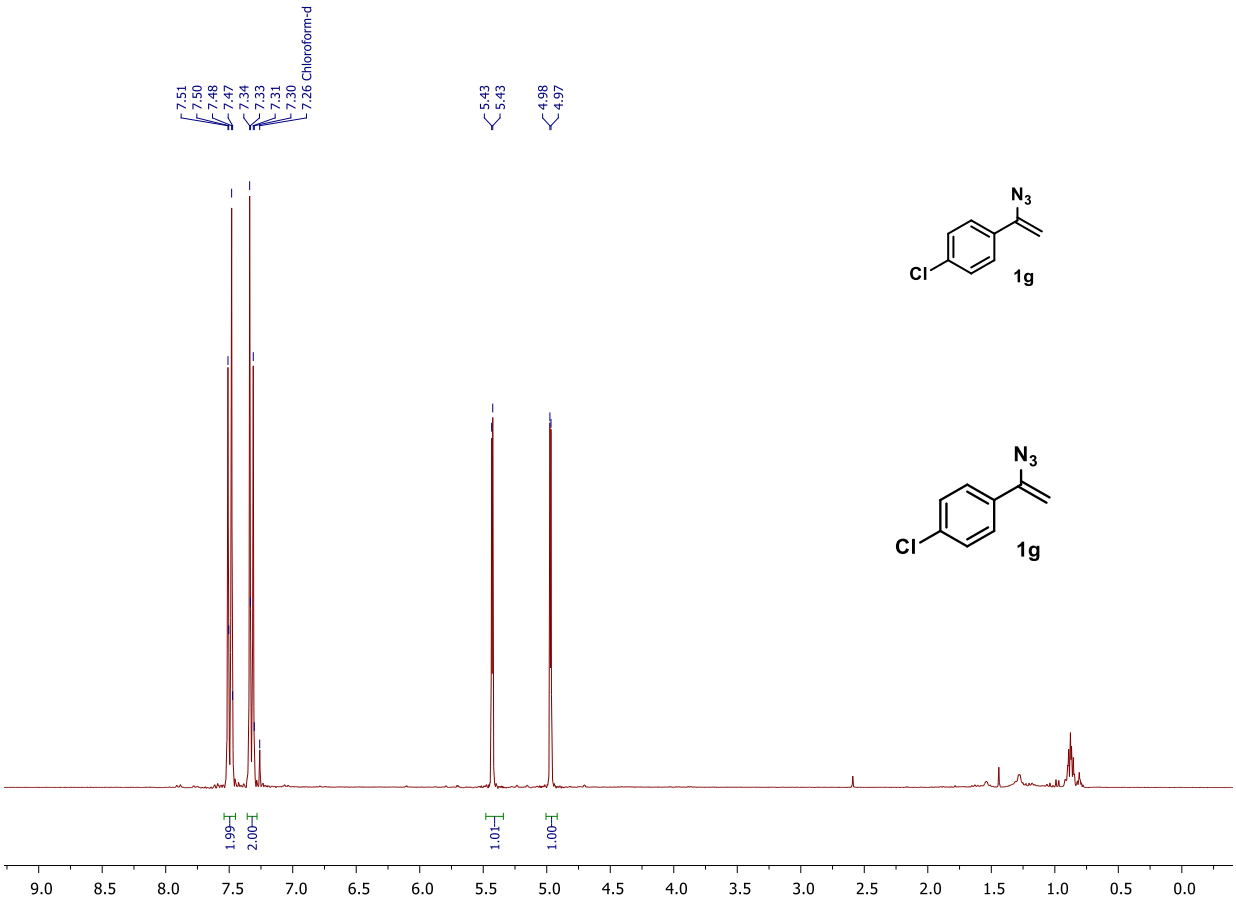
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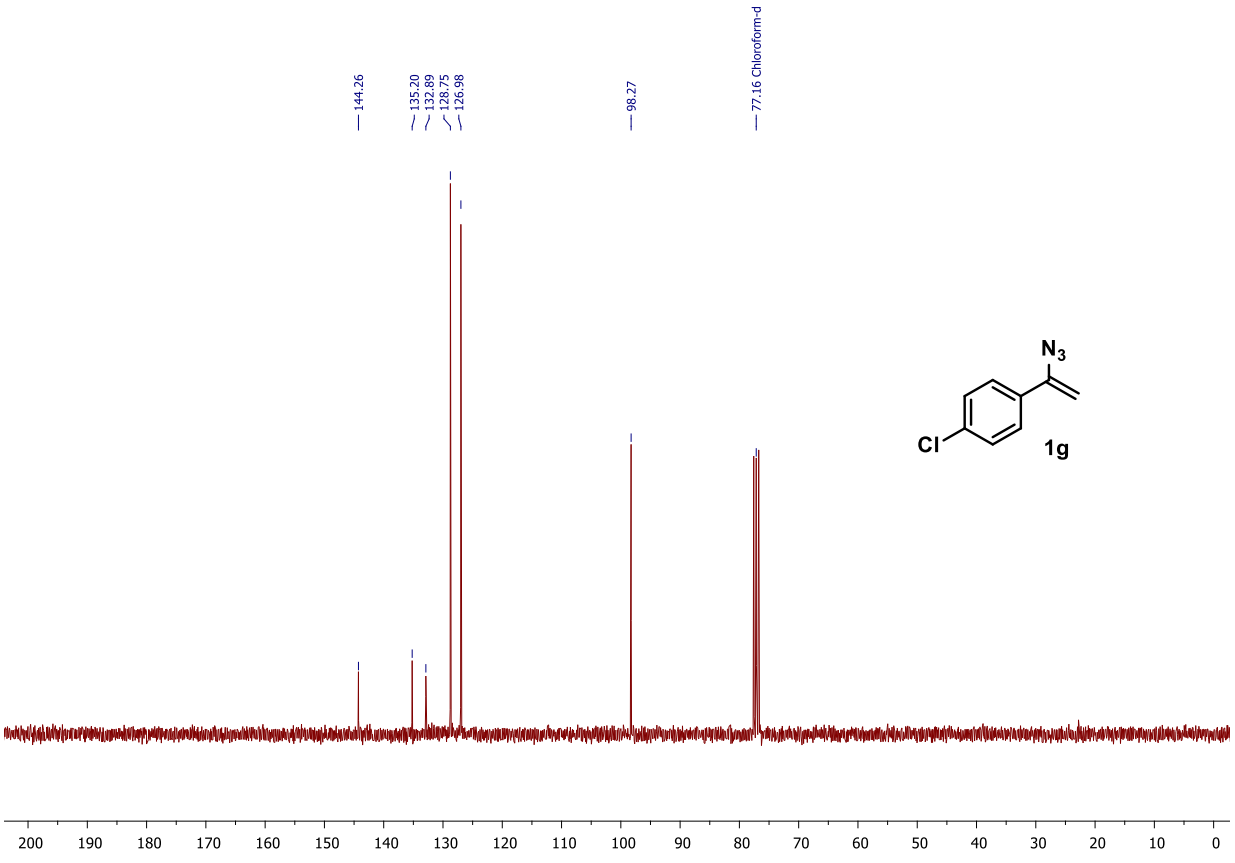
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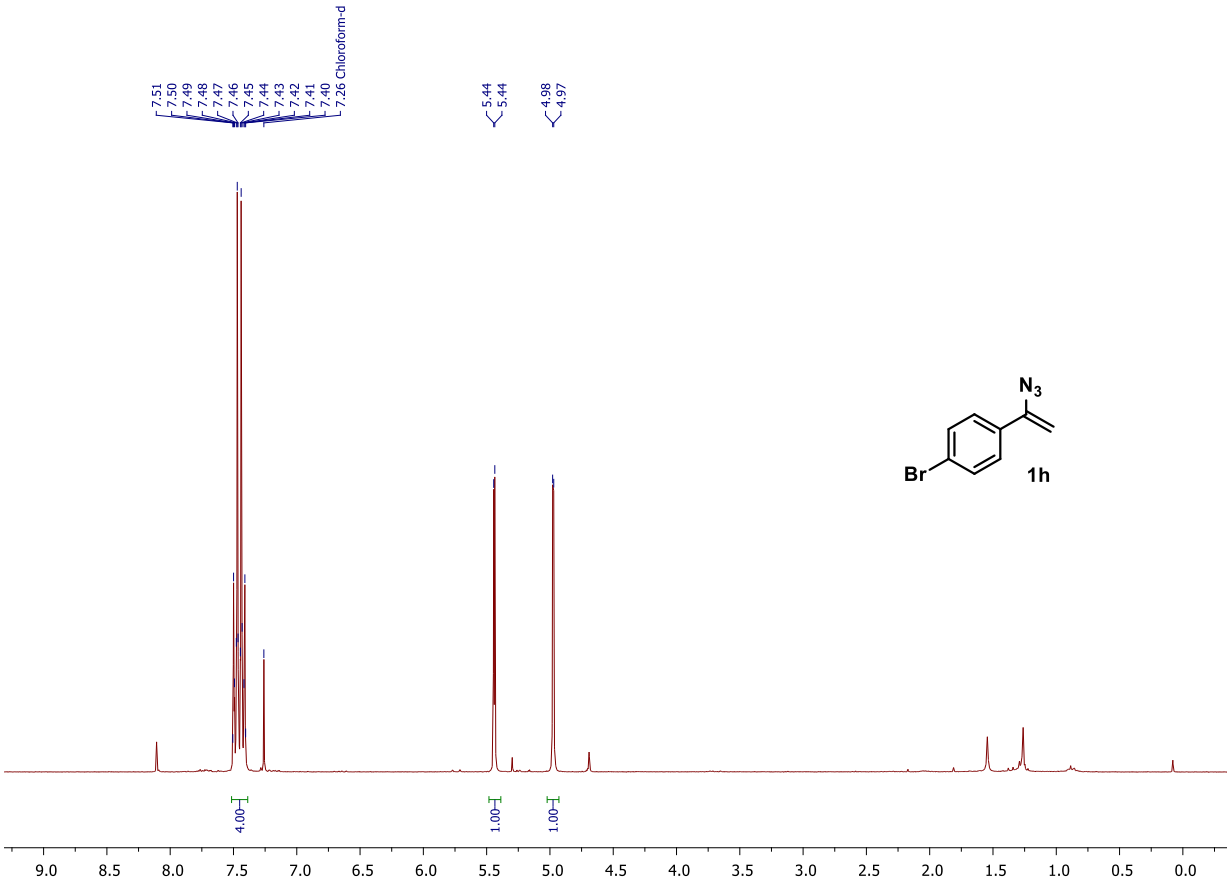
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1.00
1.00
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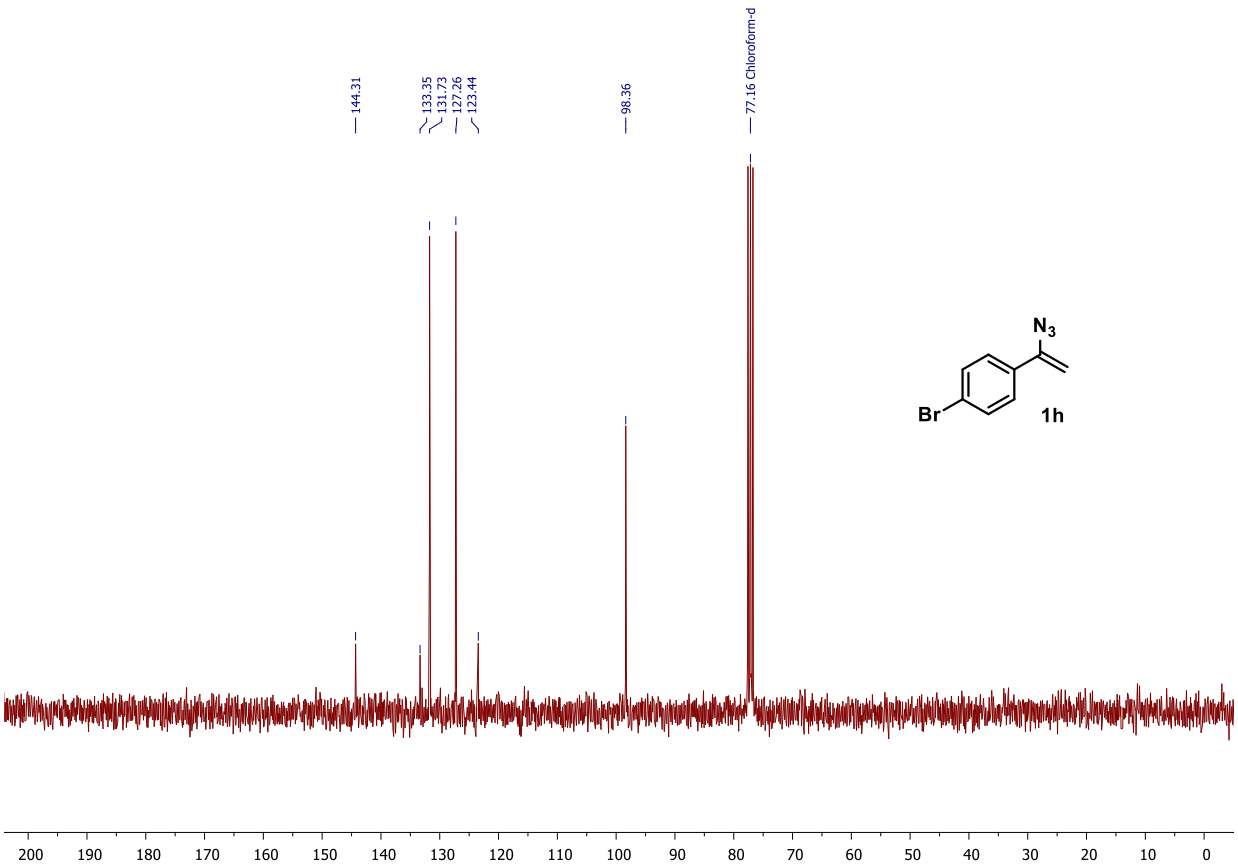
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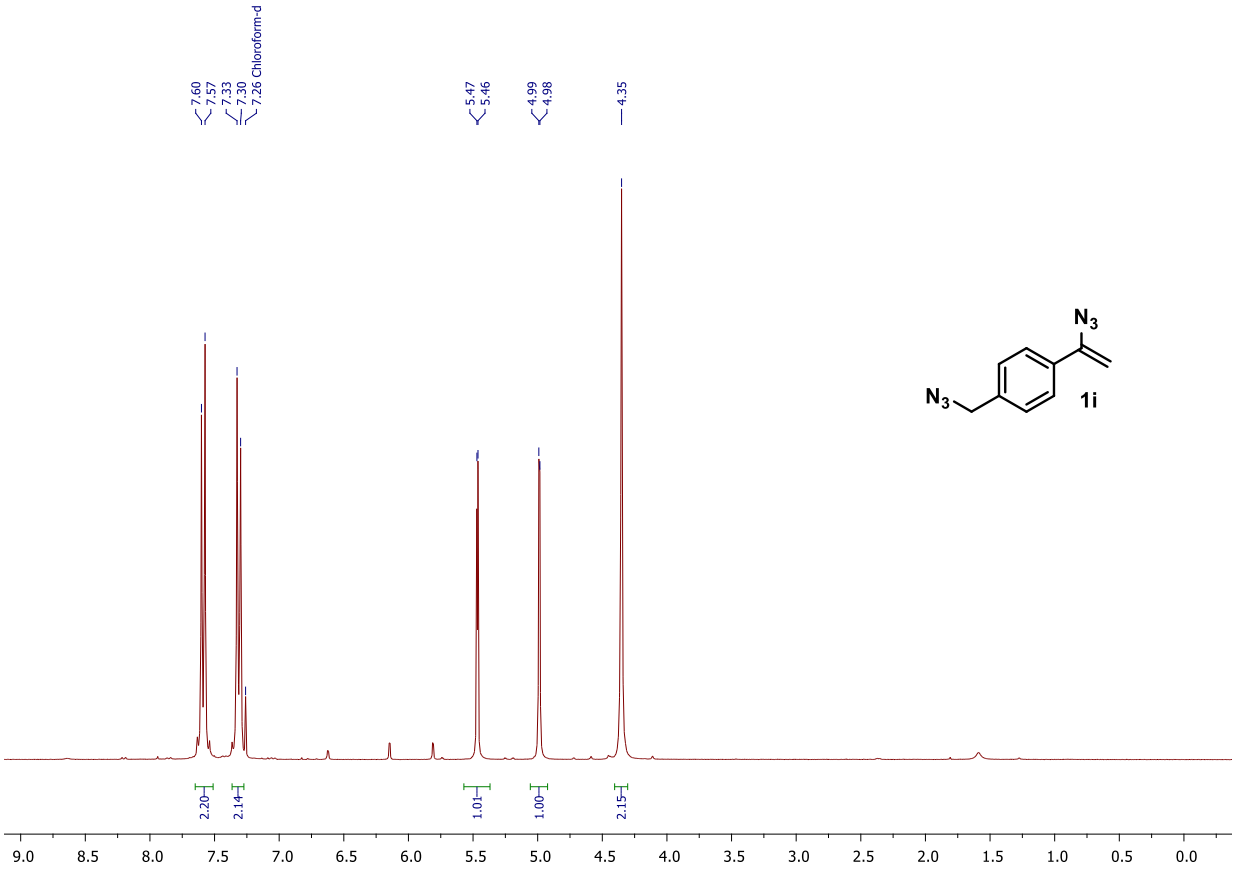
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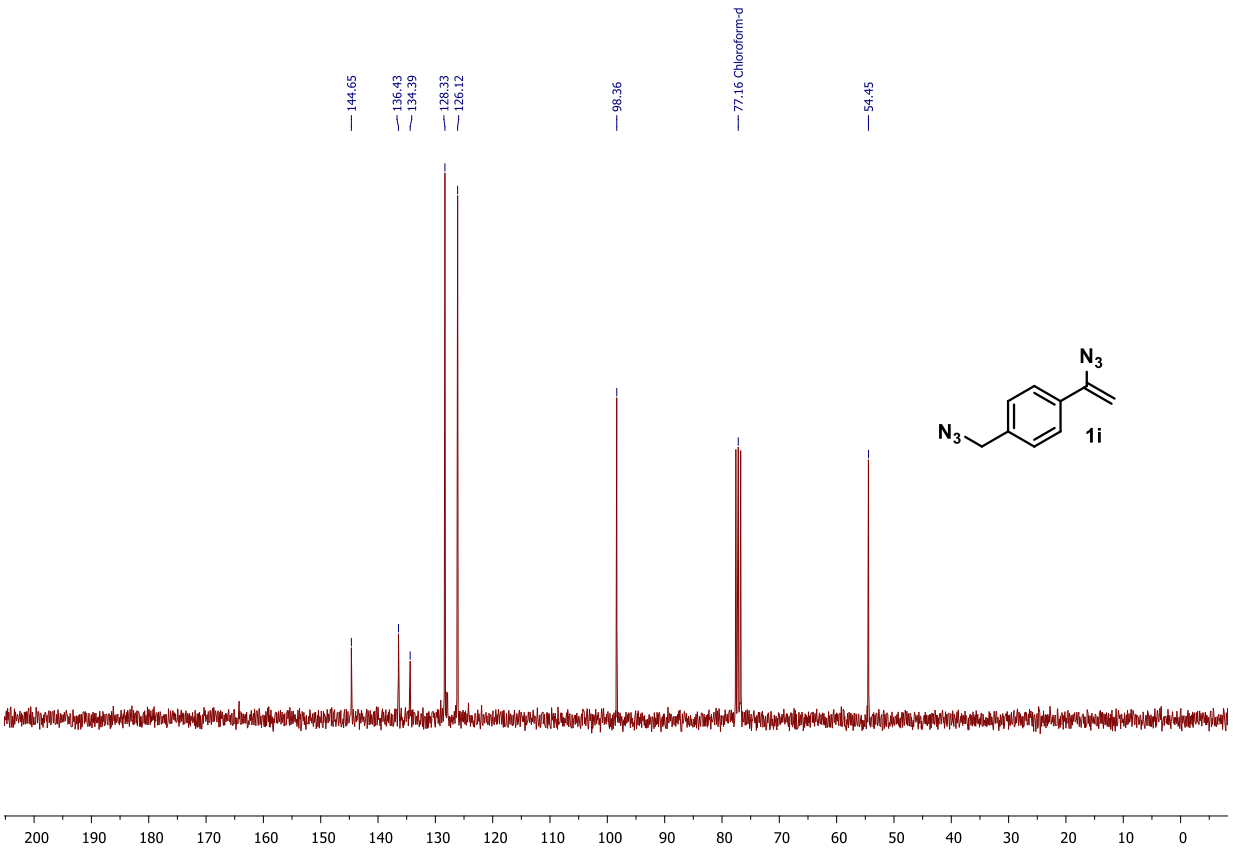
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N3
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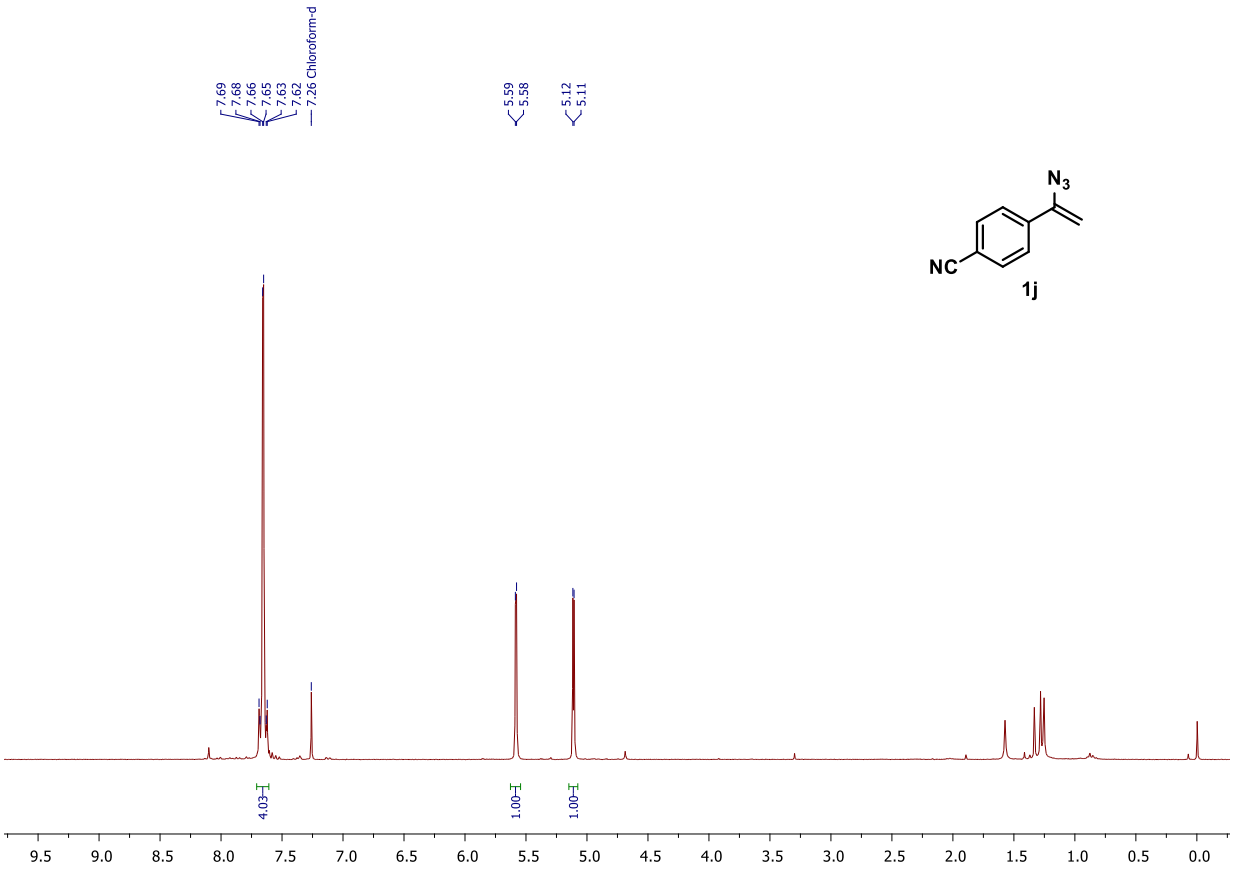
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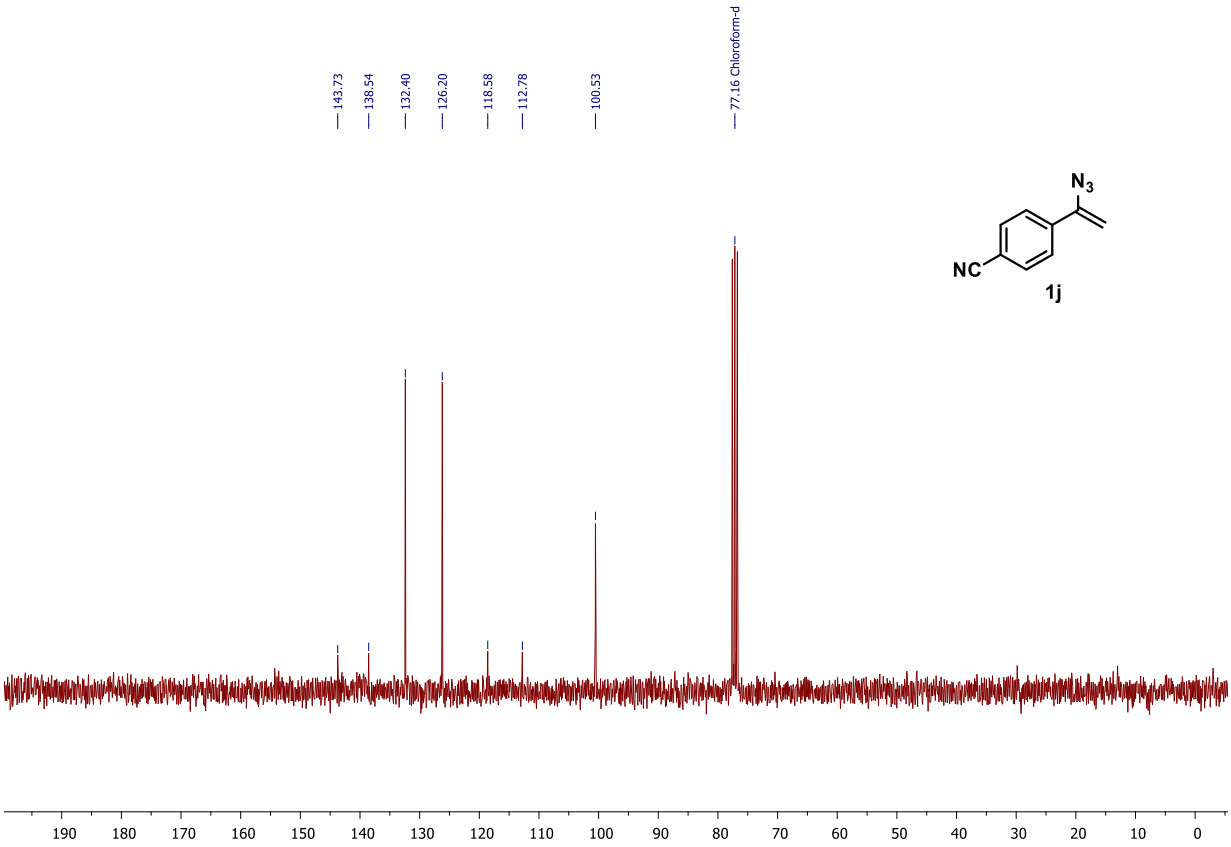
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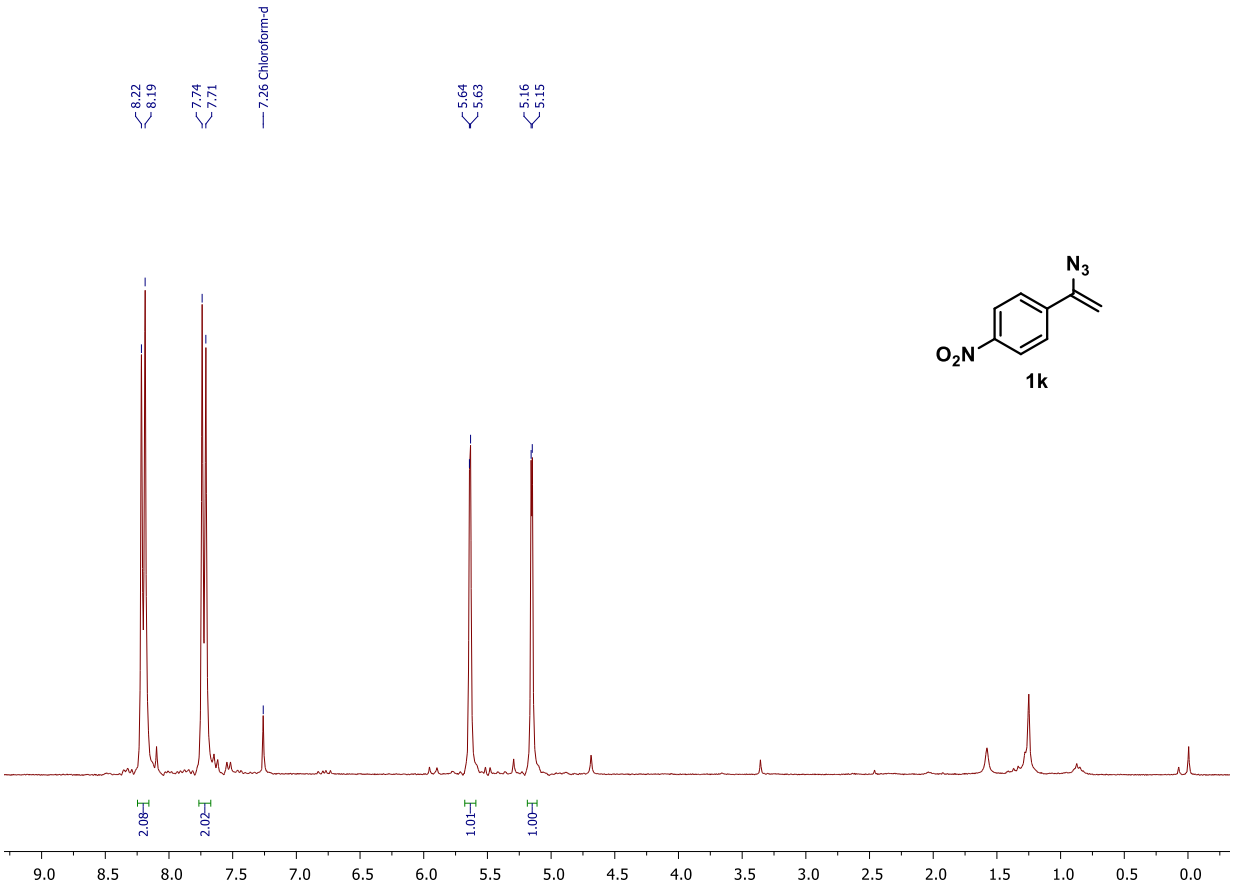
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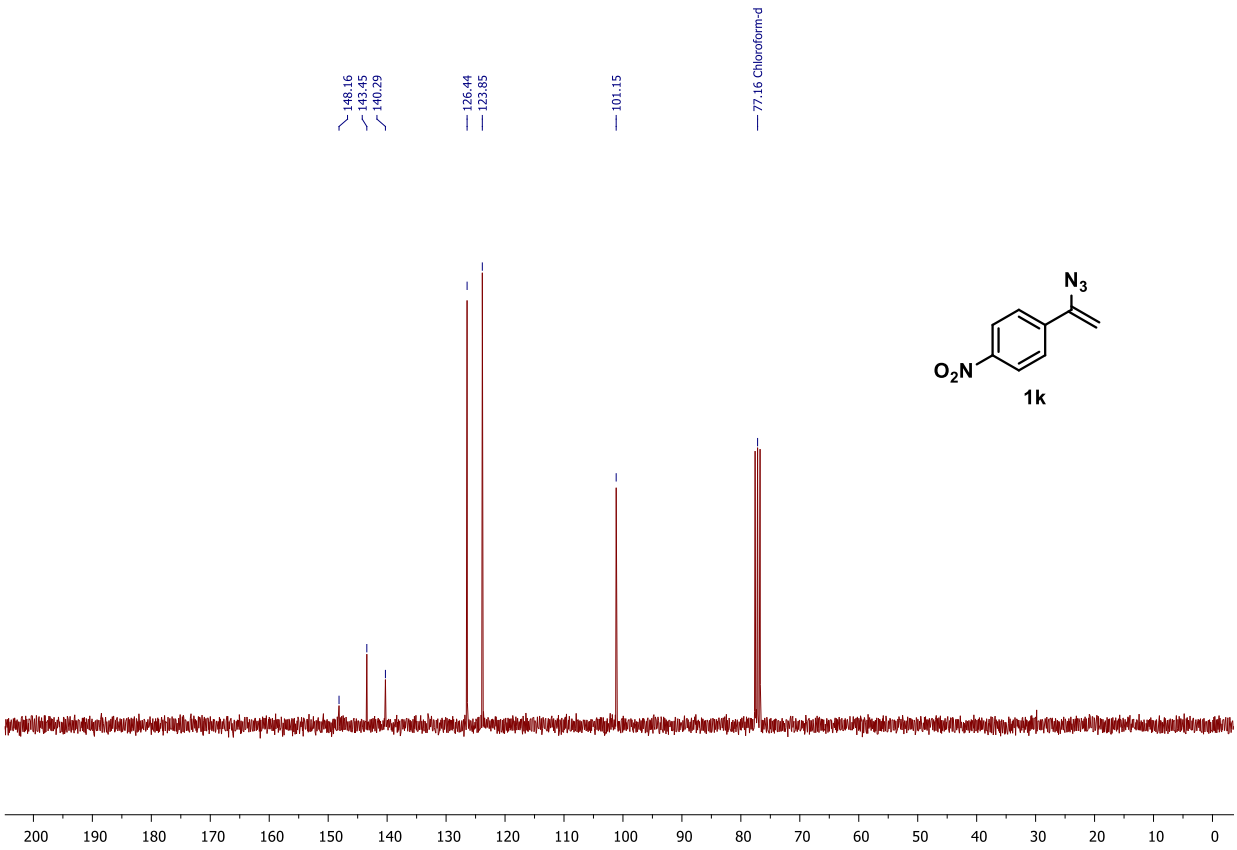
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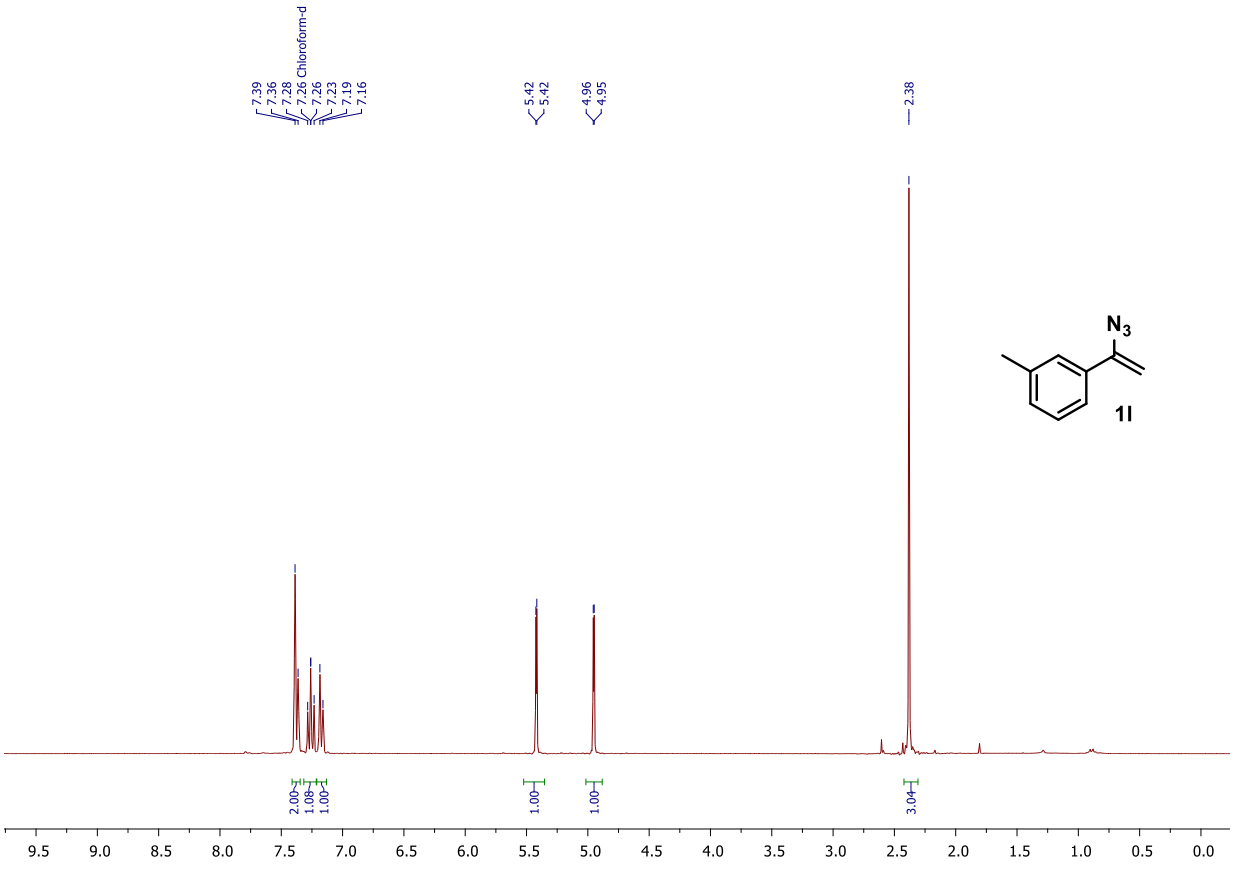
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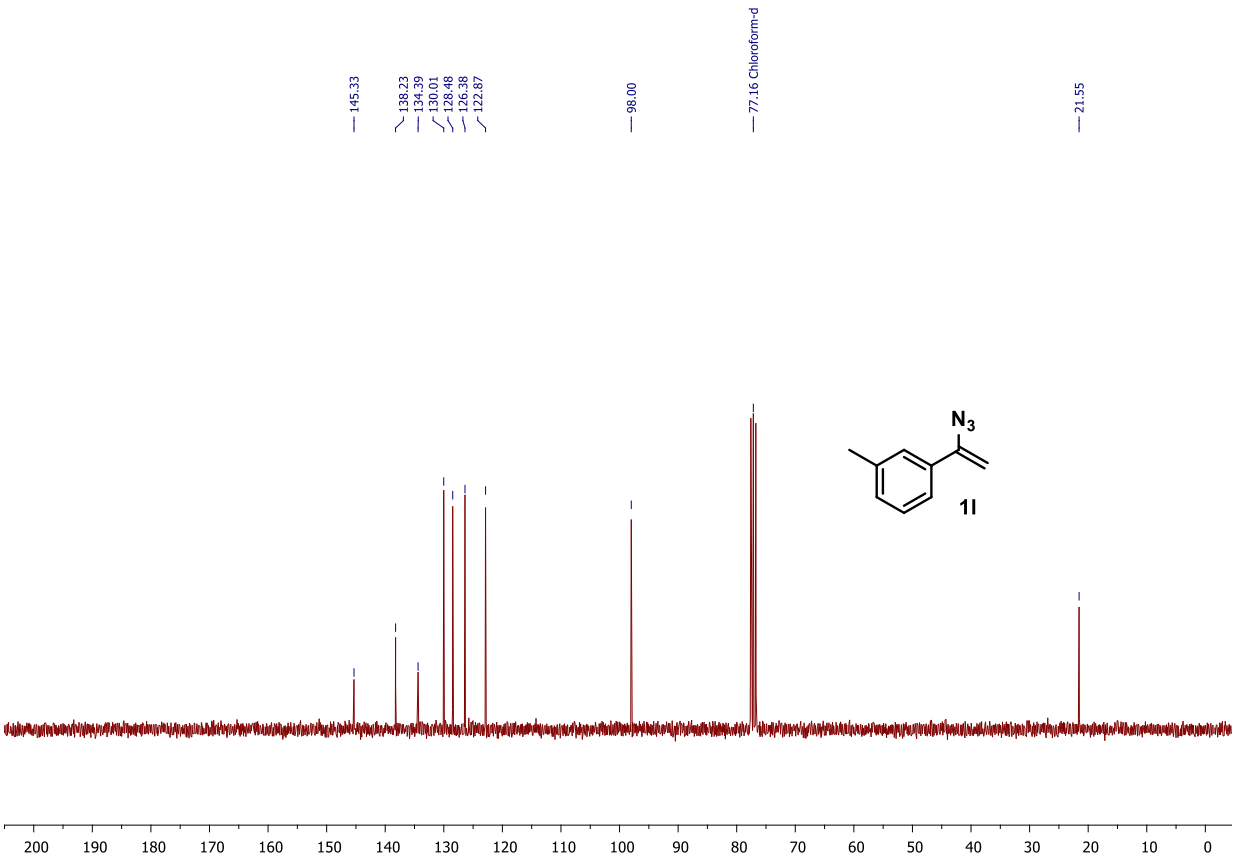
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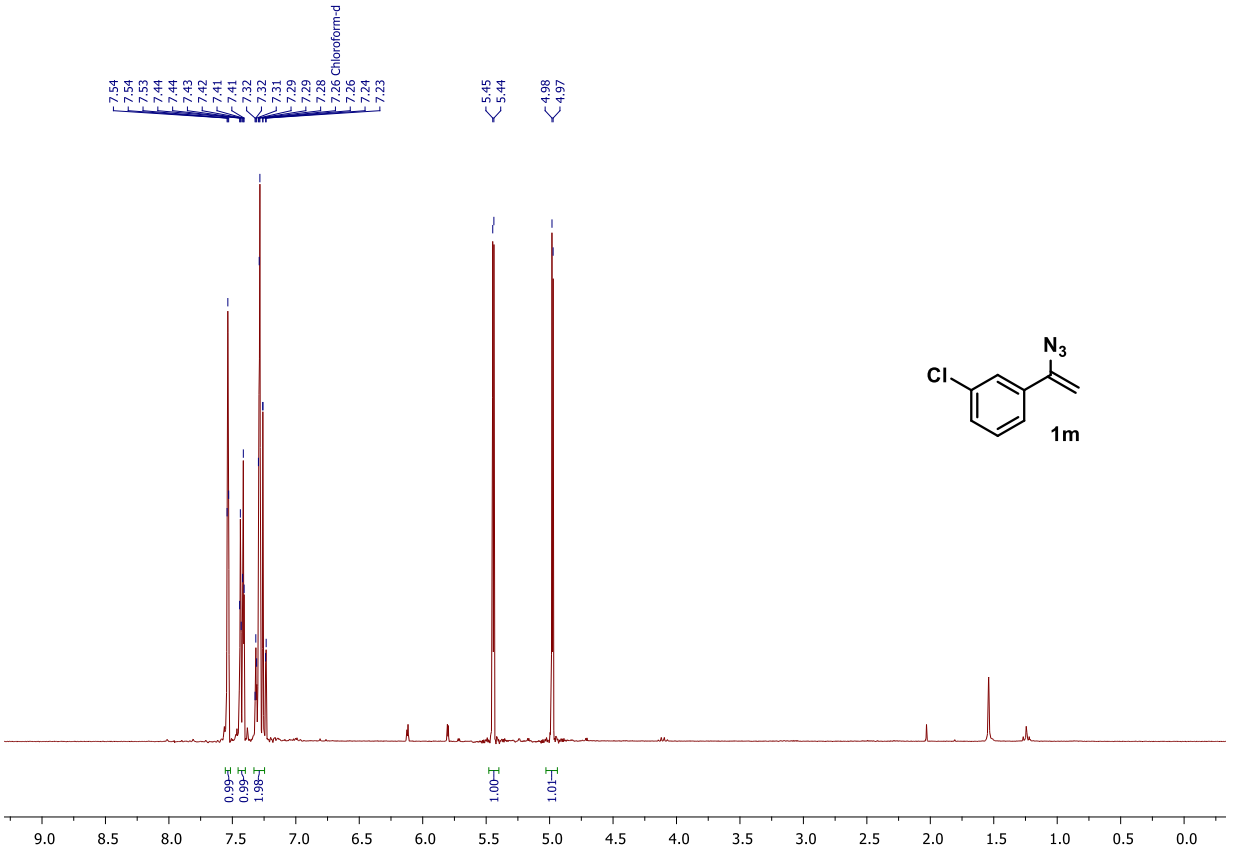
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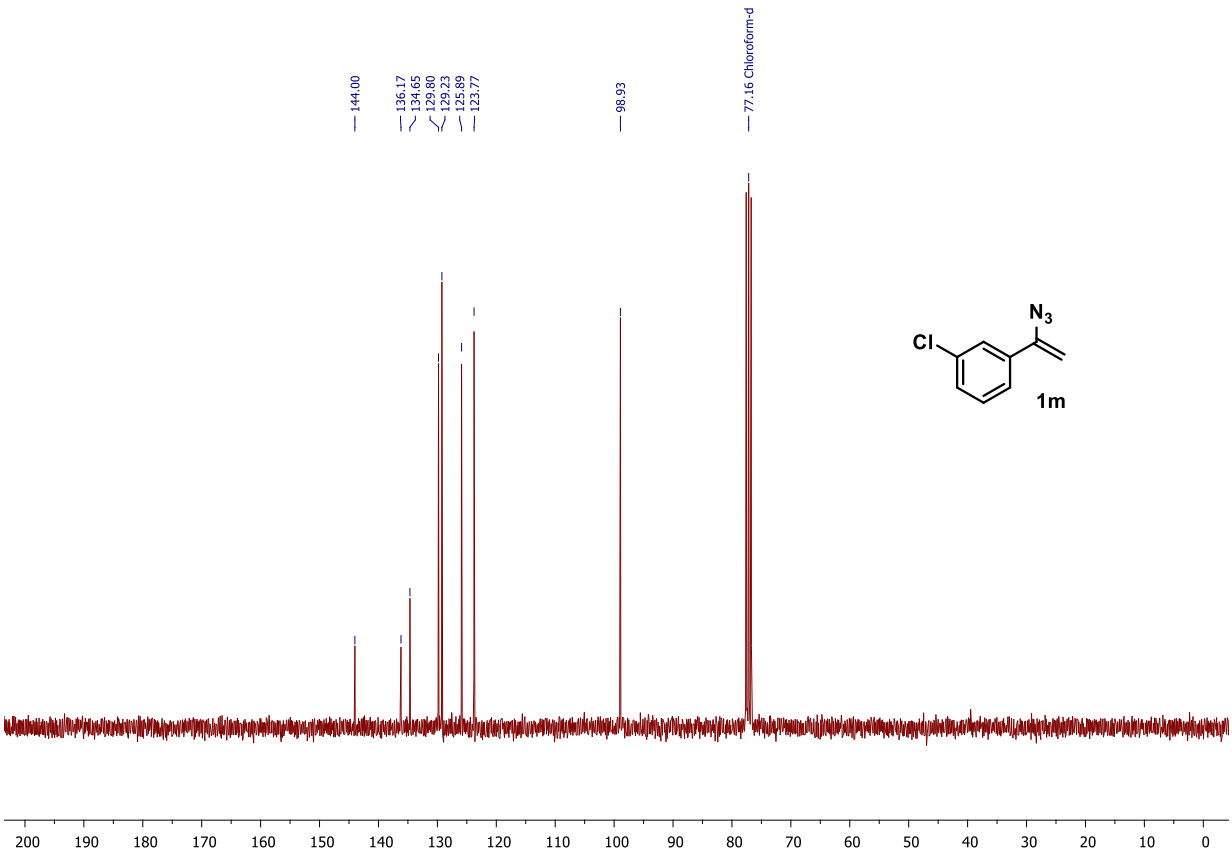
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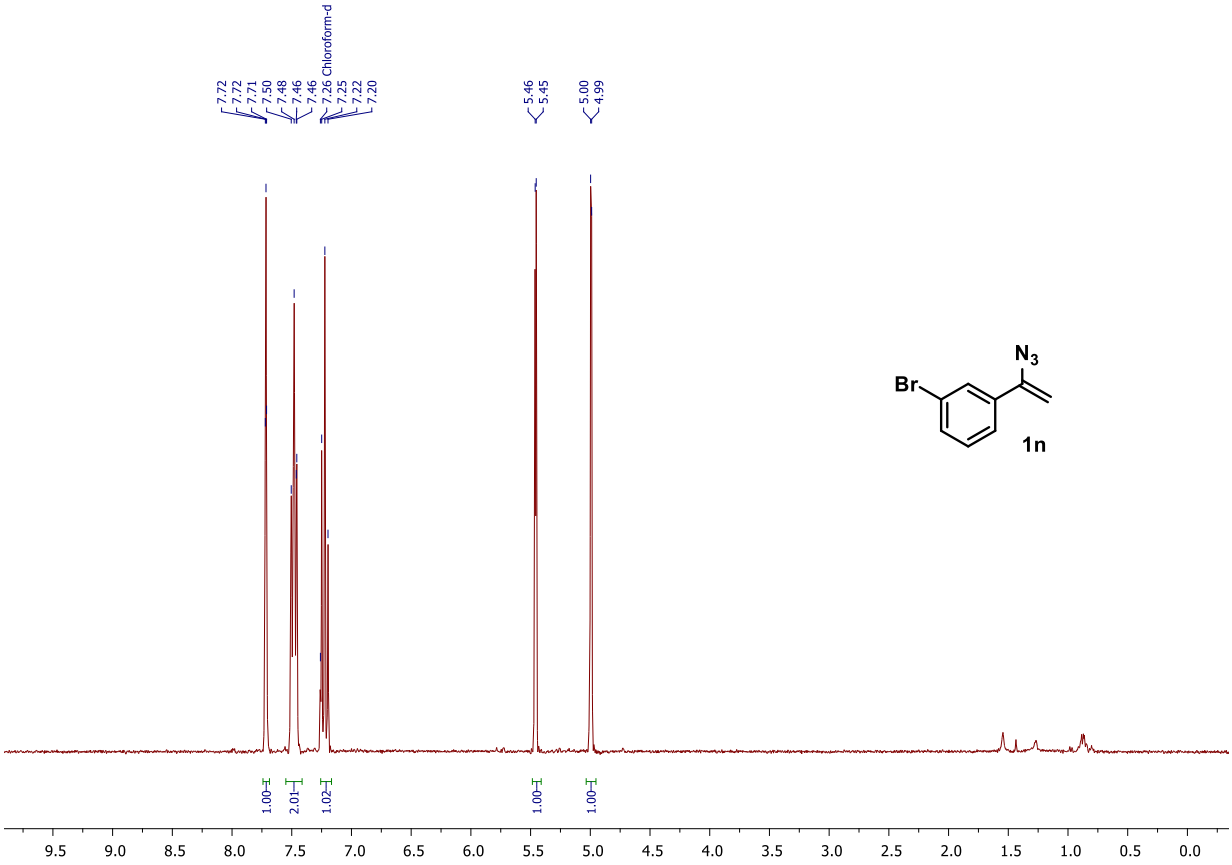
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1.00
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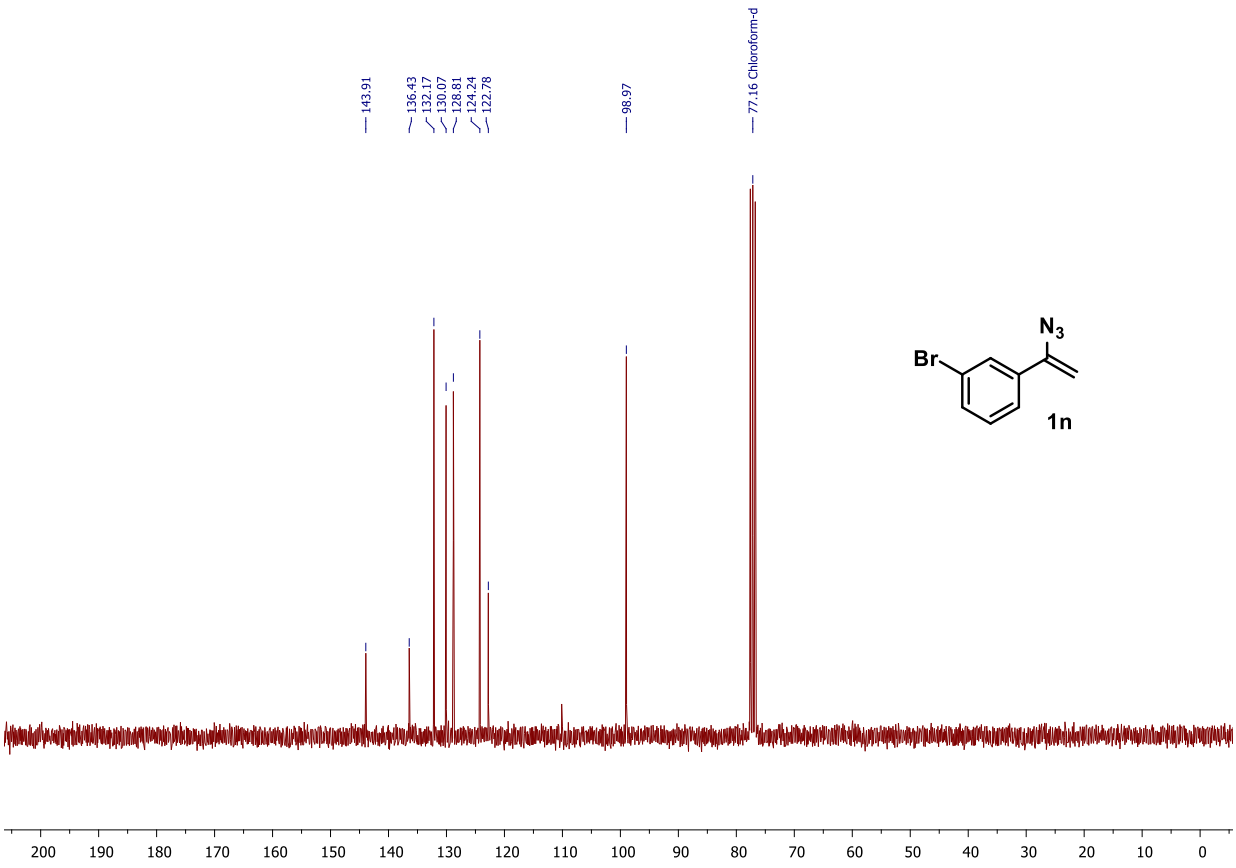
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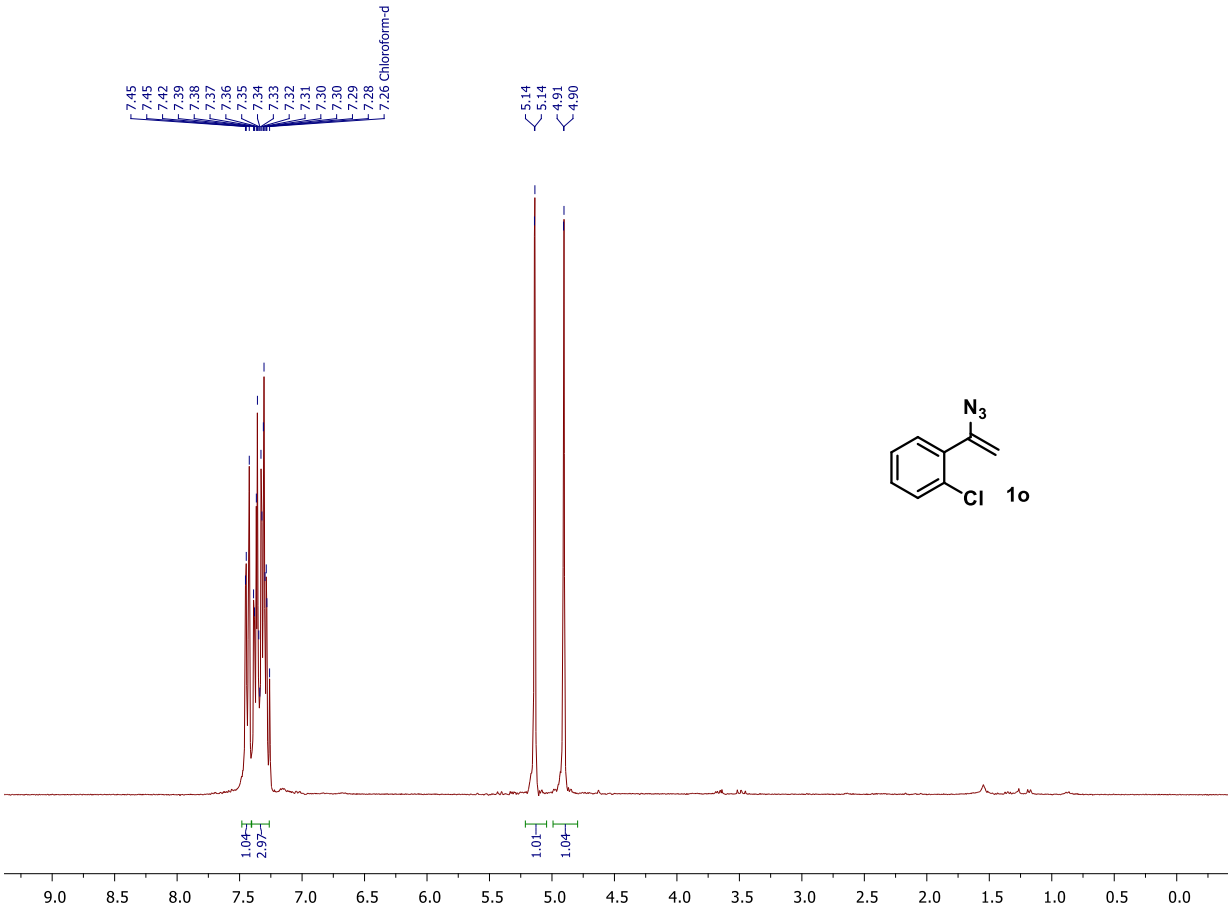
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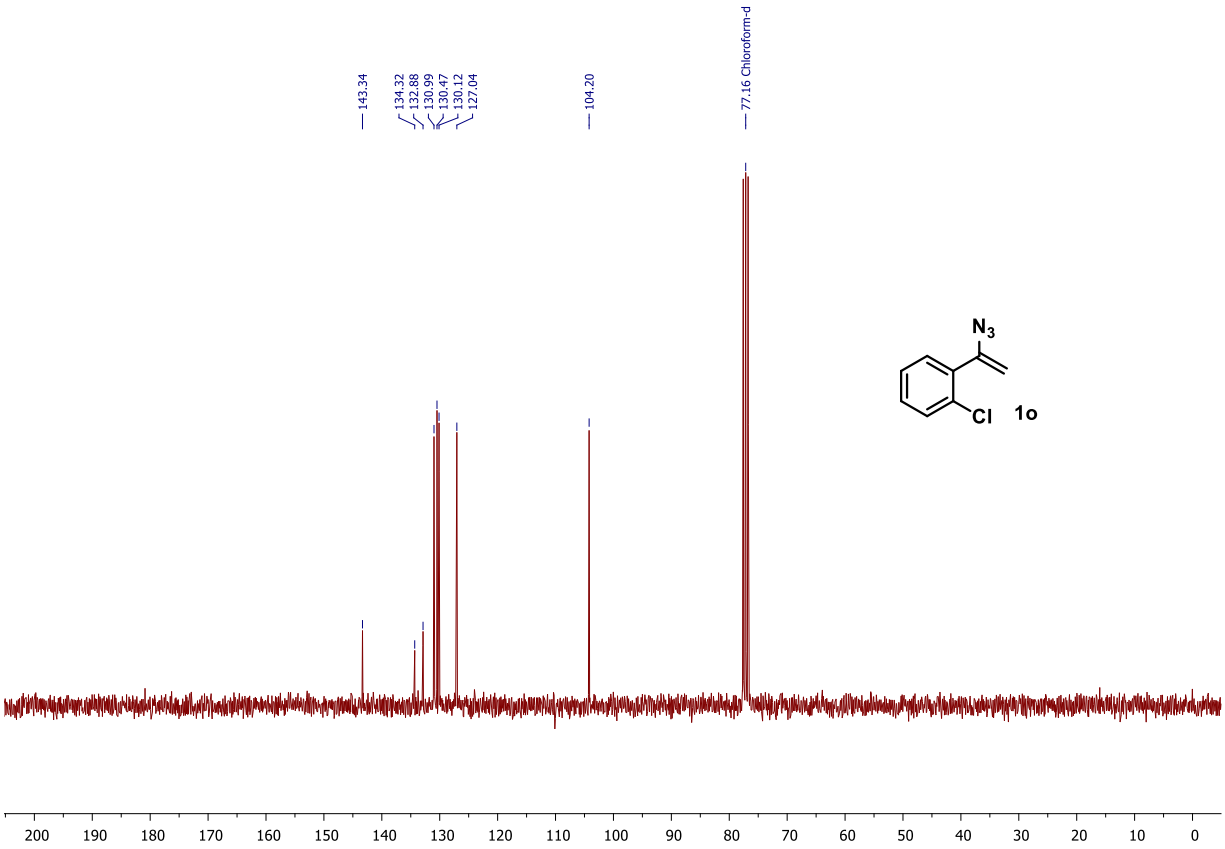
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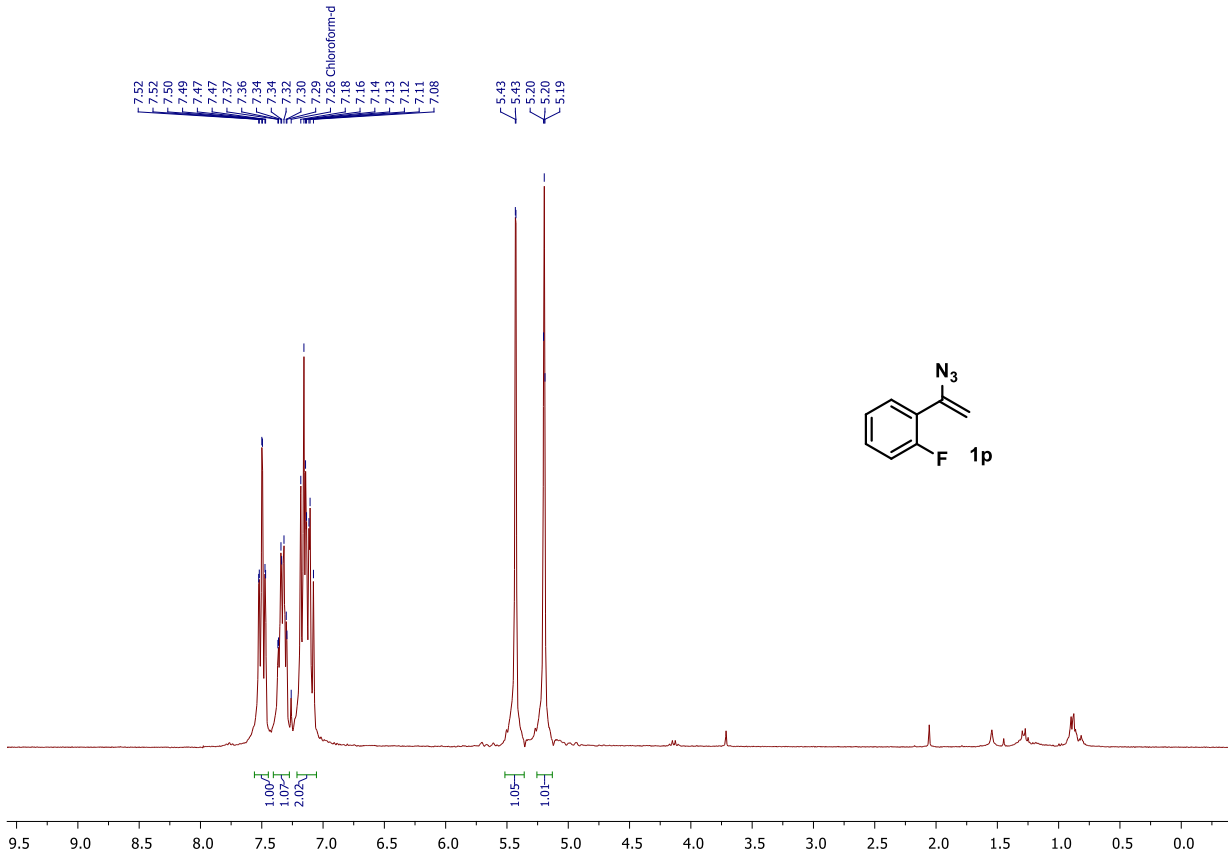
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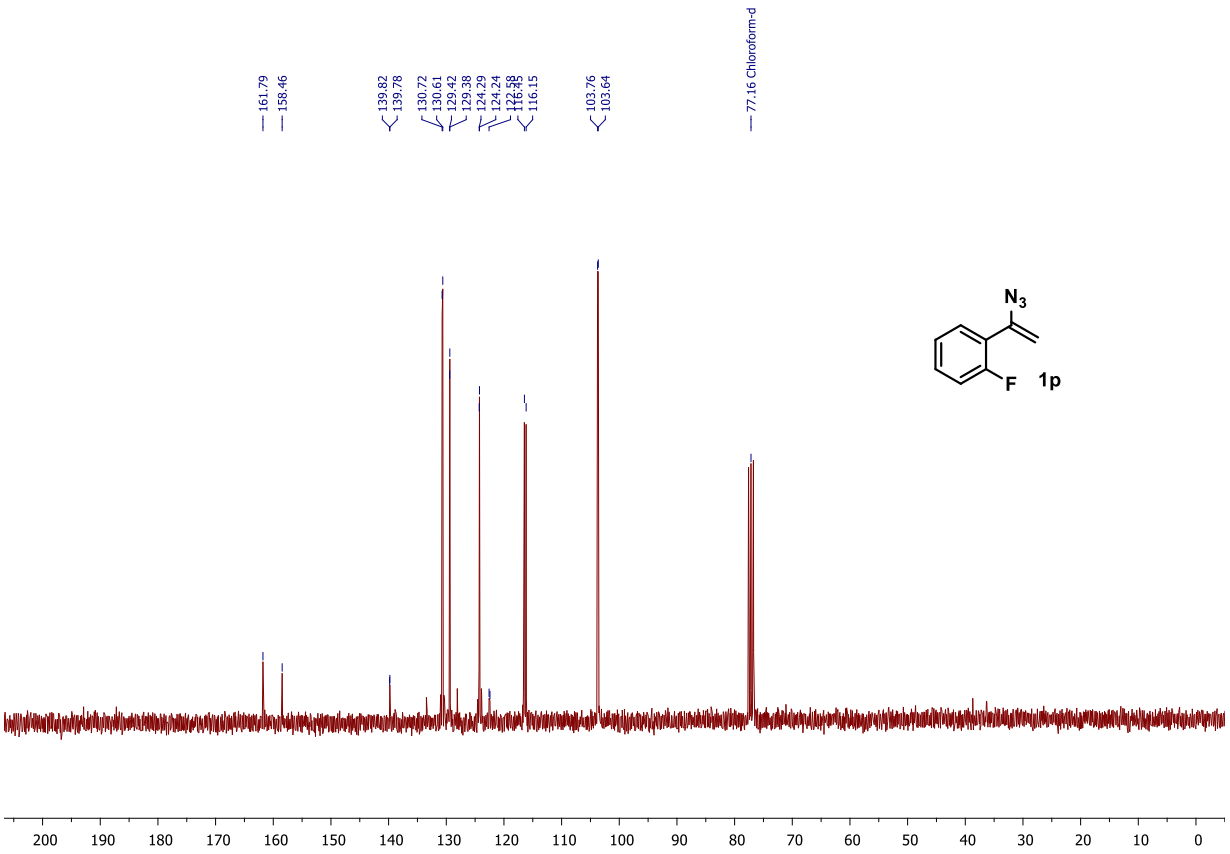
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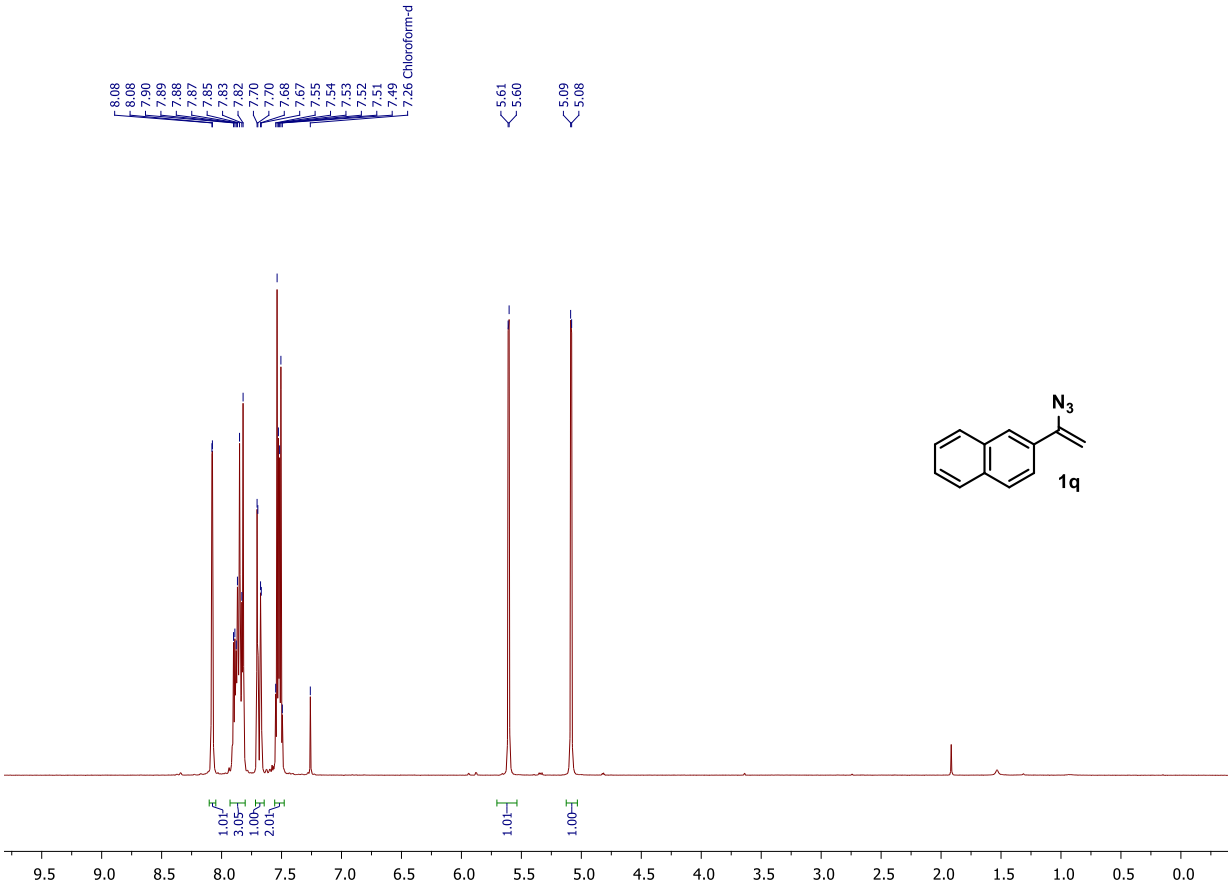
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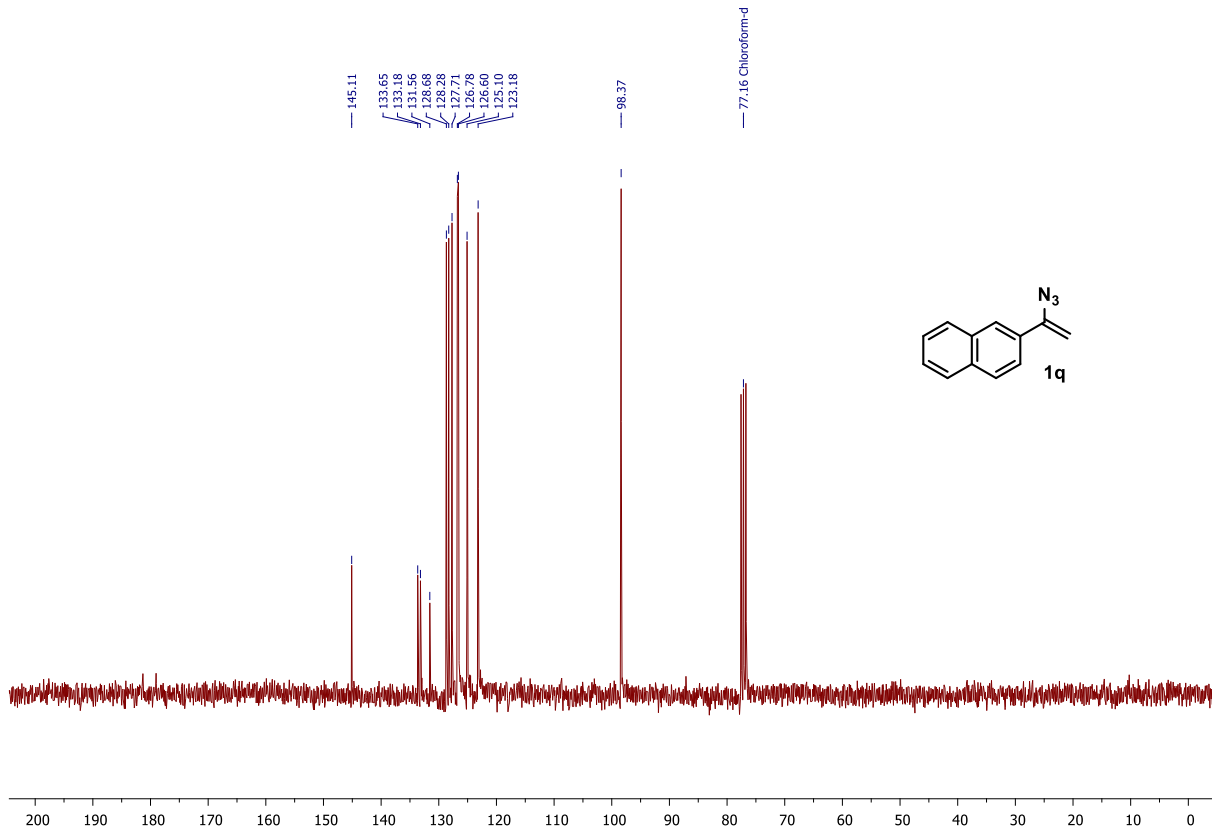
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N3
1q
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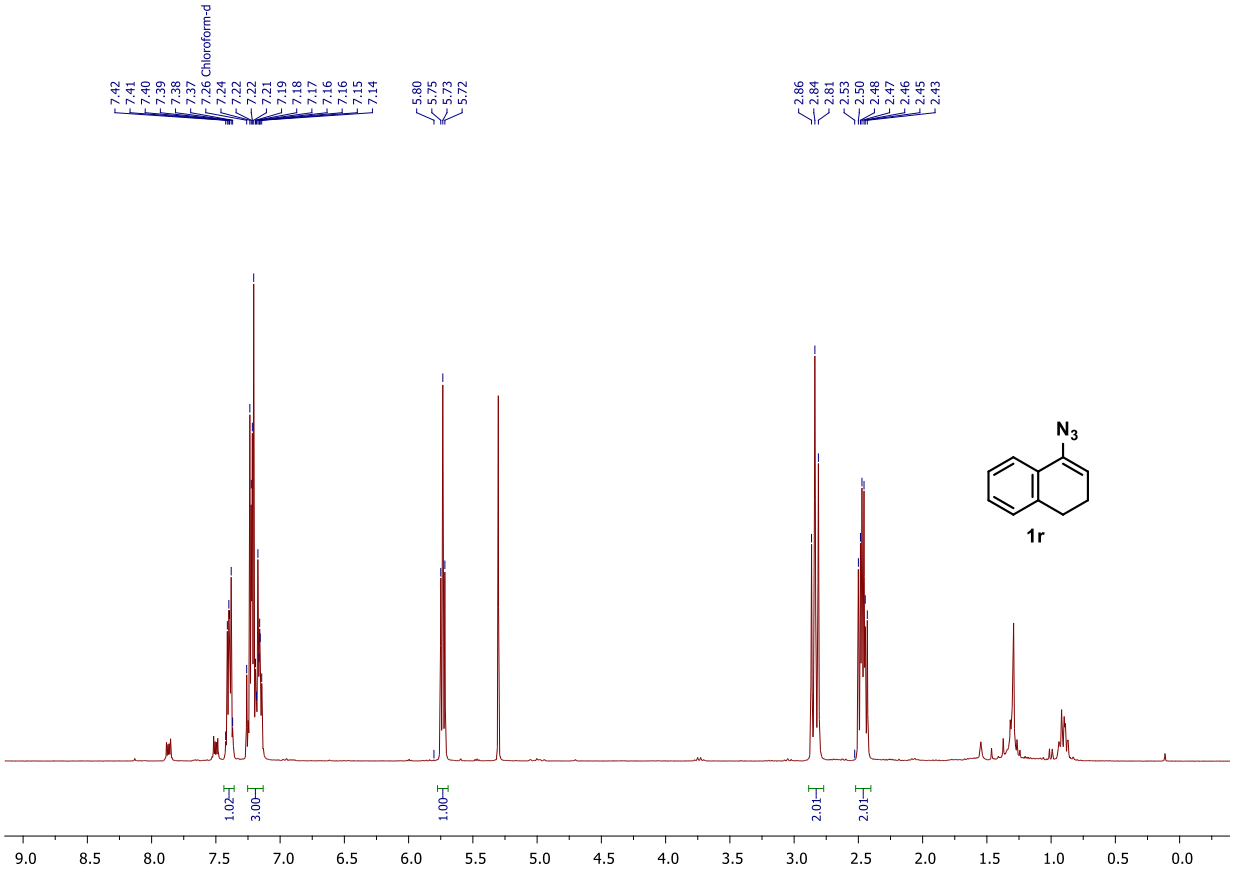
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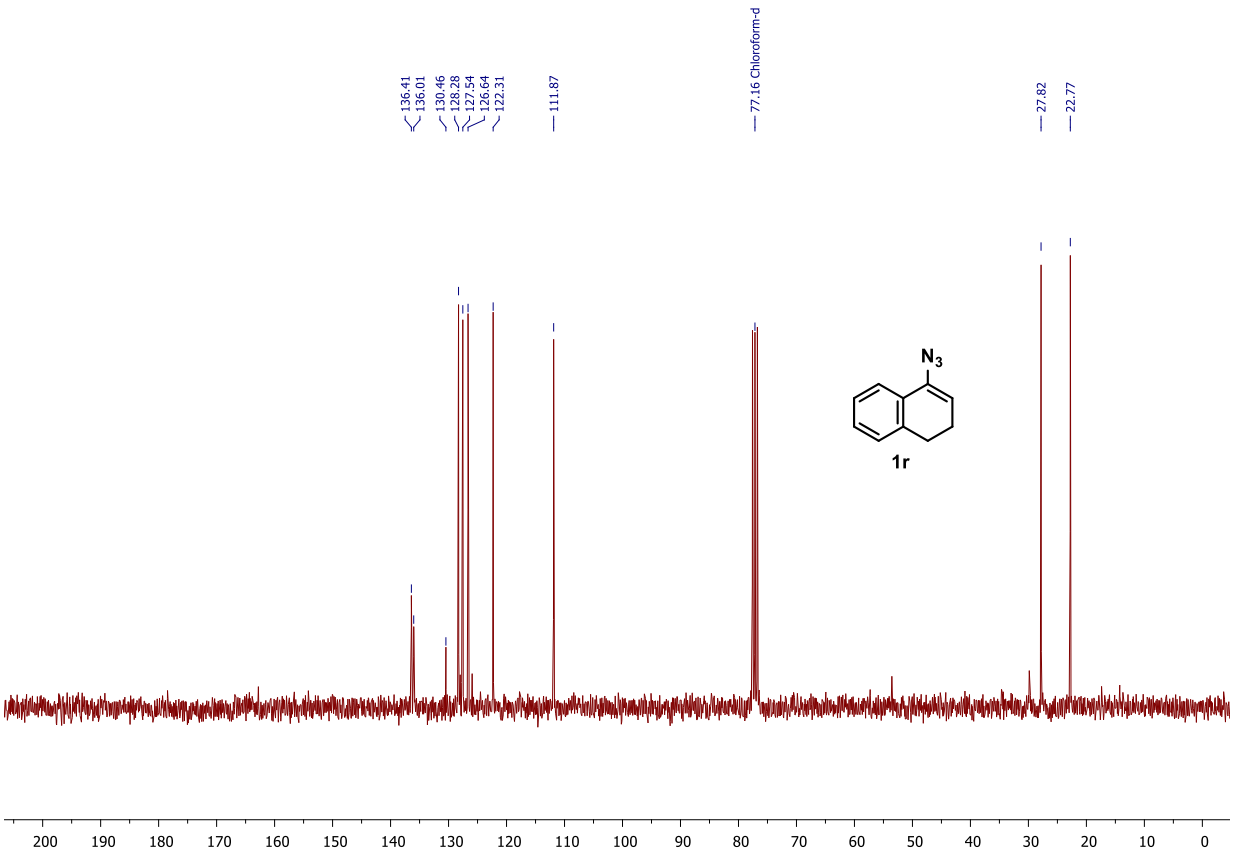
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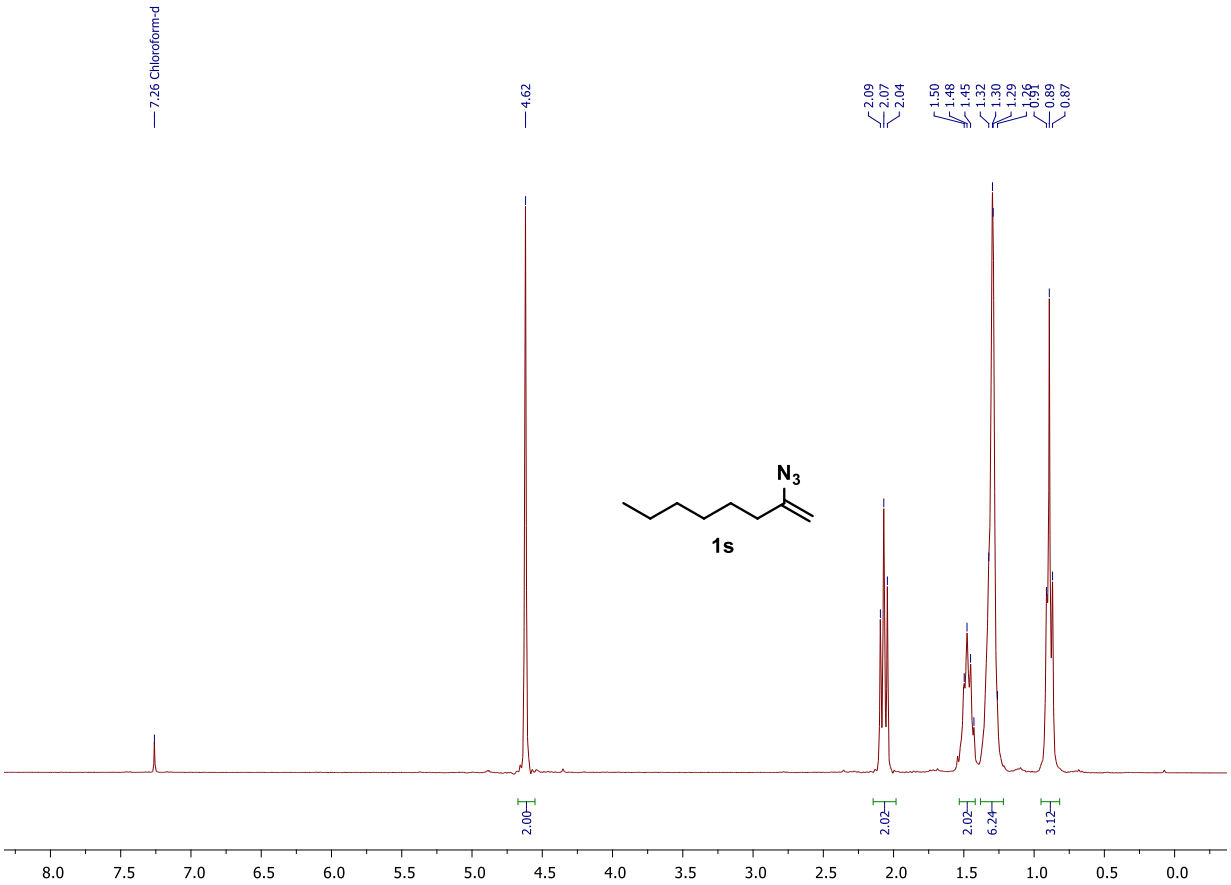
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1.26
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2.02
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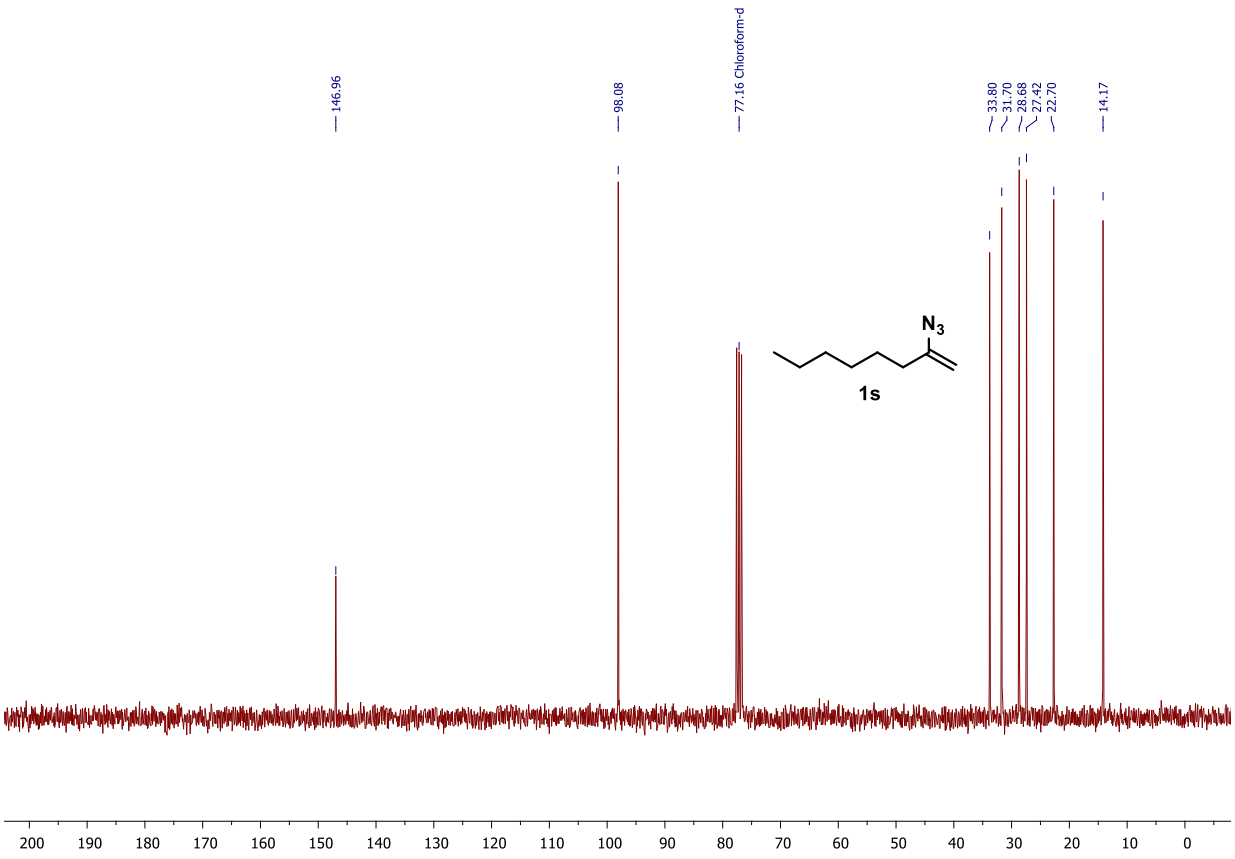
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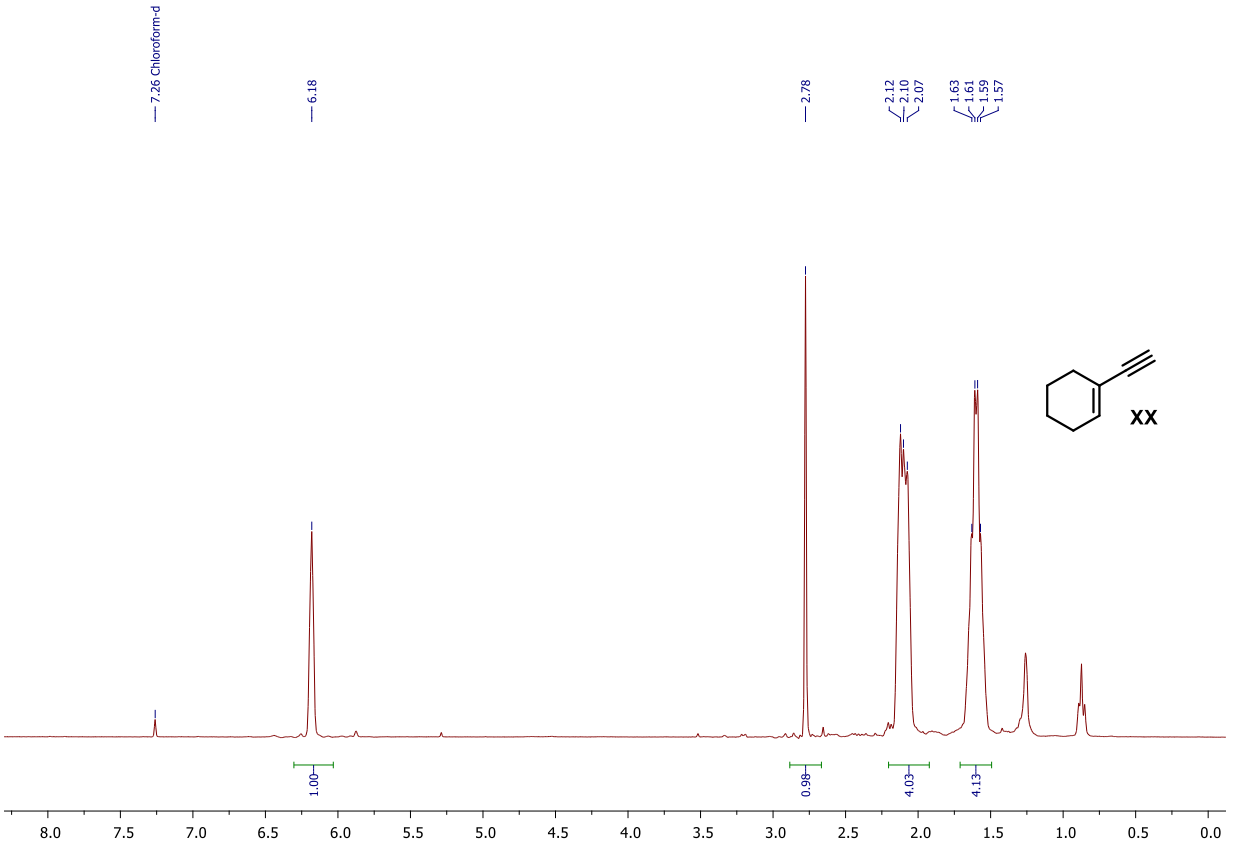
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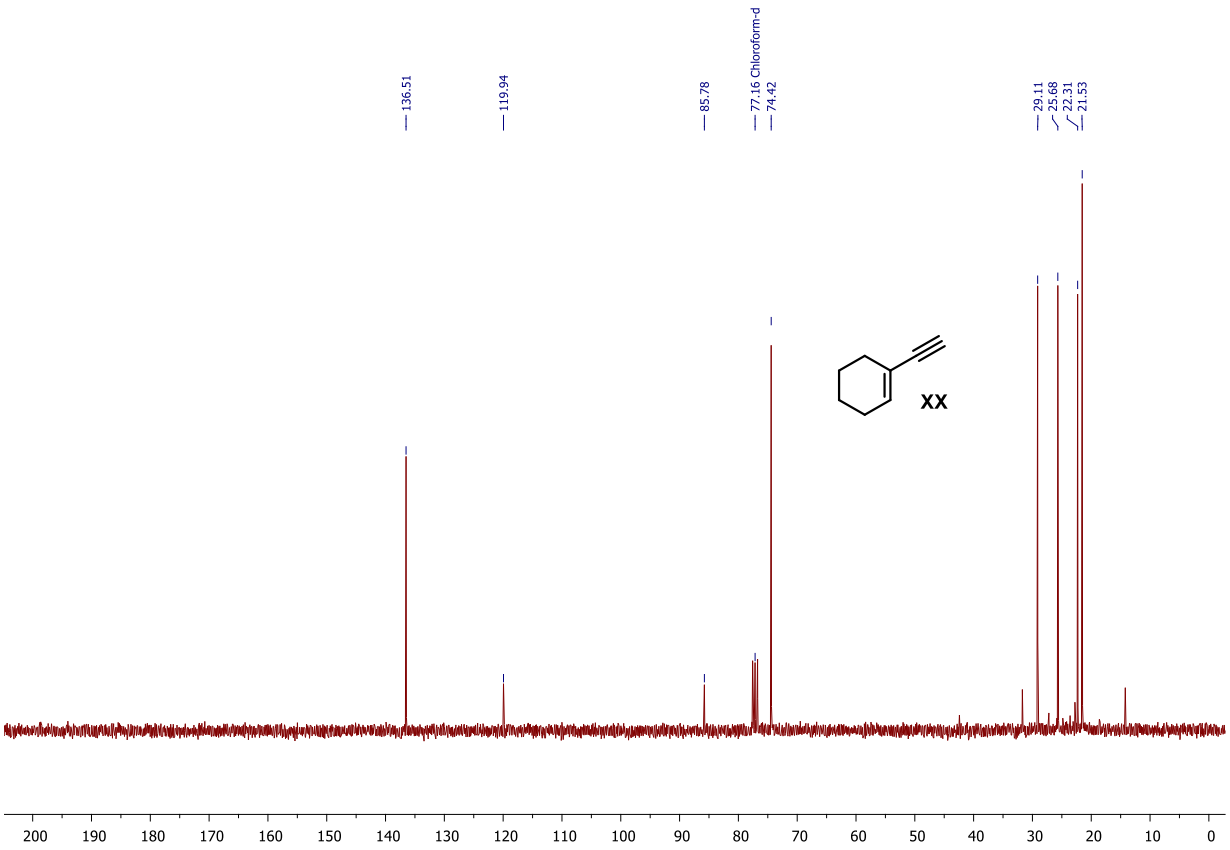
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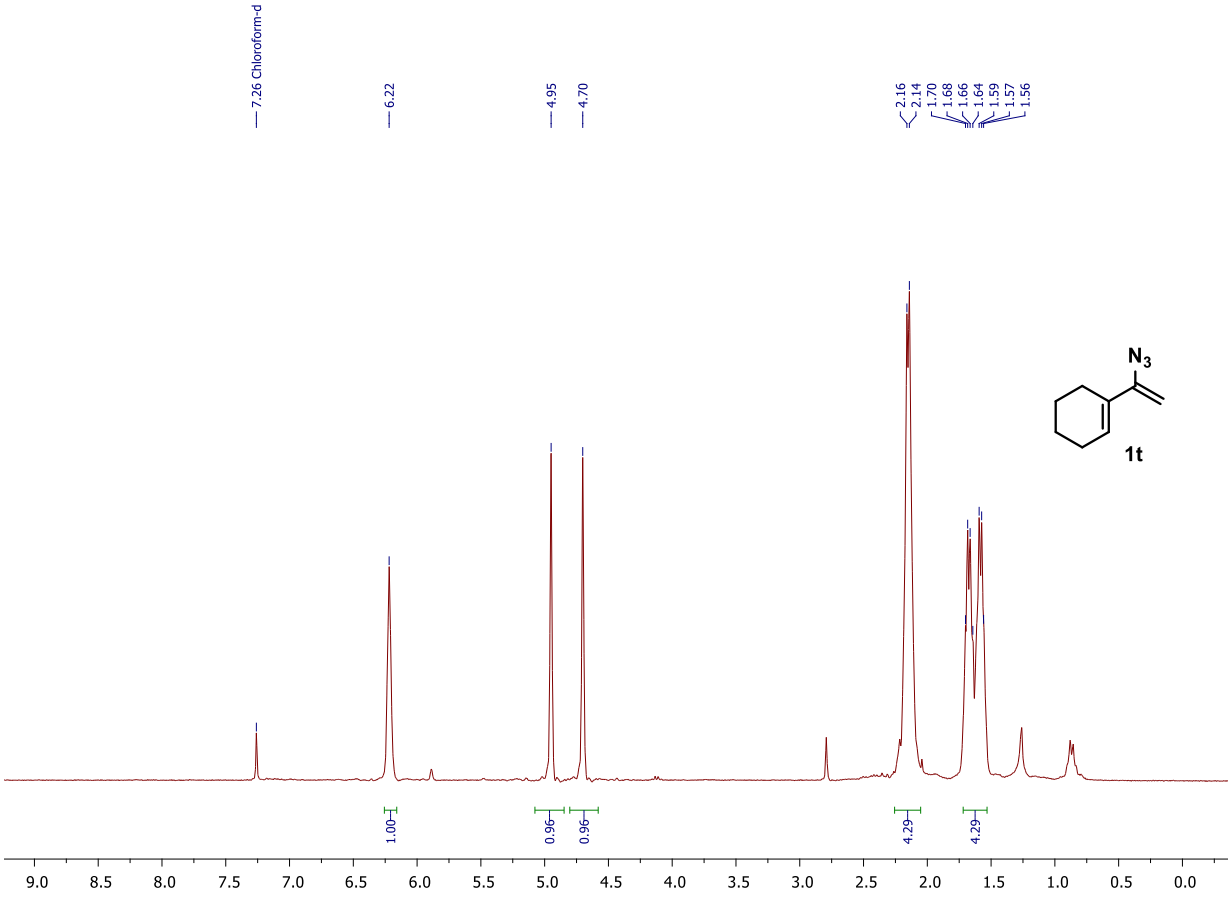
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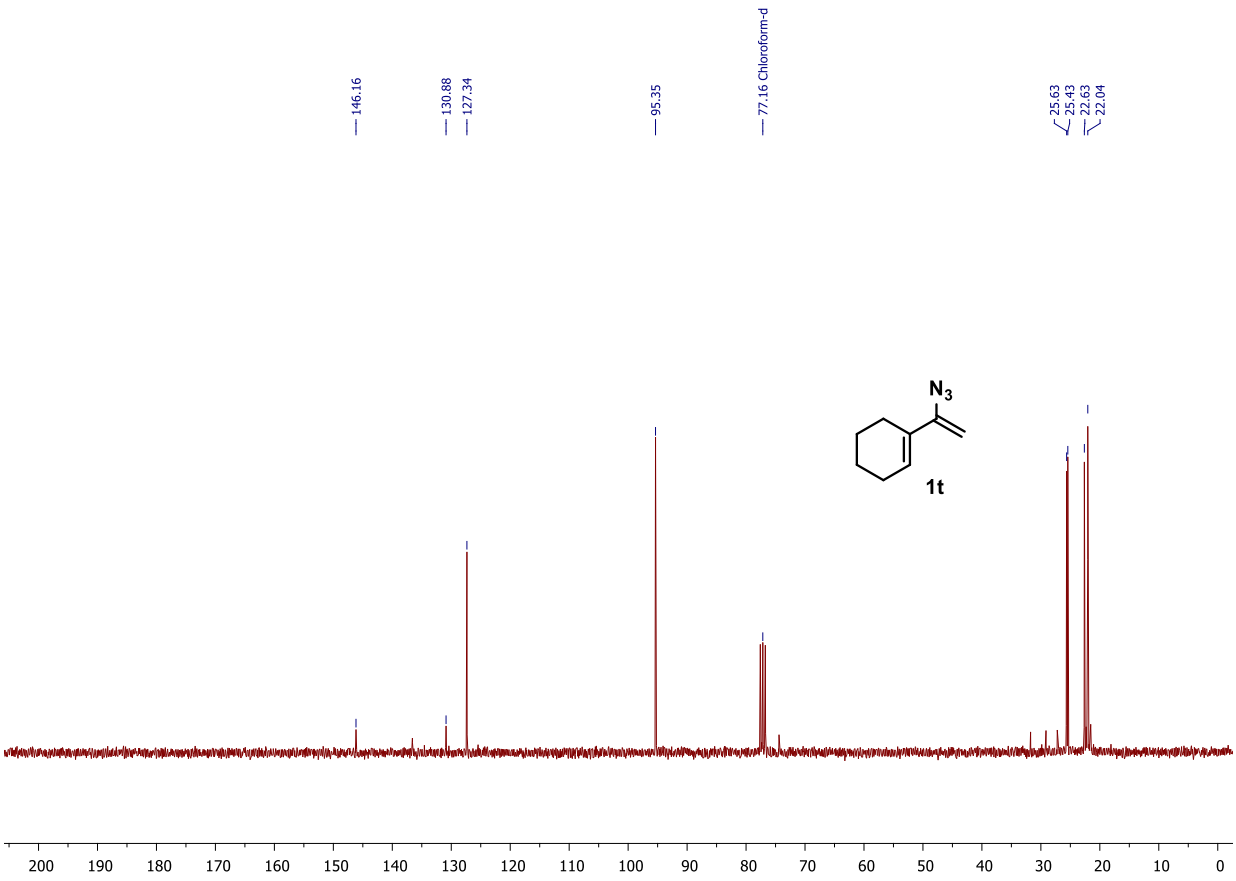
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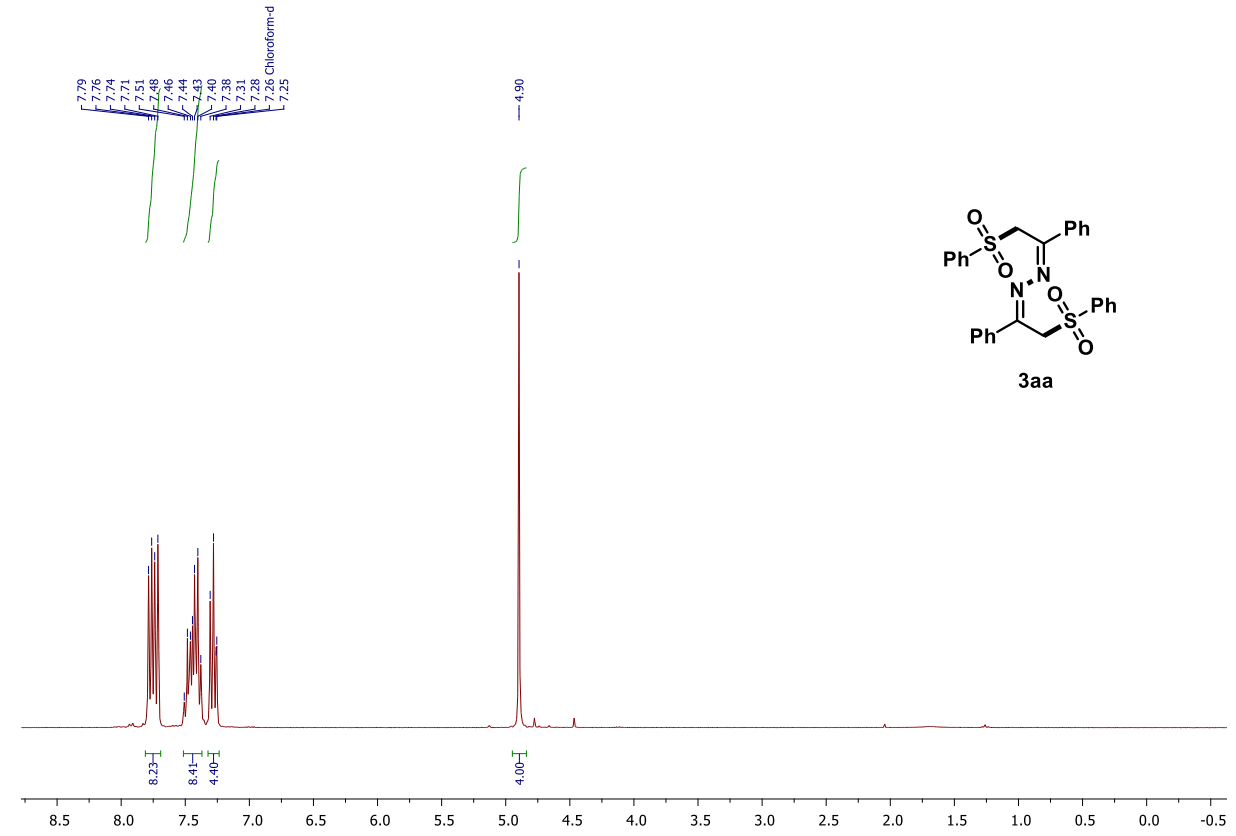
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Ph
Ph
Ph
3aa
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4.40
4.00
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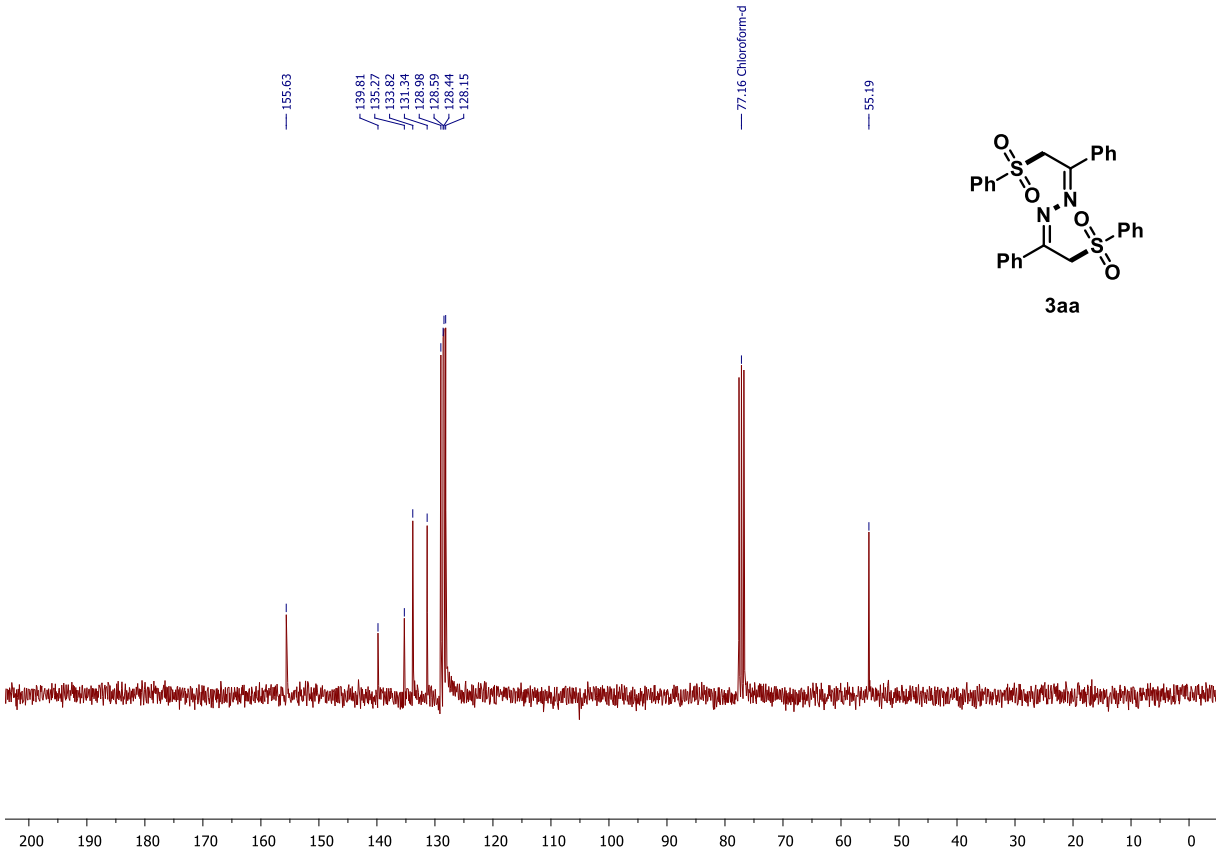
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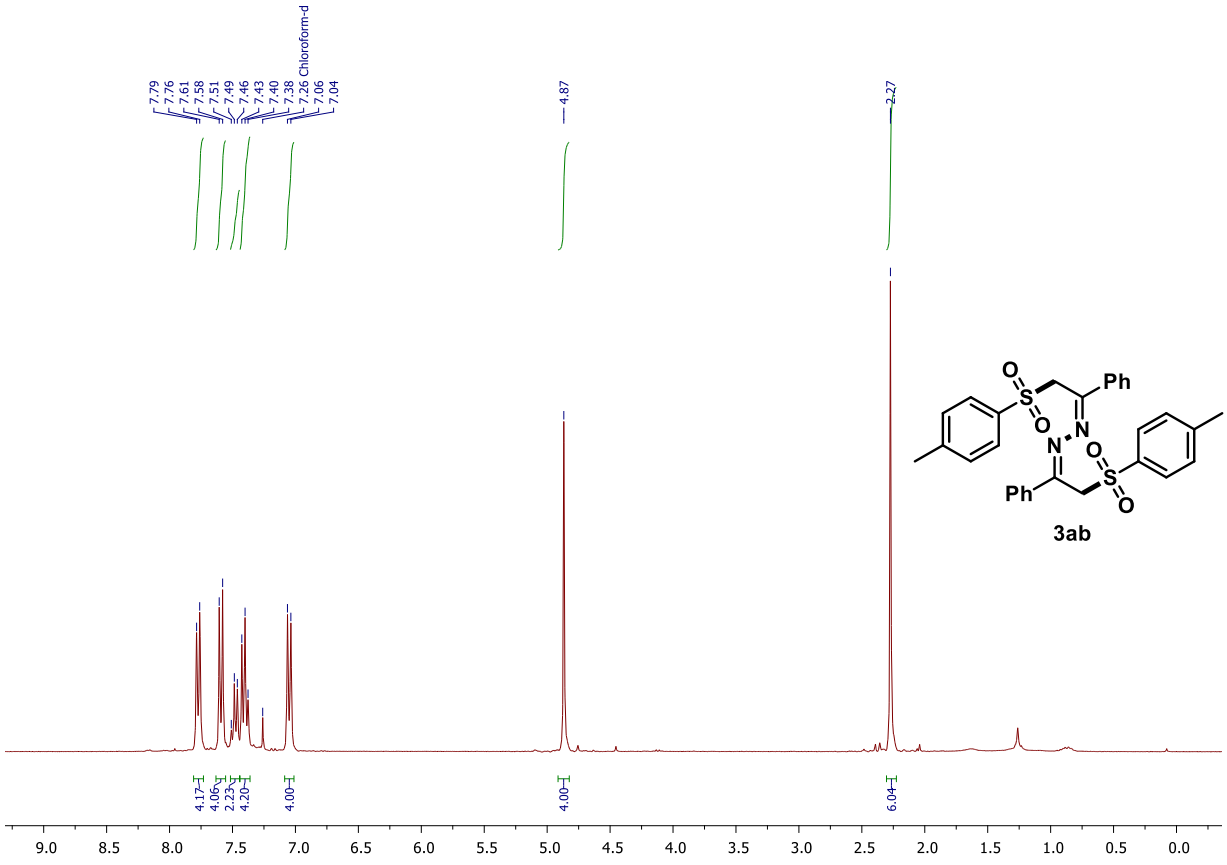
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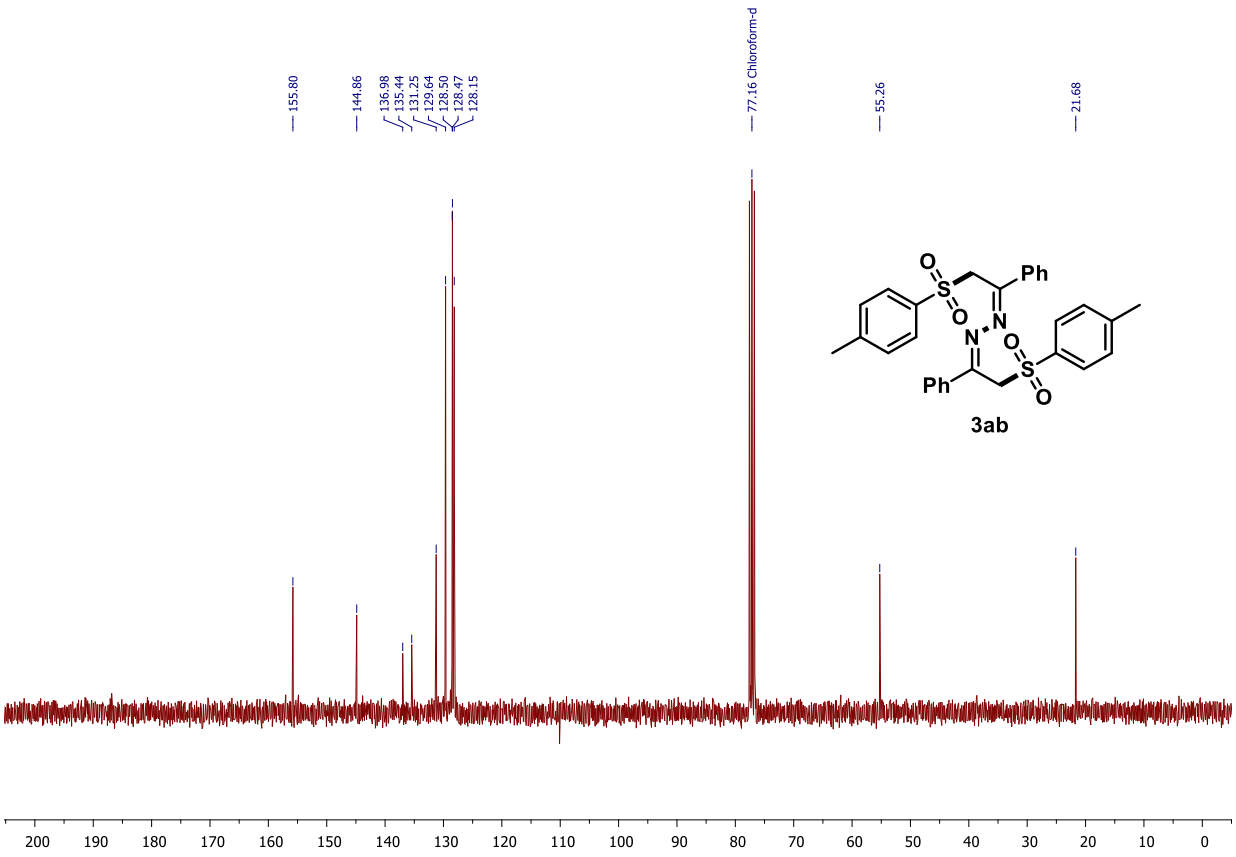
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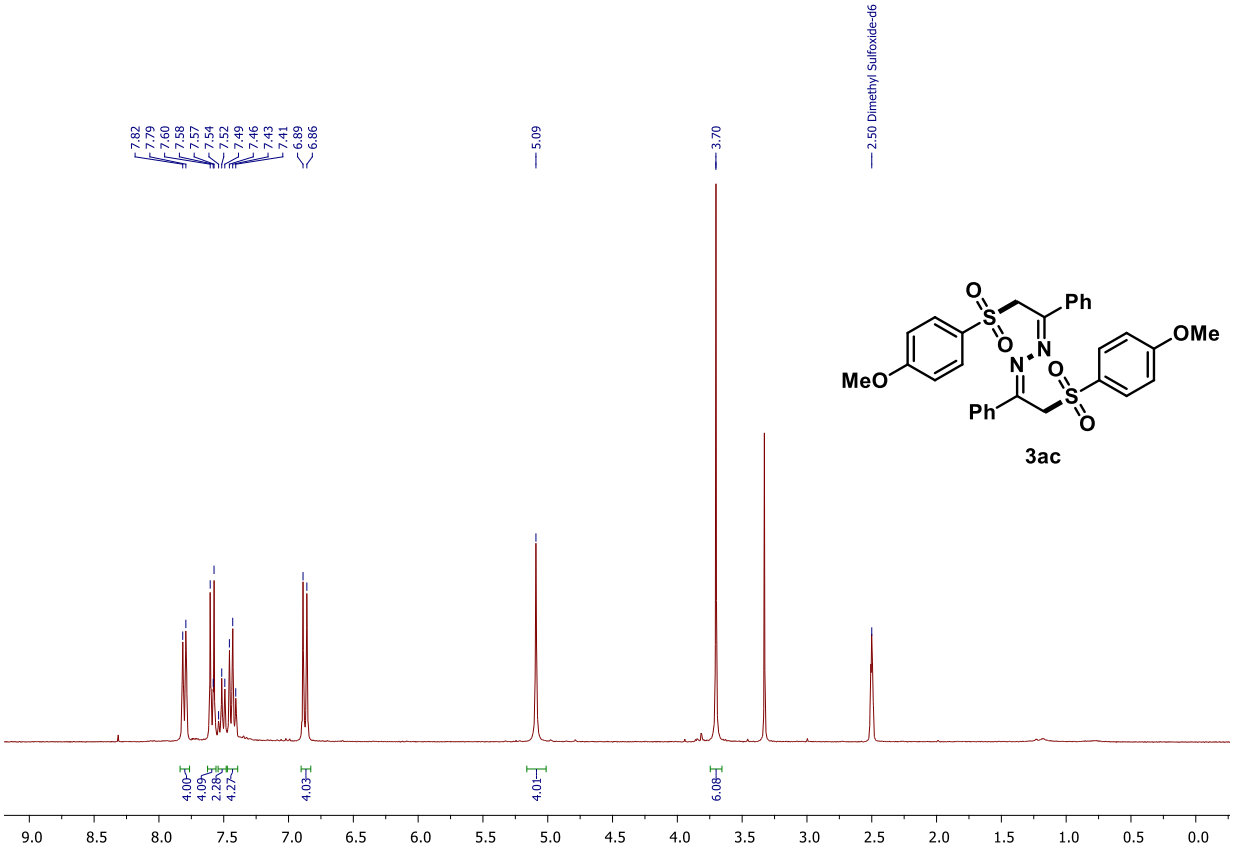
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3.70
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4.09
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4.03
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6.08
MeO
OMe
Ph
Ph
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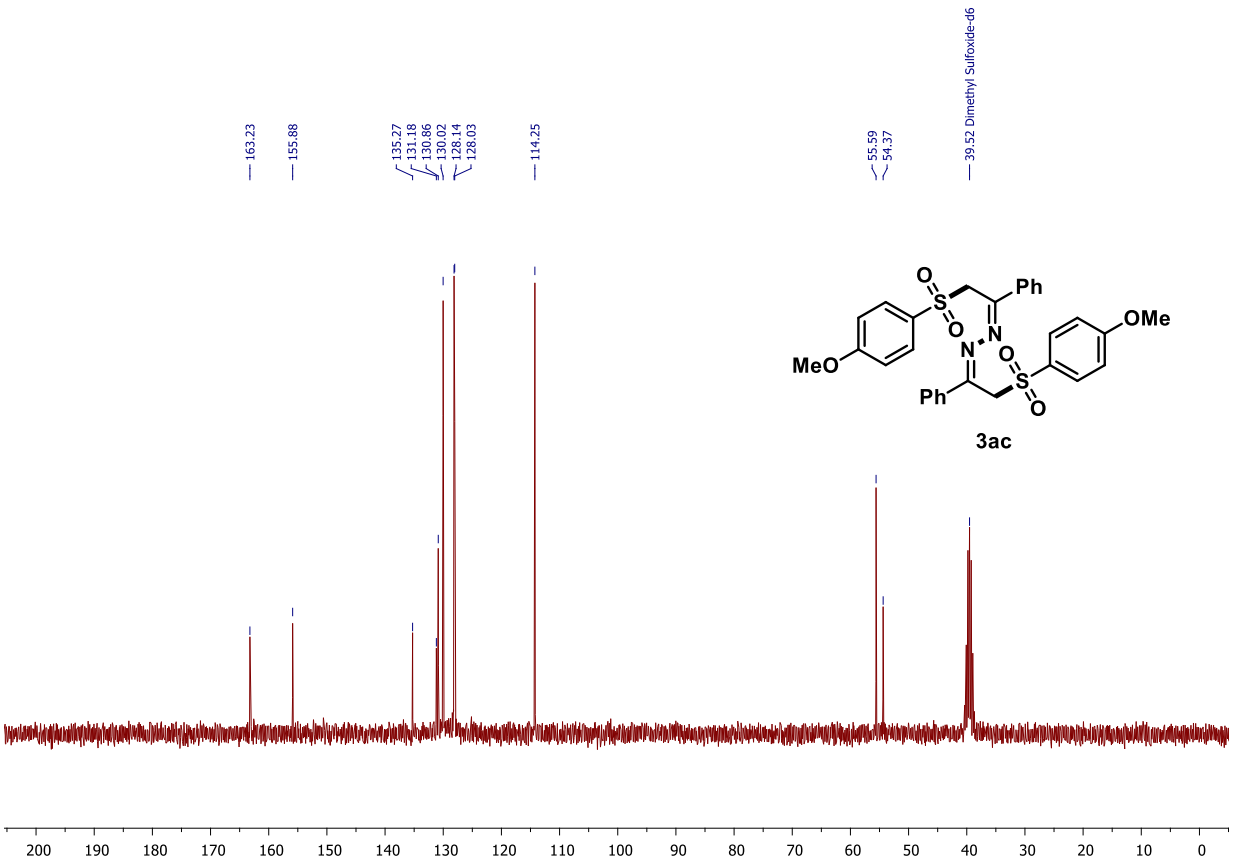
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OMe
Ph
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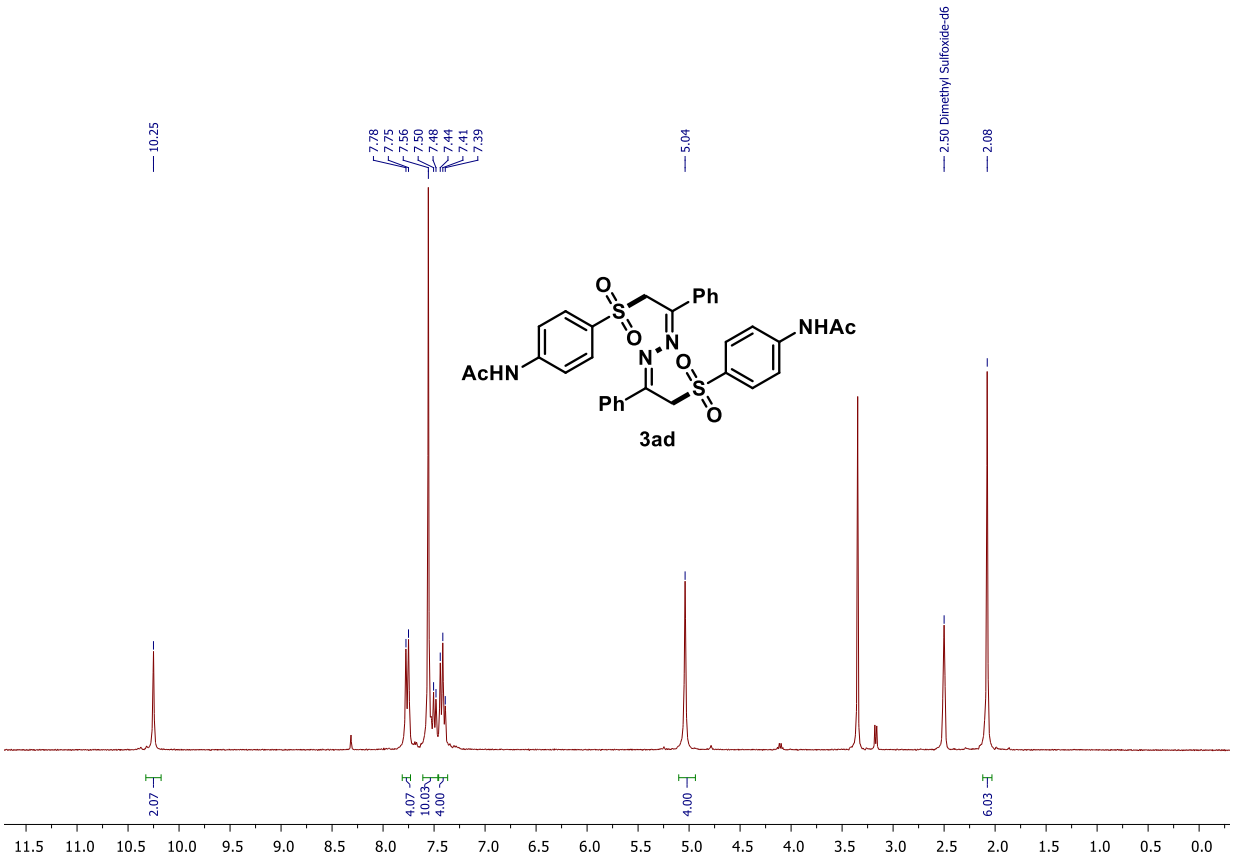
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2.08
AcHN
NHAc
Ph
Ph
3ad
2.07
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10.03
4.00
4.00
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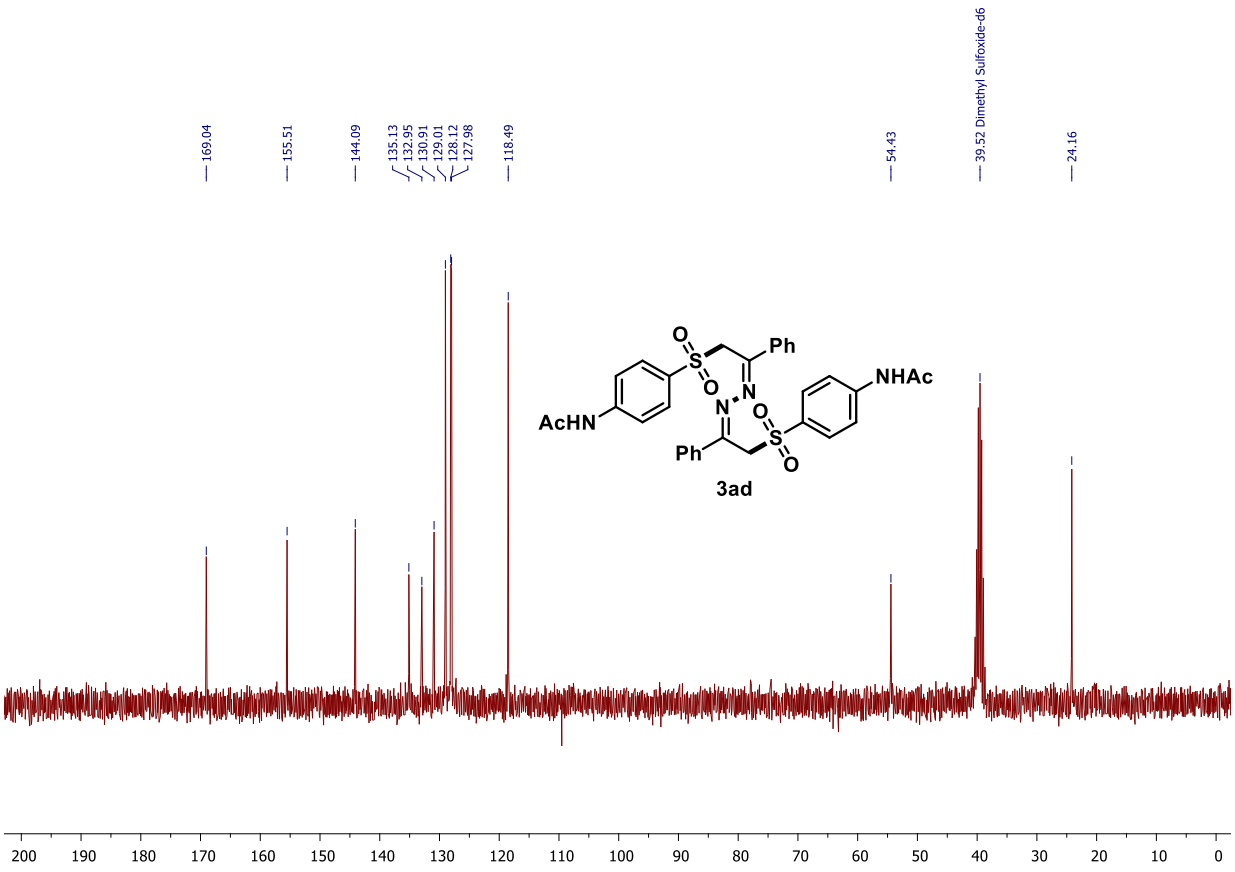
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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24.16
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Ph
Ph
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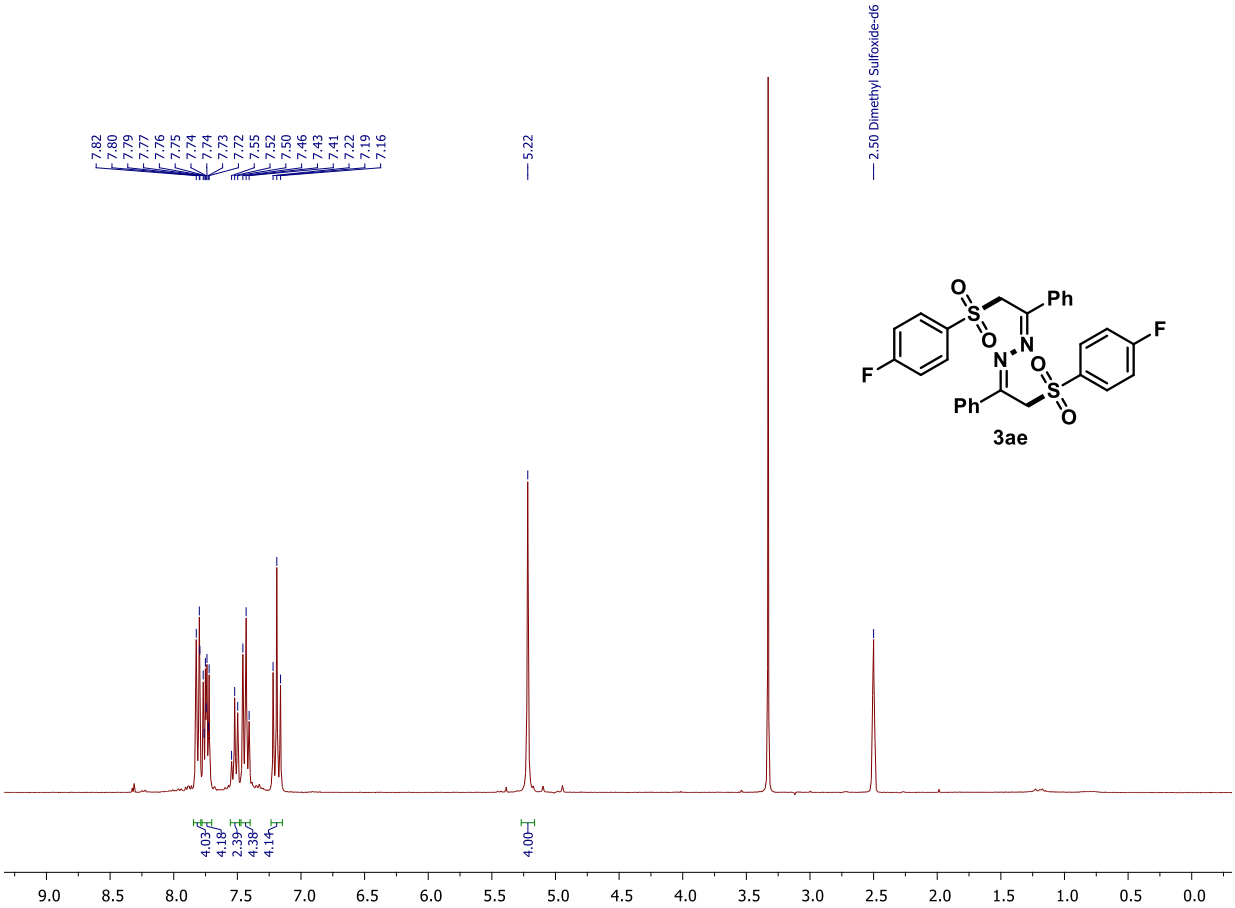
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7.46
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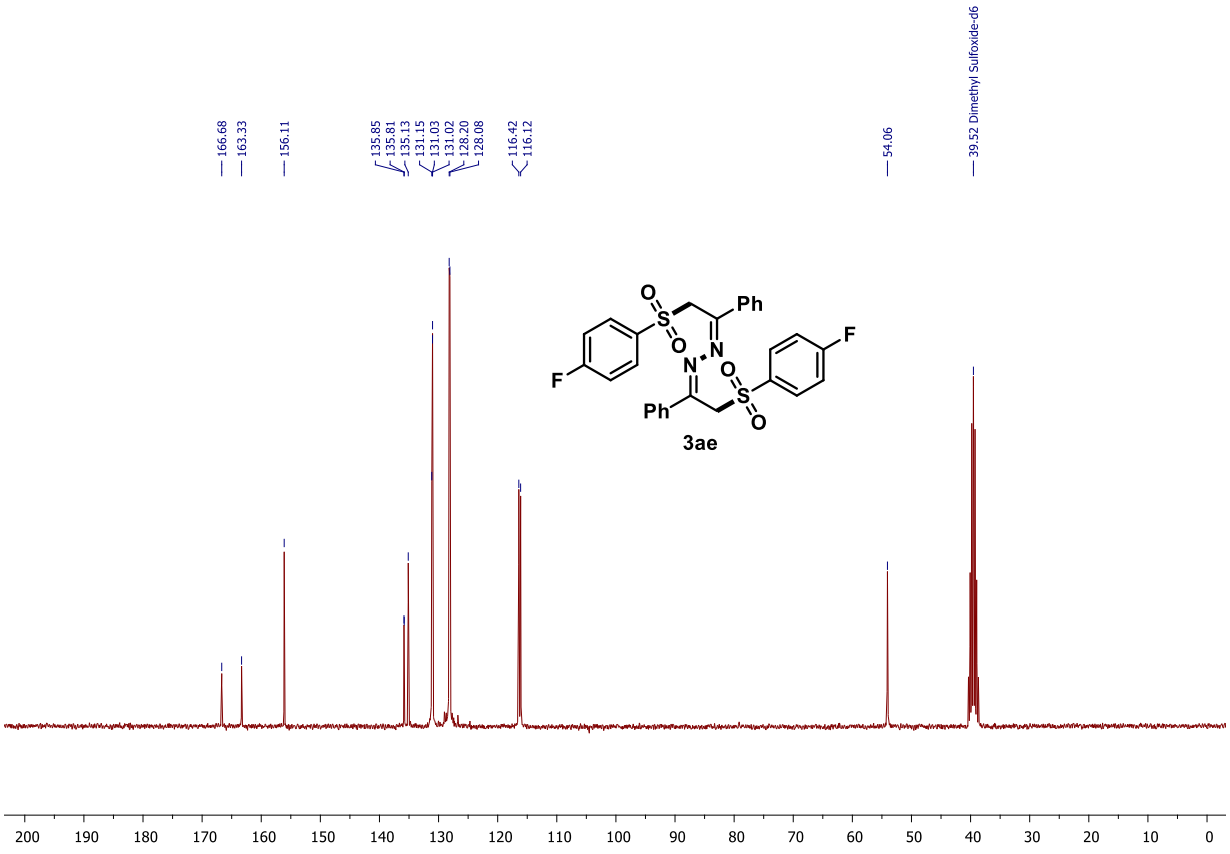
Ph
Ph
3ae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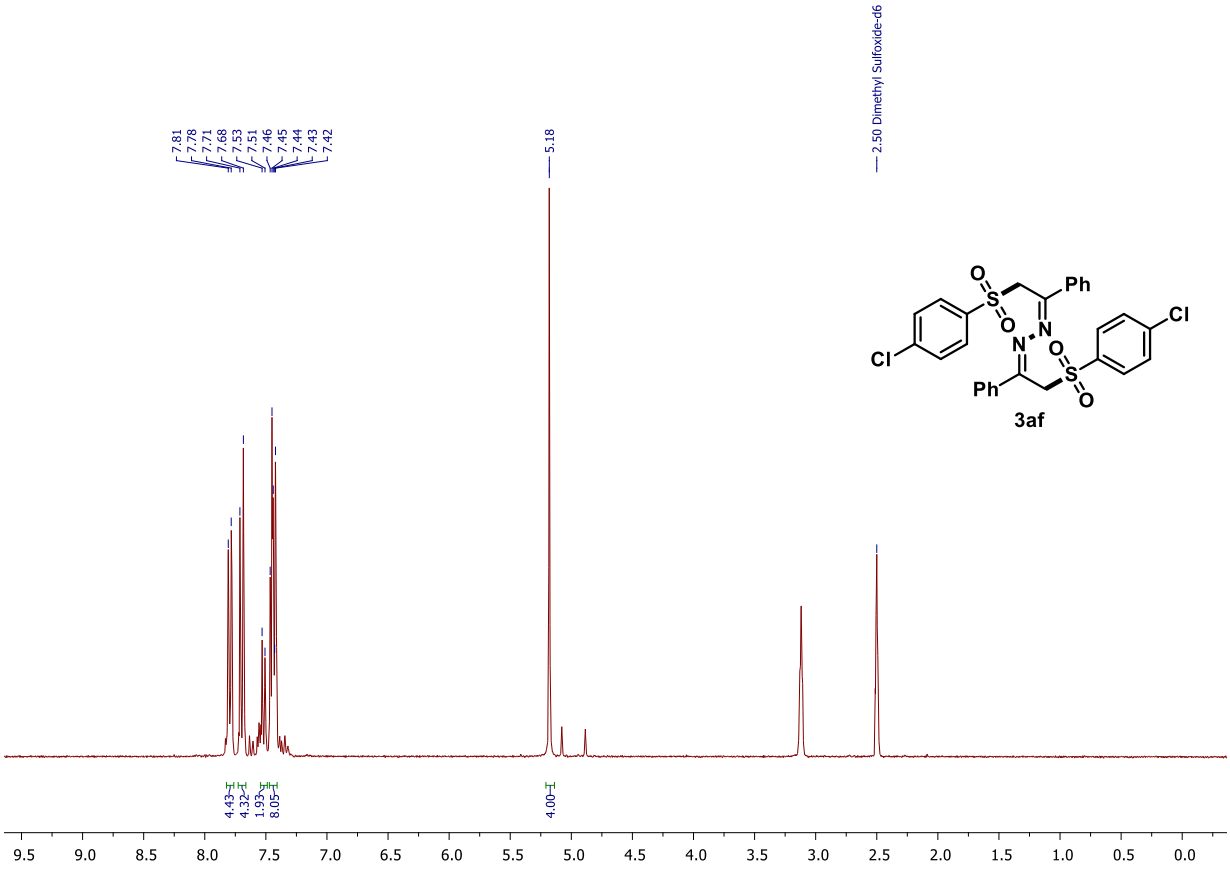
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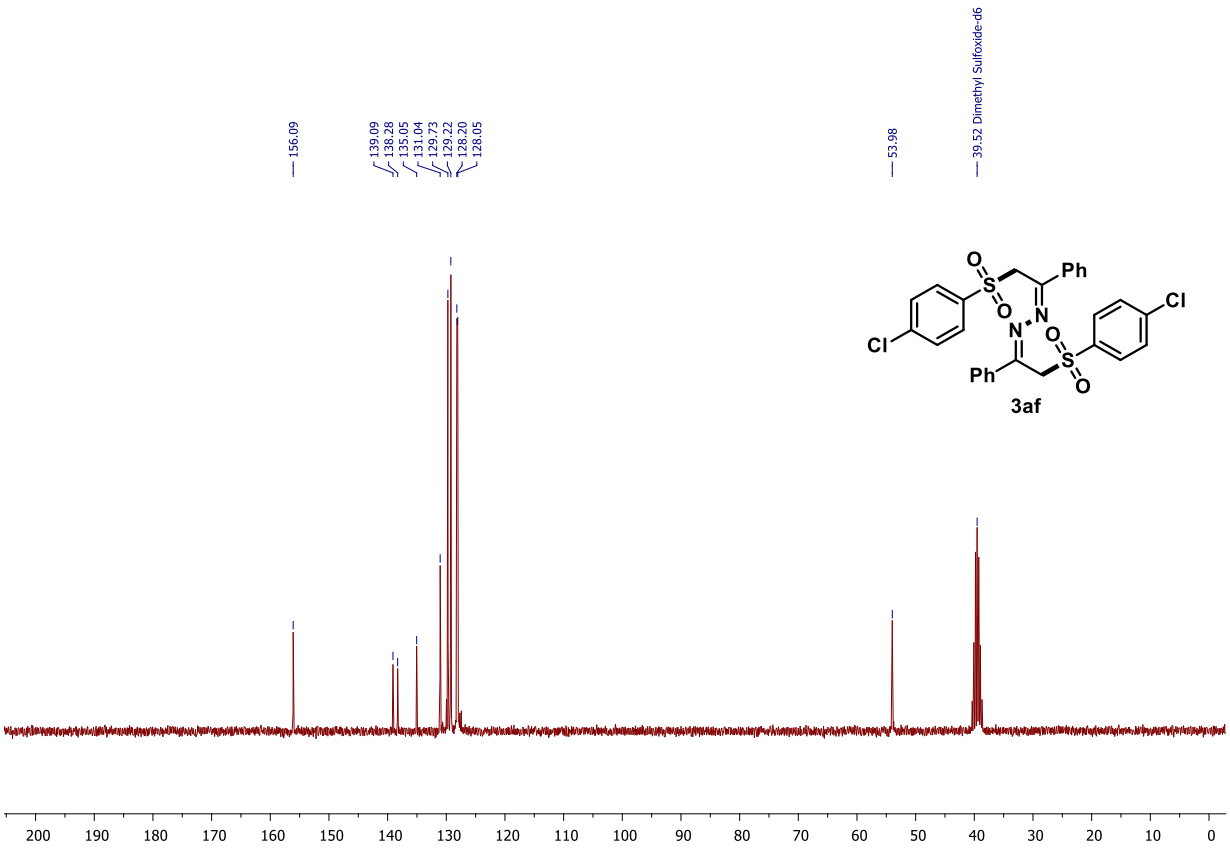
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Cl
Cl
Ph
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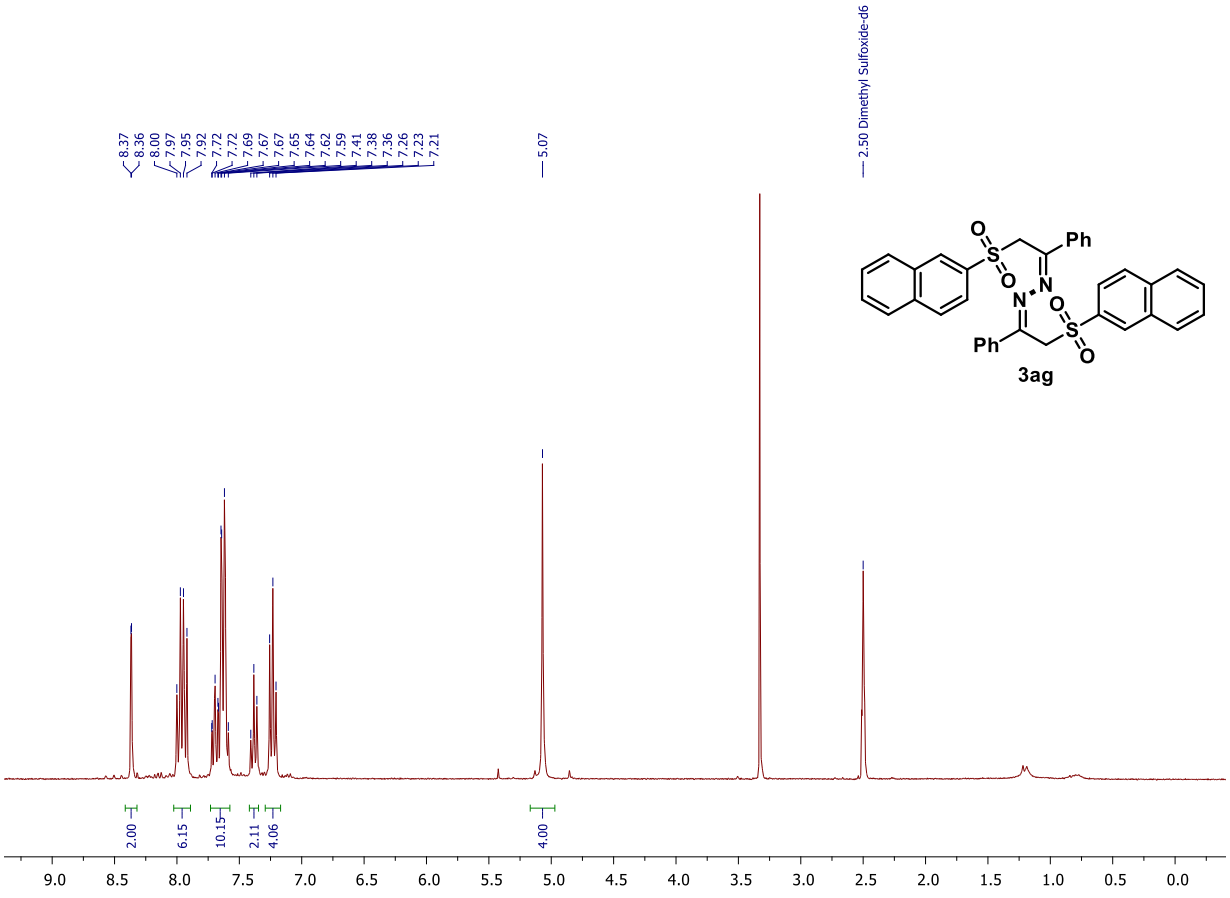
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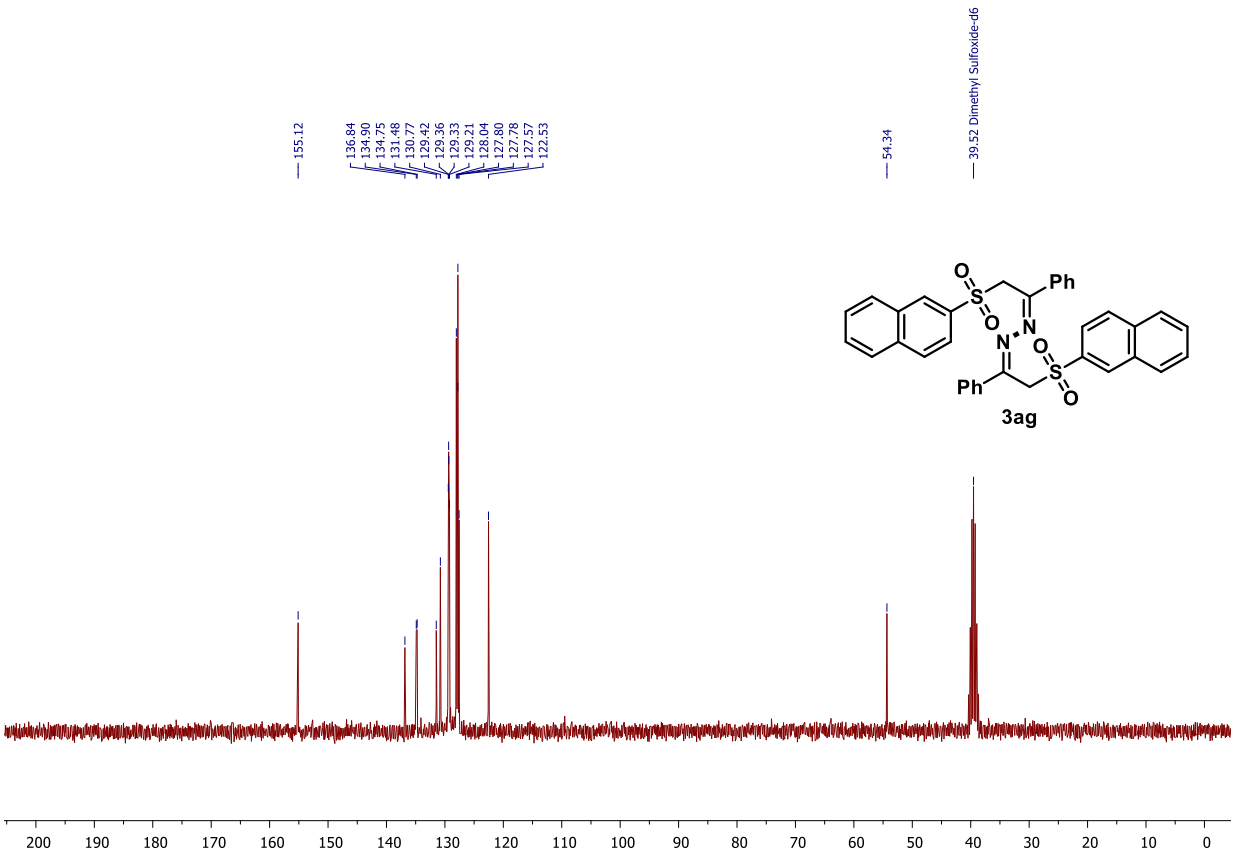
4.00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122.53
54.34
39.52 Dimethyl Sulfoxide-d6
Ph
Ph
3ag
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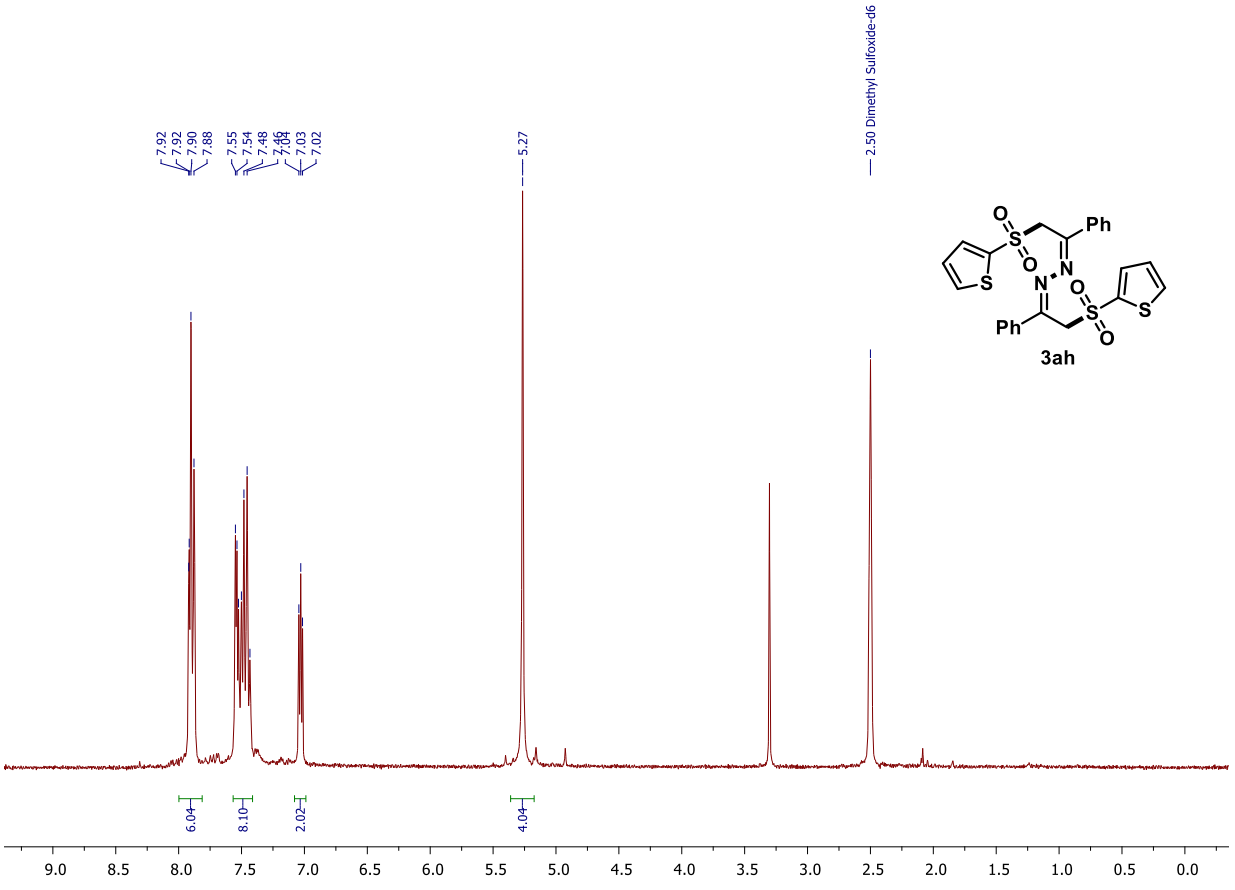
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Ph
Ph
3ah
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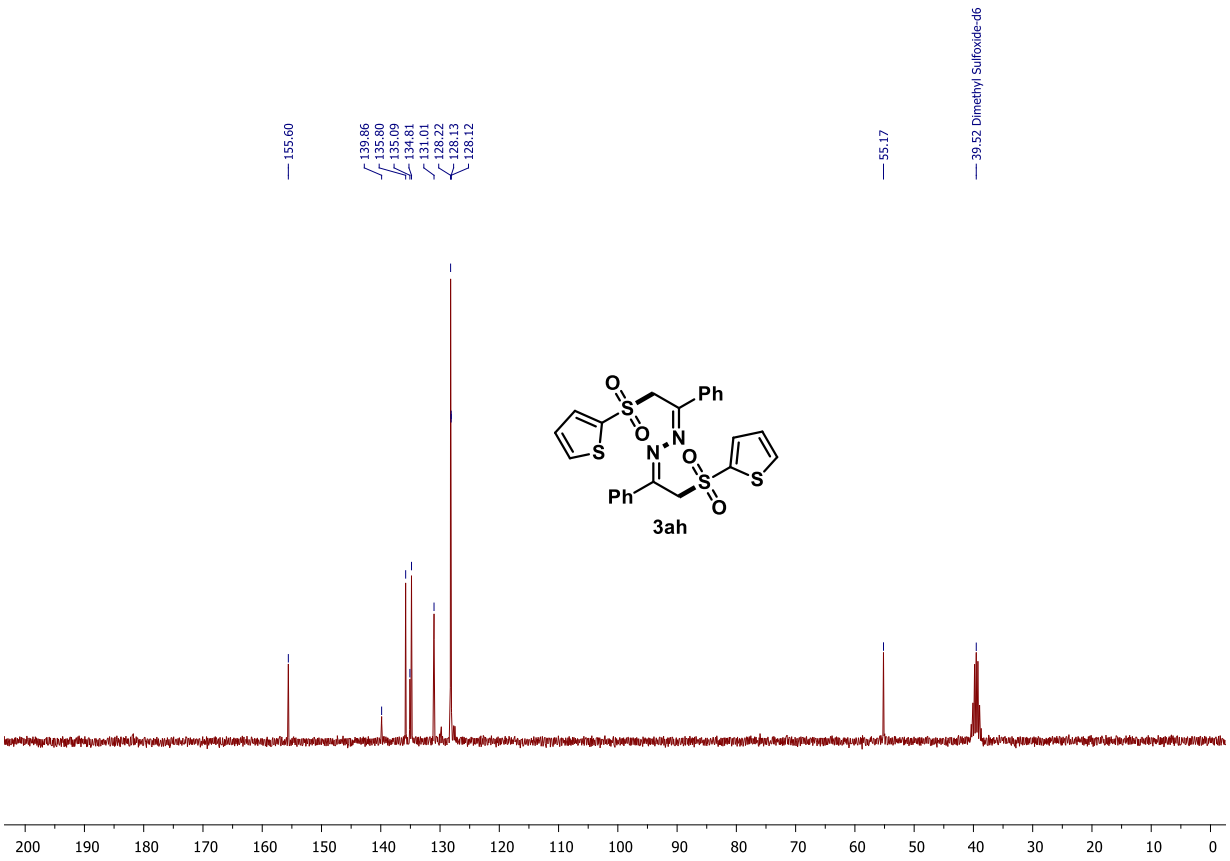
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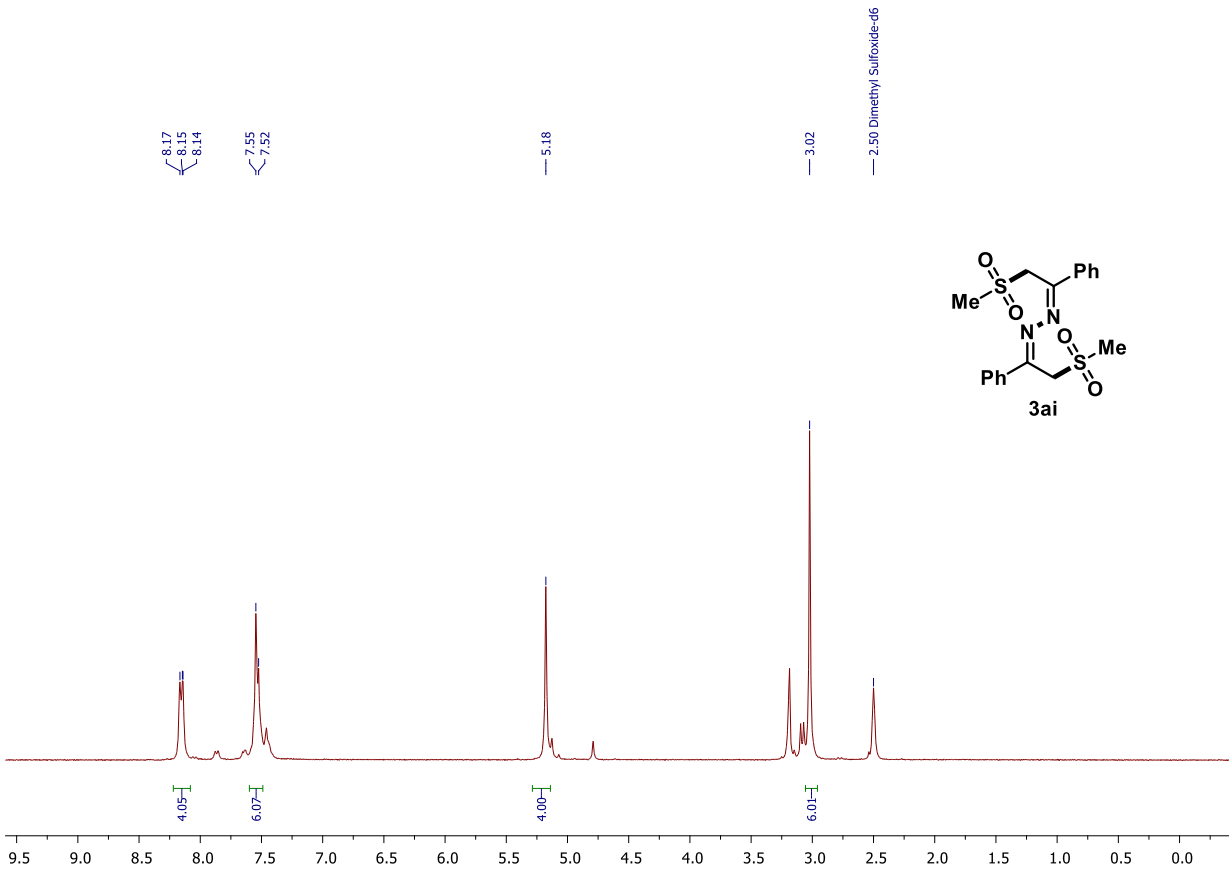
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4.00
6.01
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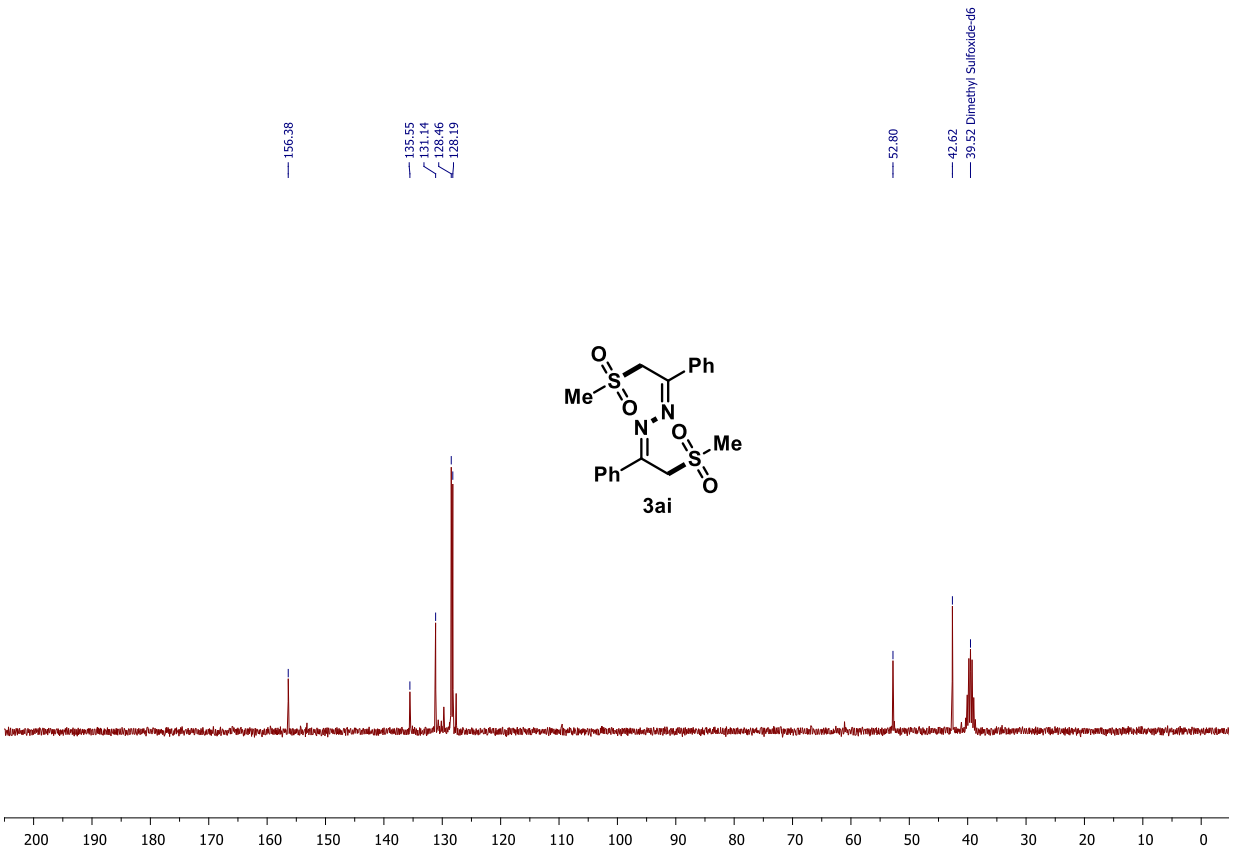
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Ph
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Me
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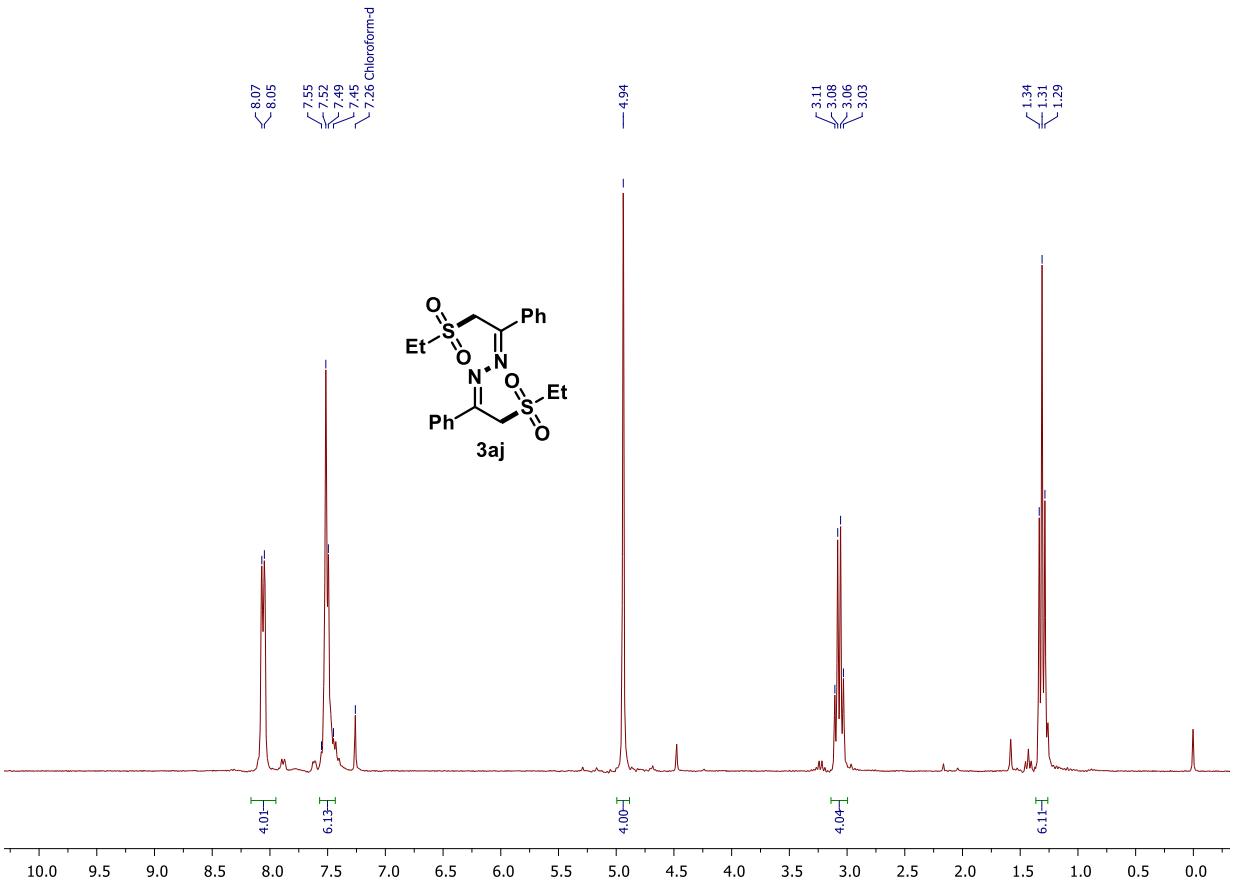
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1.31
1.29
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Ph
Ph
Et
3aj
4.01
6.13
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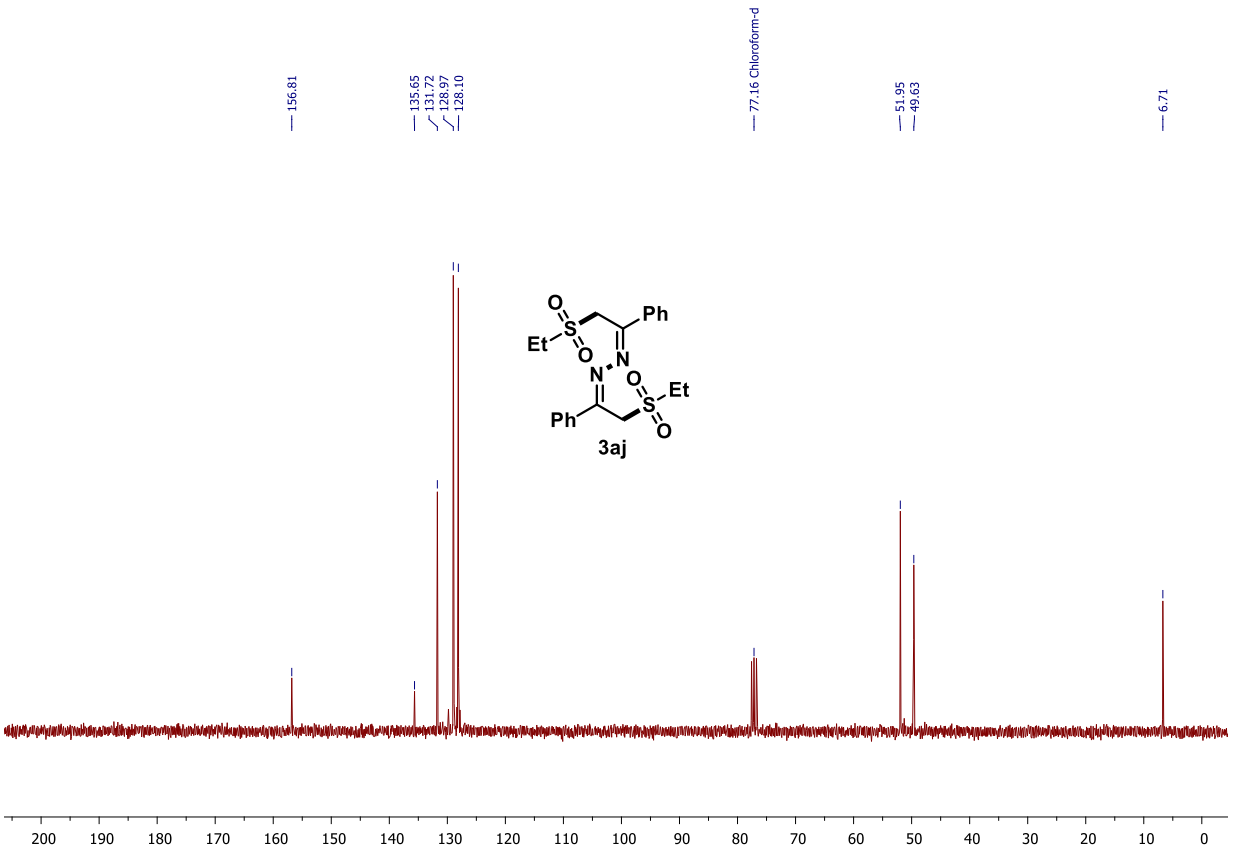
4.04
6.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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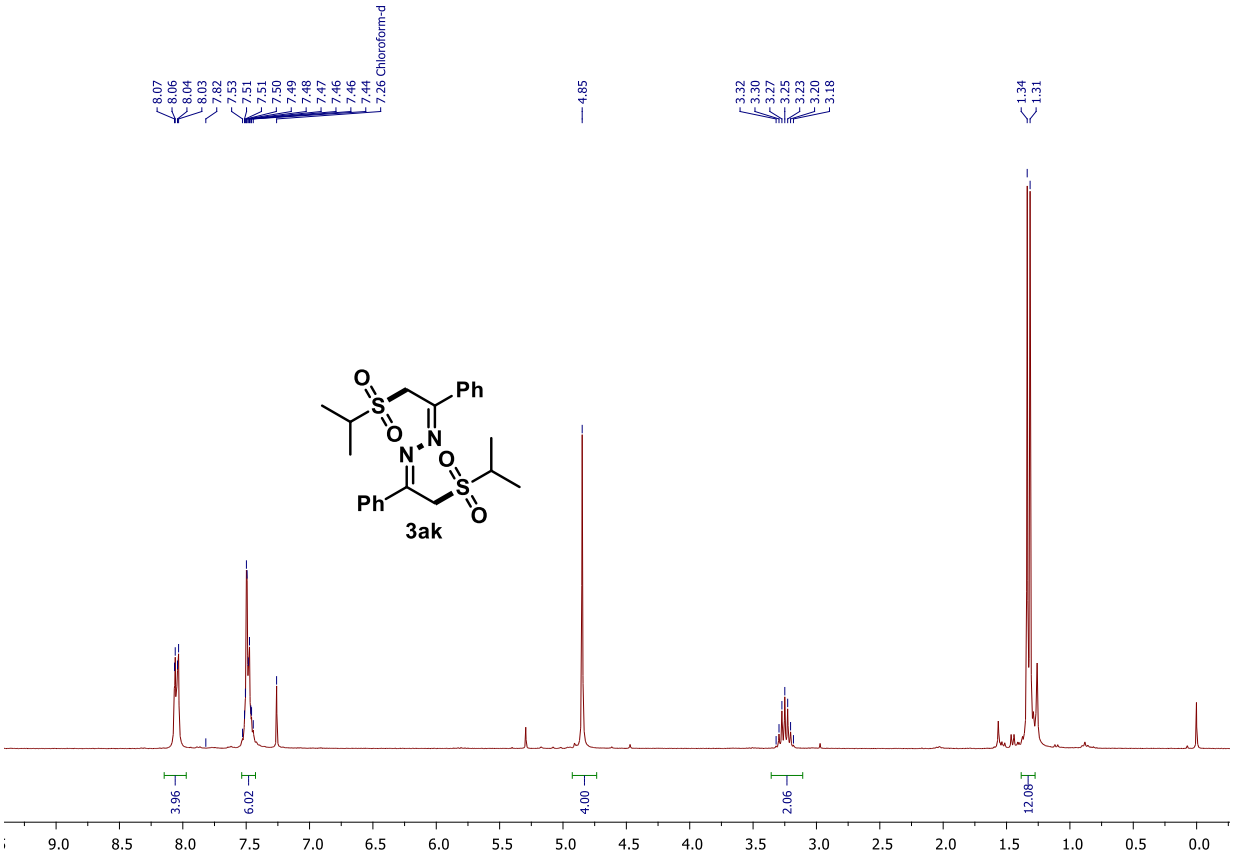
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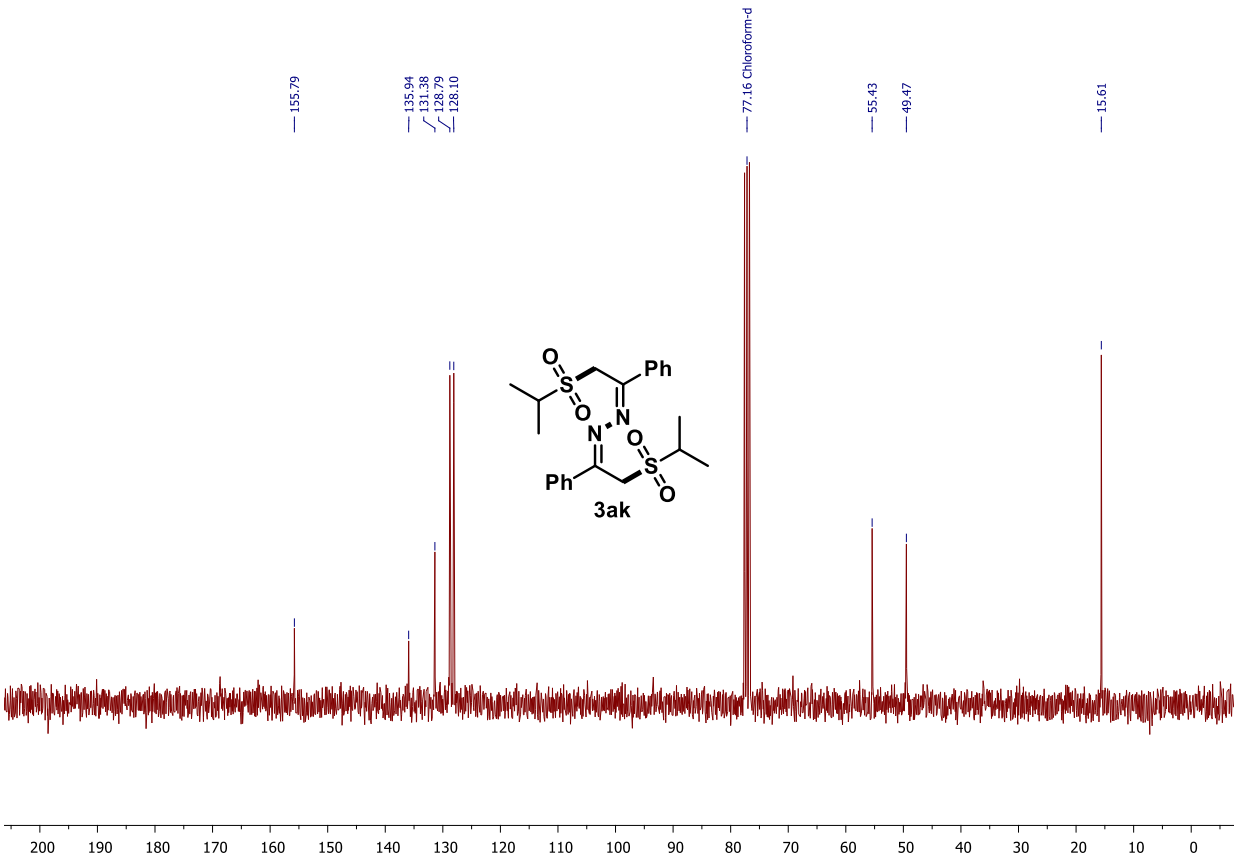
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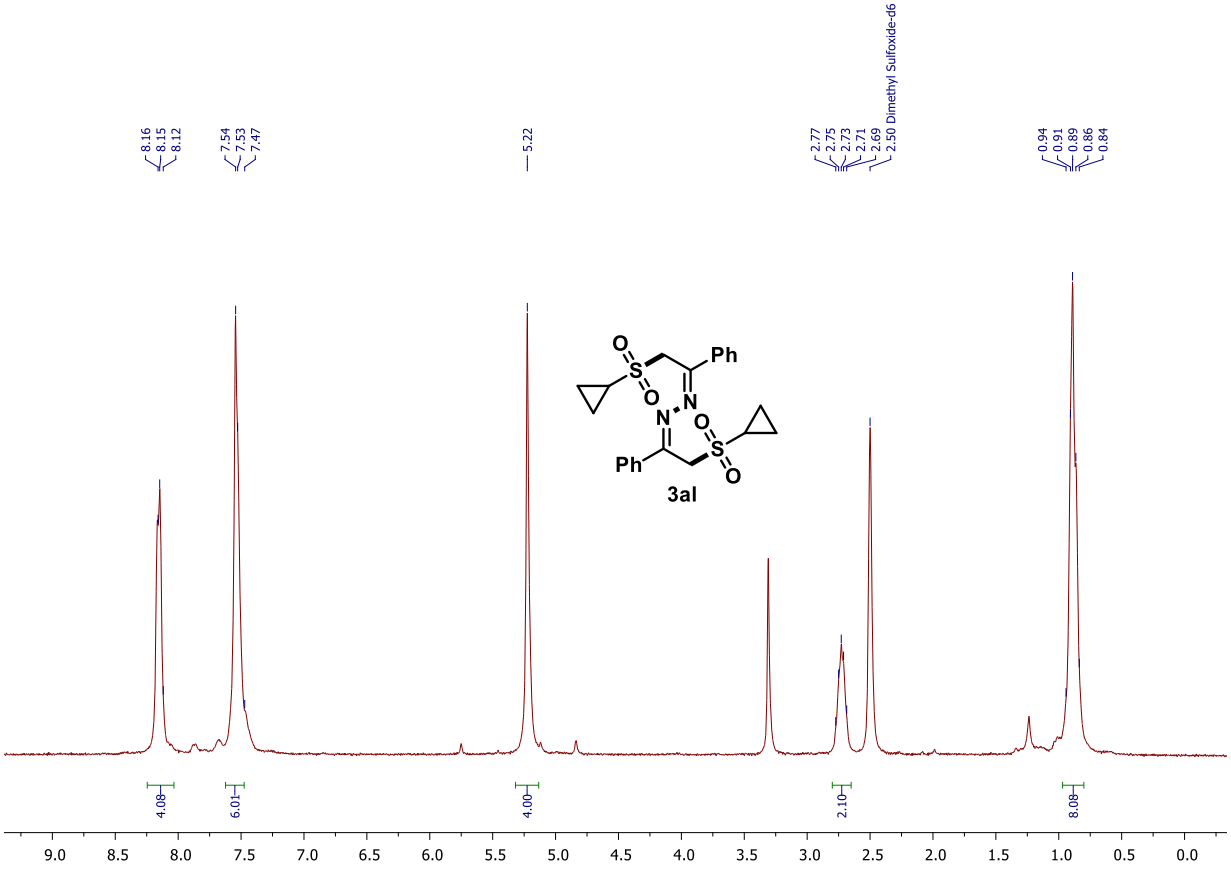
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2.77
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2.73
2.71
2.69
2.50 Dimethyl Sulfoxide-d6
0.94
0.91
0.89
0.86
0.84
Ph
Ph
3al
4.08
6.01
4.00
2.10
8.08
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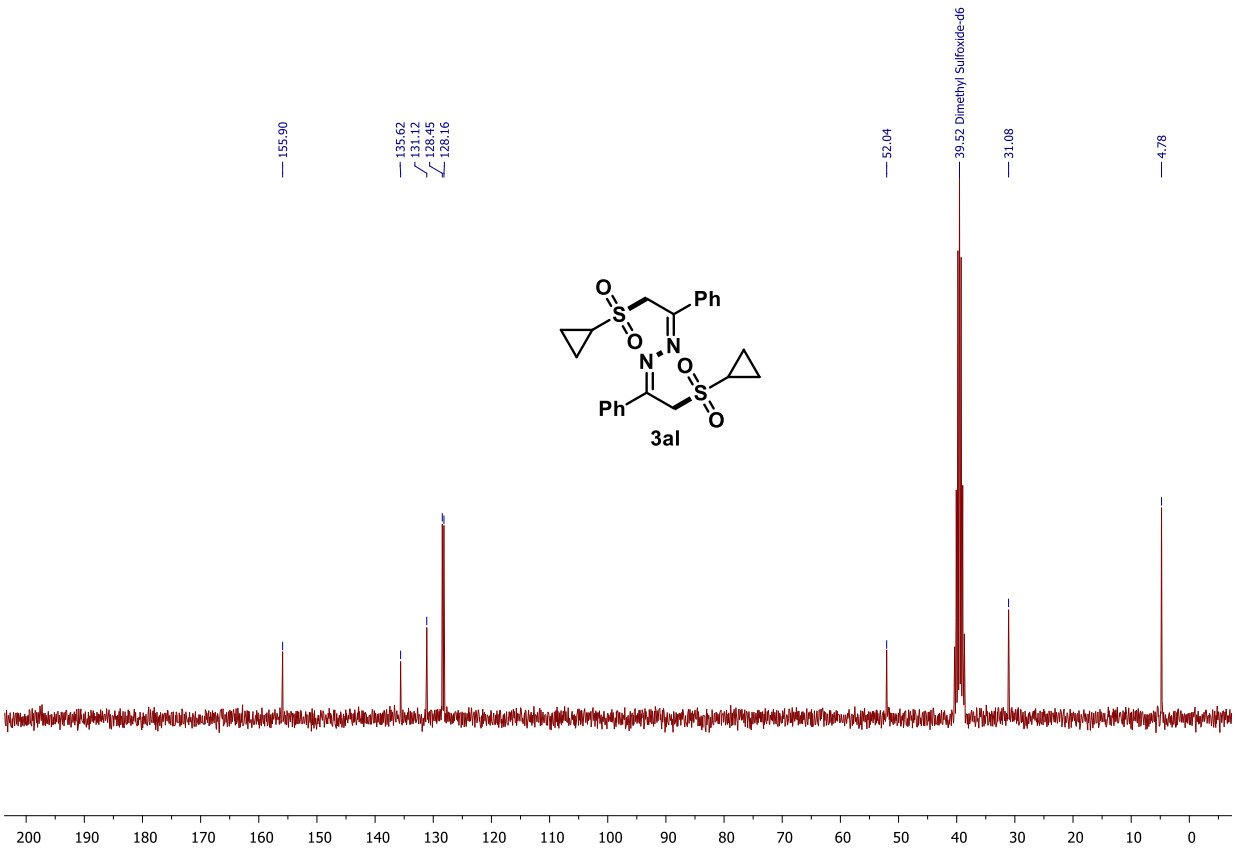
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Ph
3al
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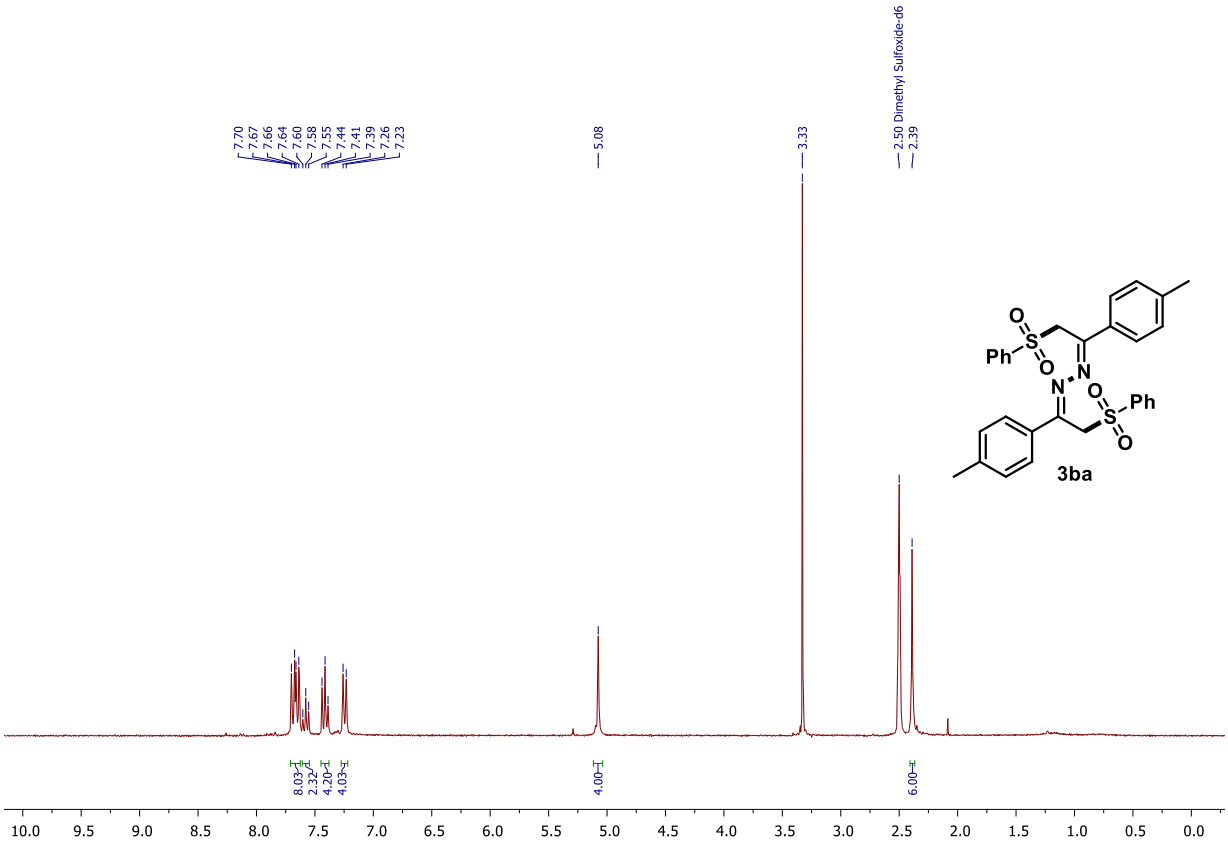
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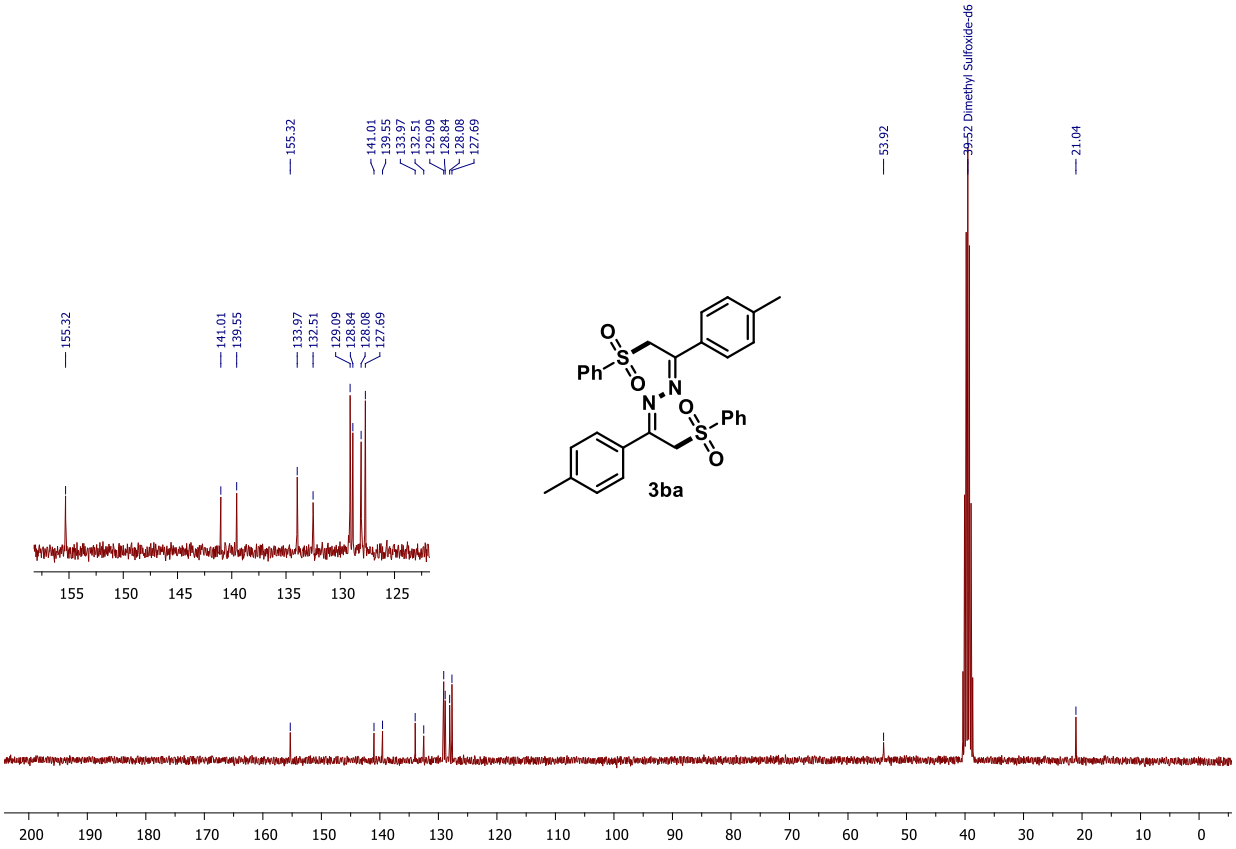
7.39
7.26
7.23
5.08
3.33
2.50 Dimethyl Sulfoxide-d6
2.39
Ph
Ph
3ba
8.03
2.32
4.20
4.03
4.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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128.08
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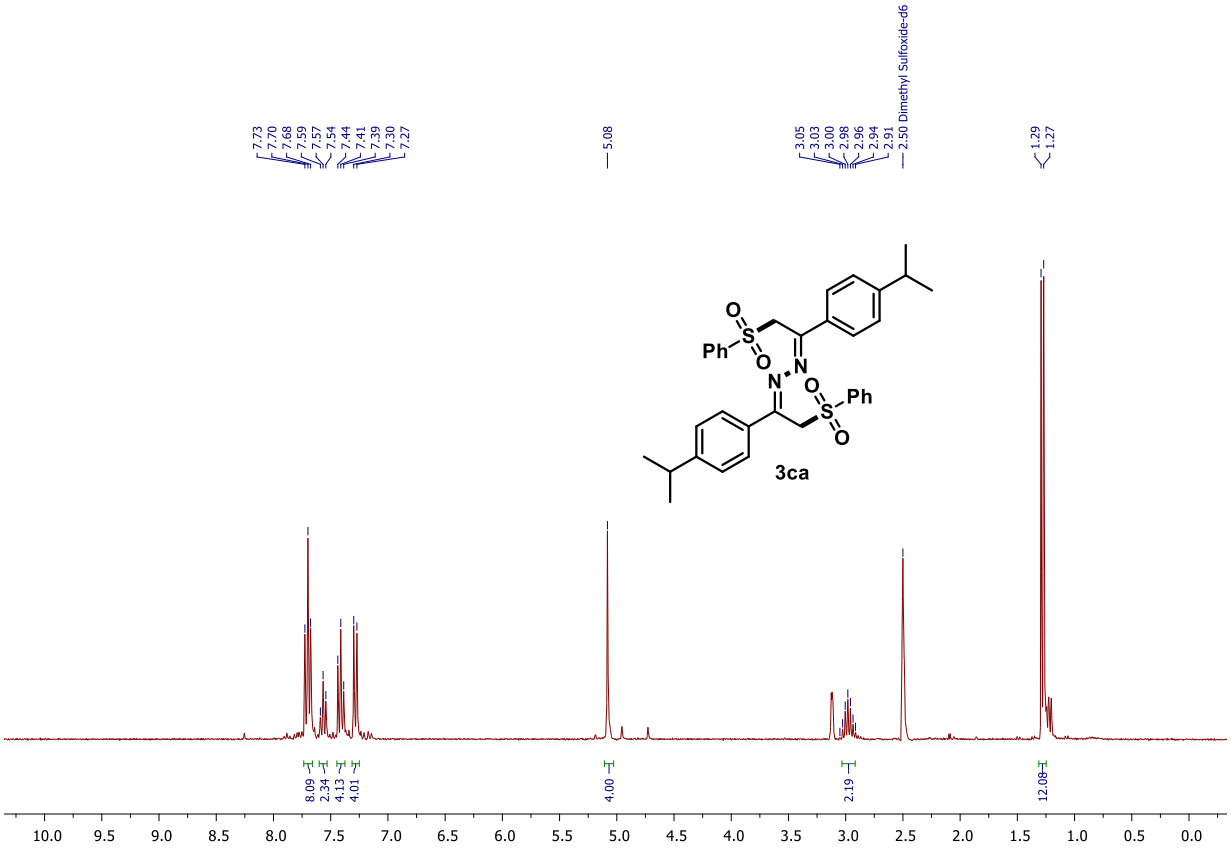
53.92
39.52 Dimethyl Sulfoxide-d6
21.04
3ba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3.05
3.03
3.00
2.98
2.96
2.94
2.91
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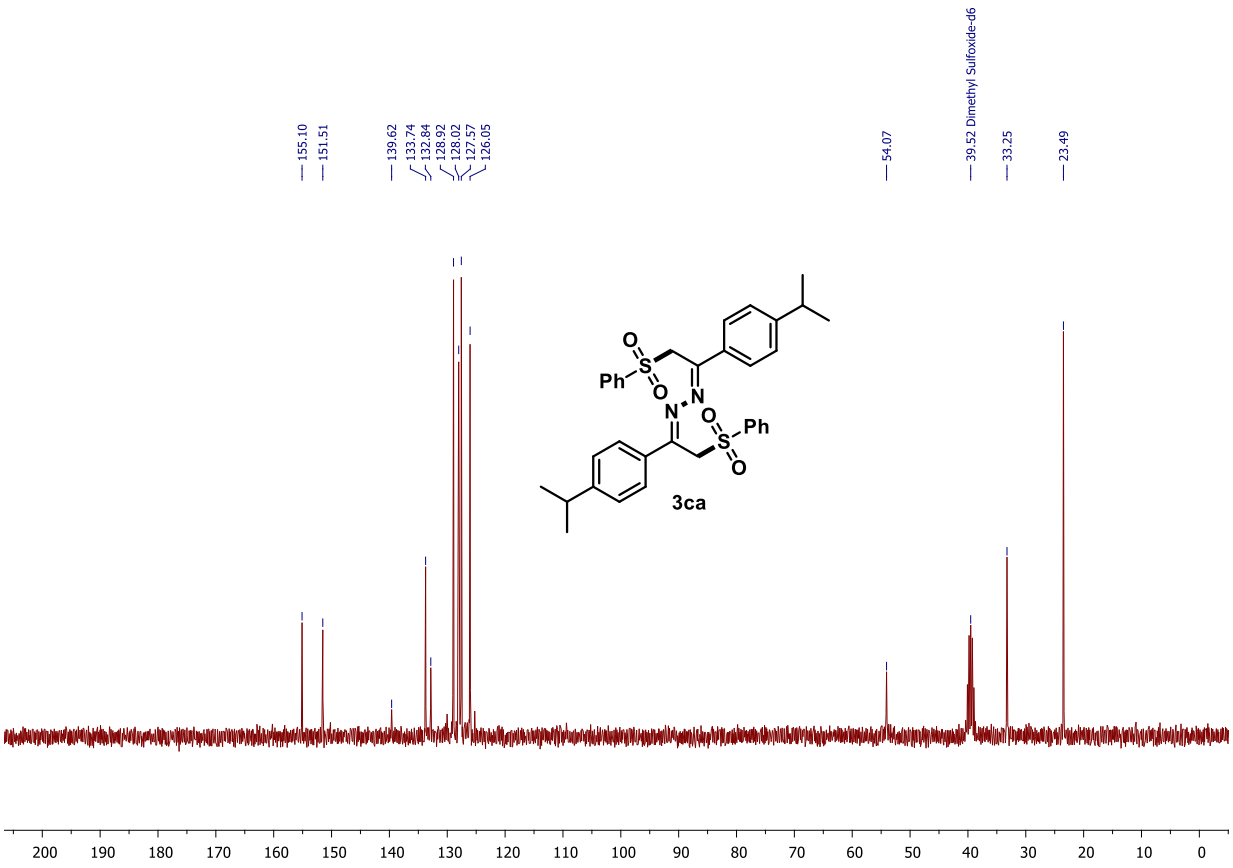
12.08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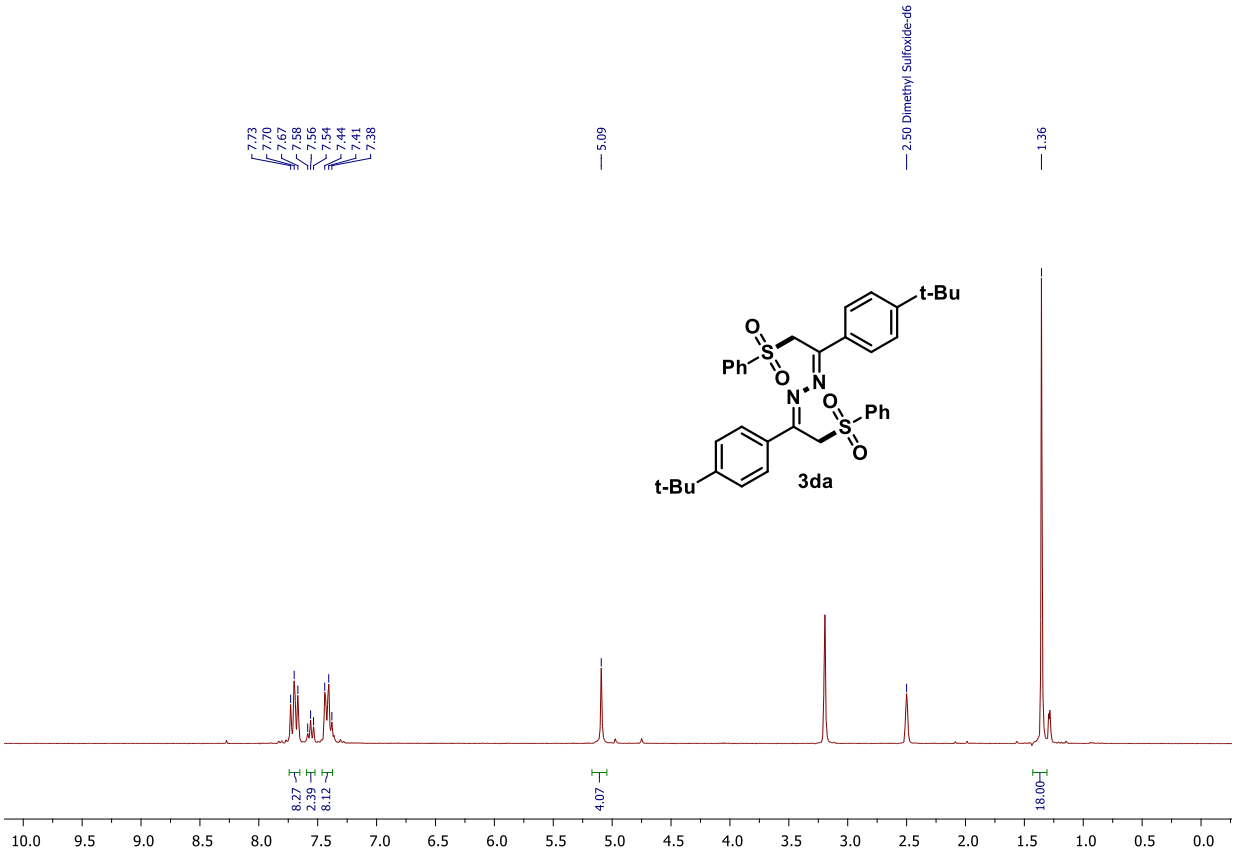
23.49
3ca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t-Bu
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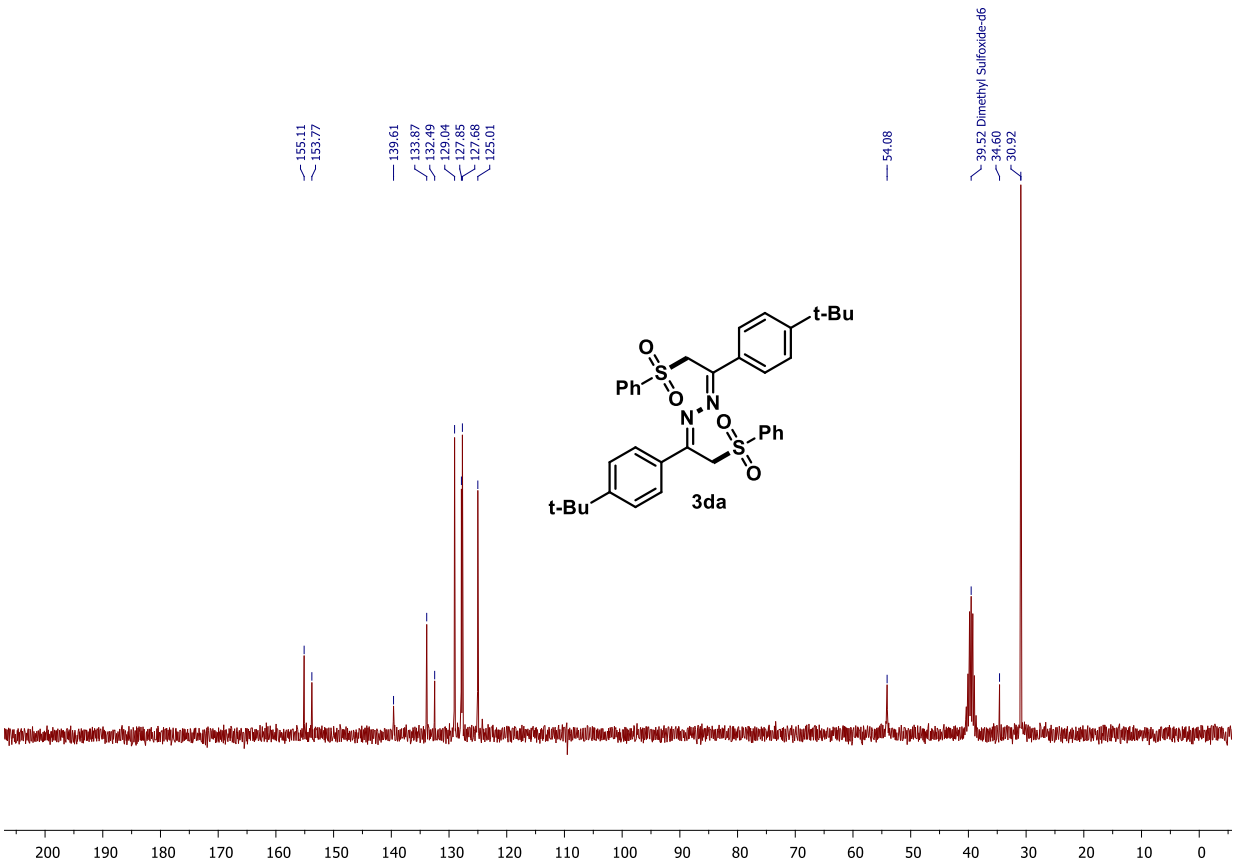
8.12
4.07
18.00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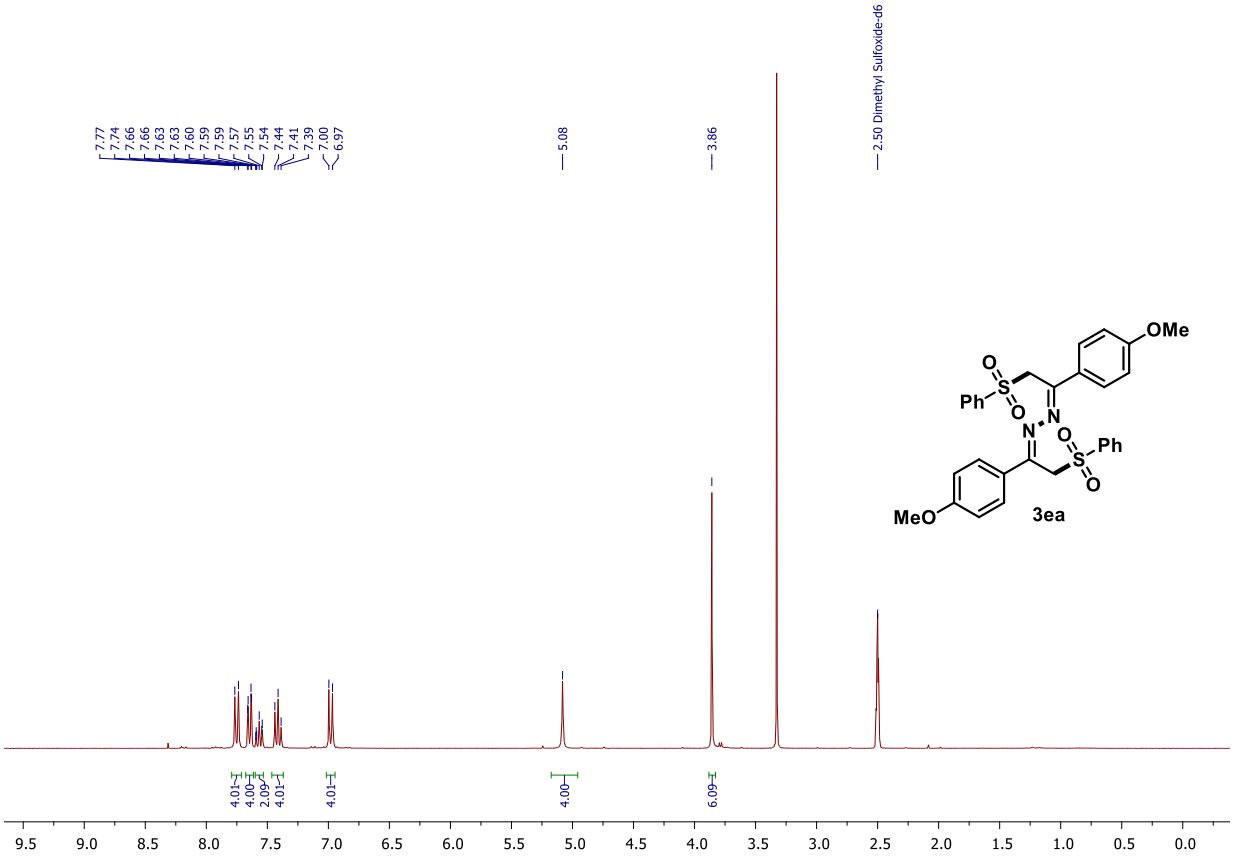
t-Bu
Ph
Ph
t-Bu
3da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7.63
7.63
7.60
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7.59
7.57
7.55
7.54
7.44
7.41
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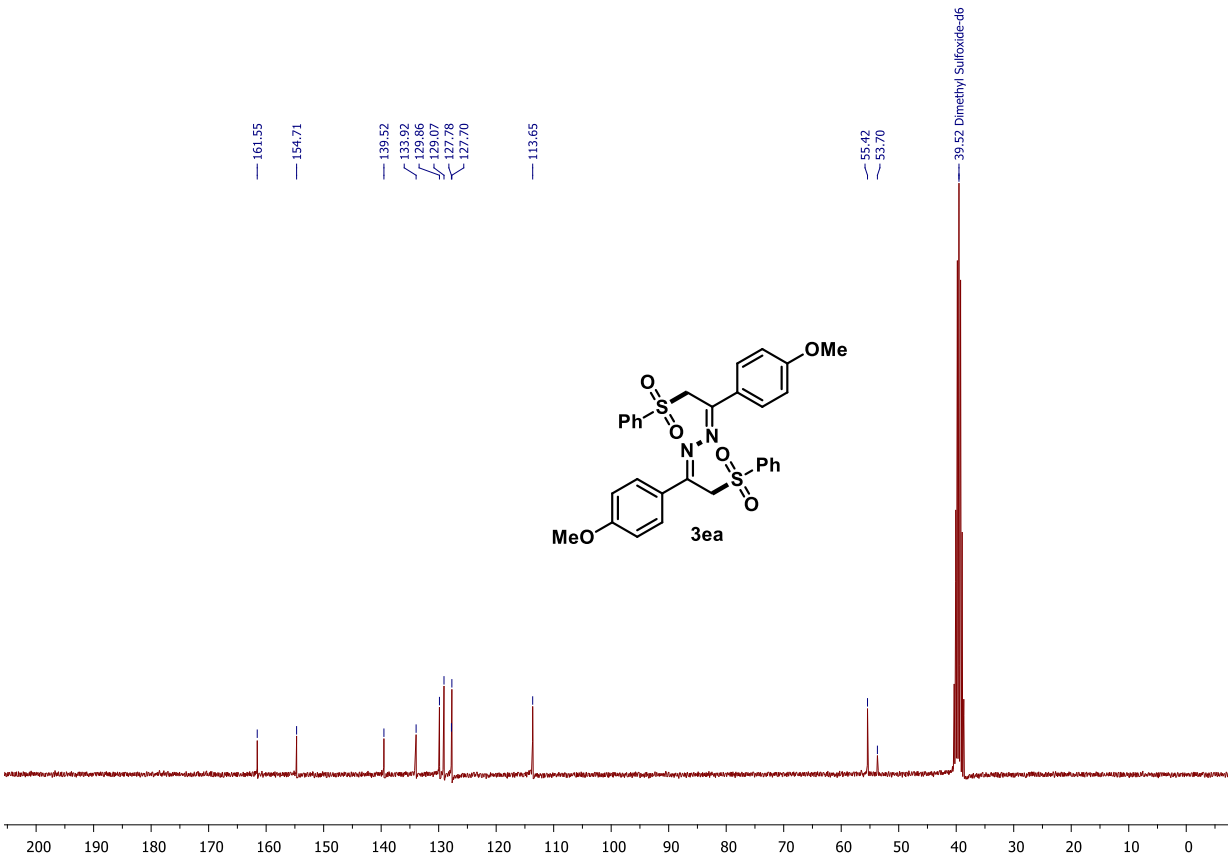
7.00
6.97
5.08
3.86
2.50 Dimethyl Sulfoxide-d6
OMe
Ph
Ph
MeO
3ea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127.70
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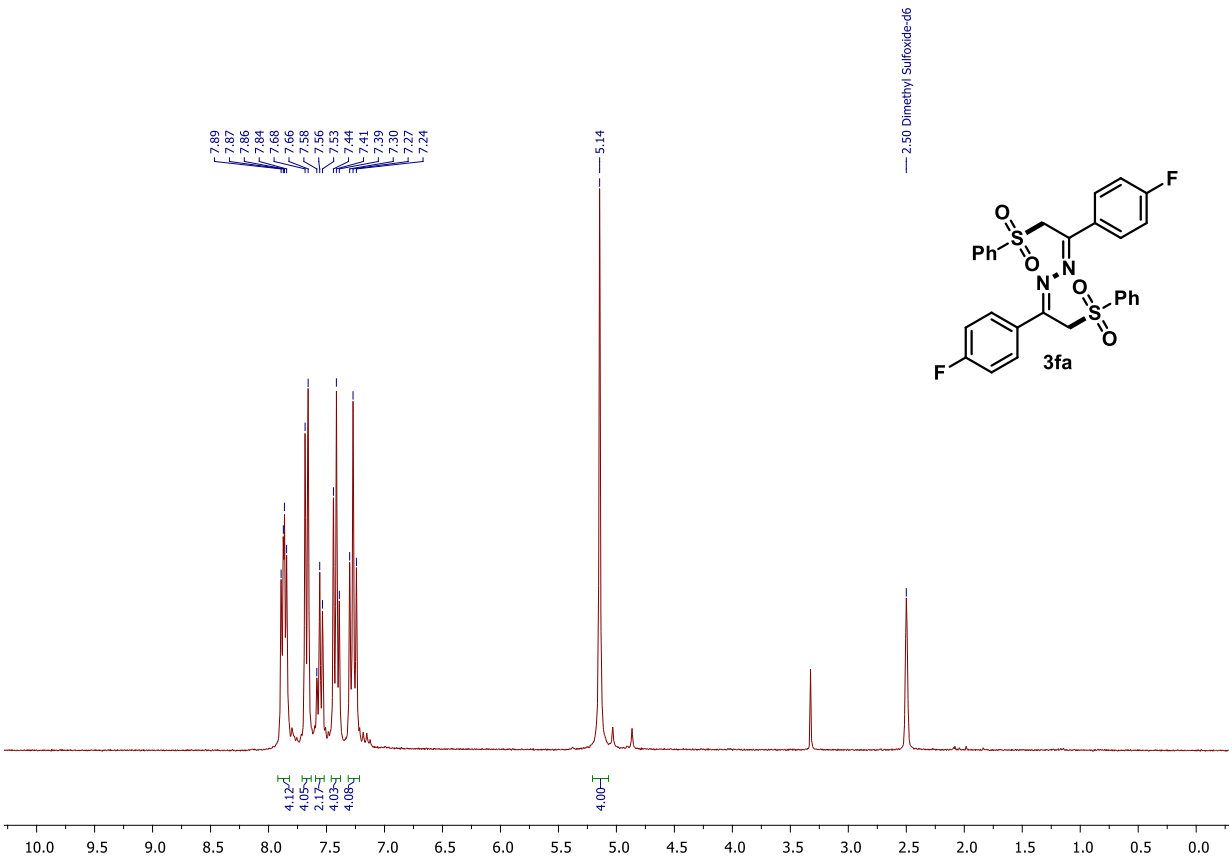
OMe
Ph
Ph
MeO
3ea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7.56
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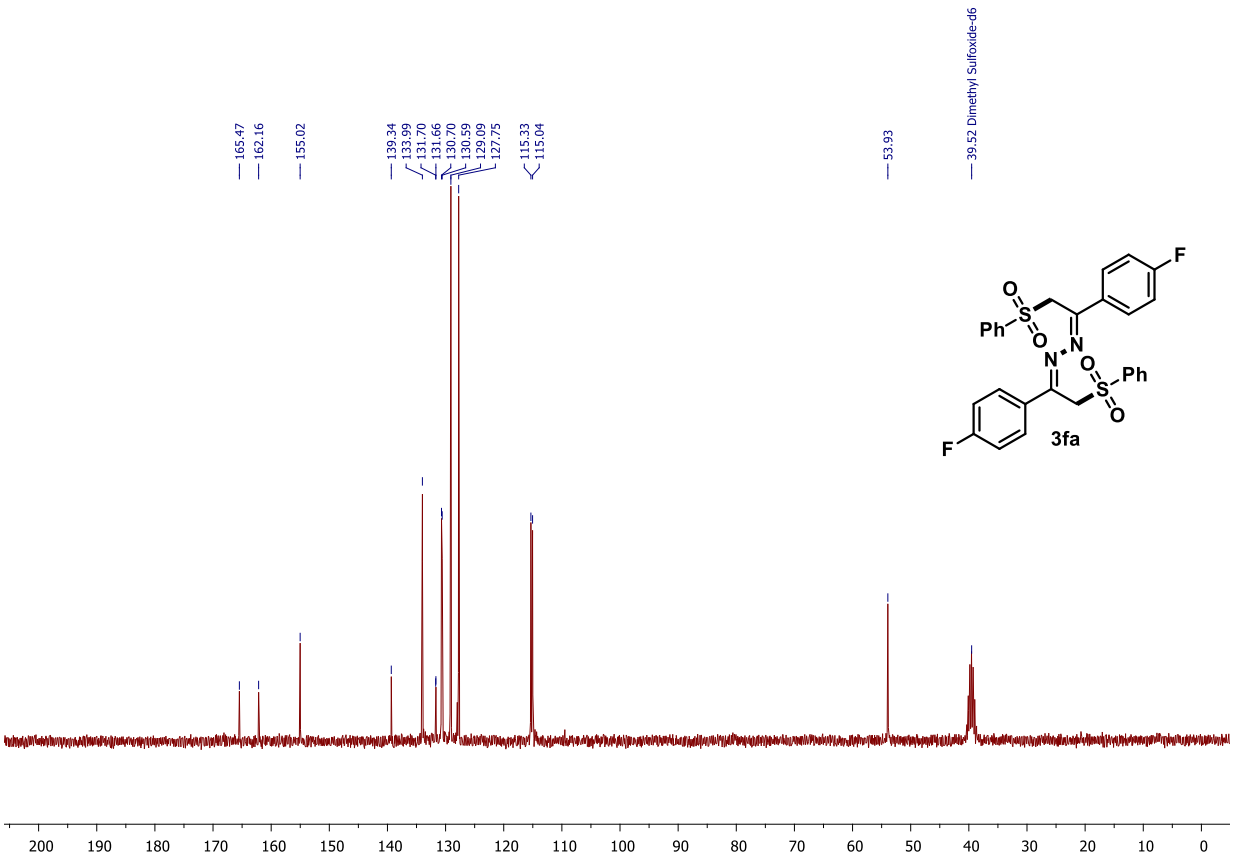
7.44
7.41
7.39
7.30
7.27
7.24
5.14
2.50 Dimethyl Sulfoxide-d6
F
Ph
Ph
F
3fa
4.12
4.05
2.17
4.03
4.08
4.00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127.75
115.33
115.04
53.93
39.52 Dimethyl Sulfoxide-d6
F
O
S
Ph
O
N
N
O
Ph
S
O
F
3fa
200
190
180
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150
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10
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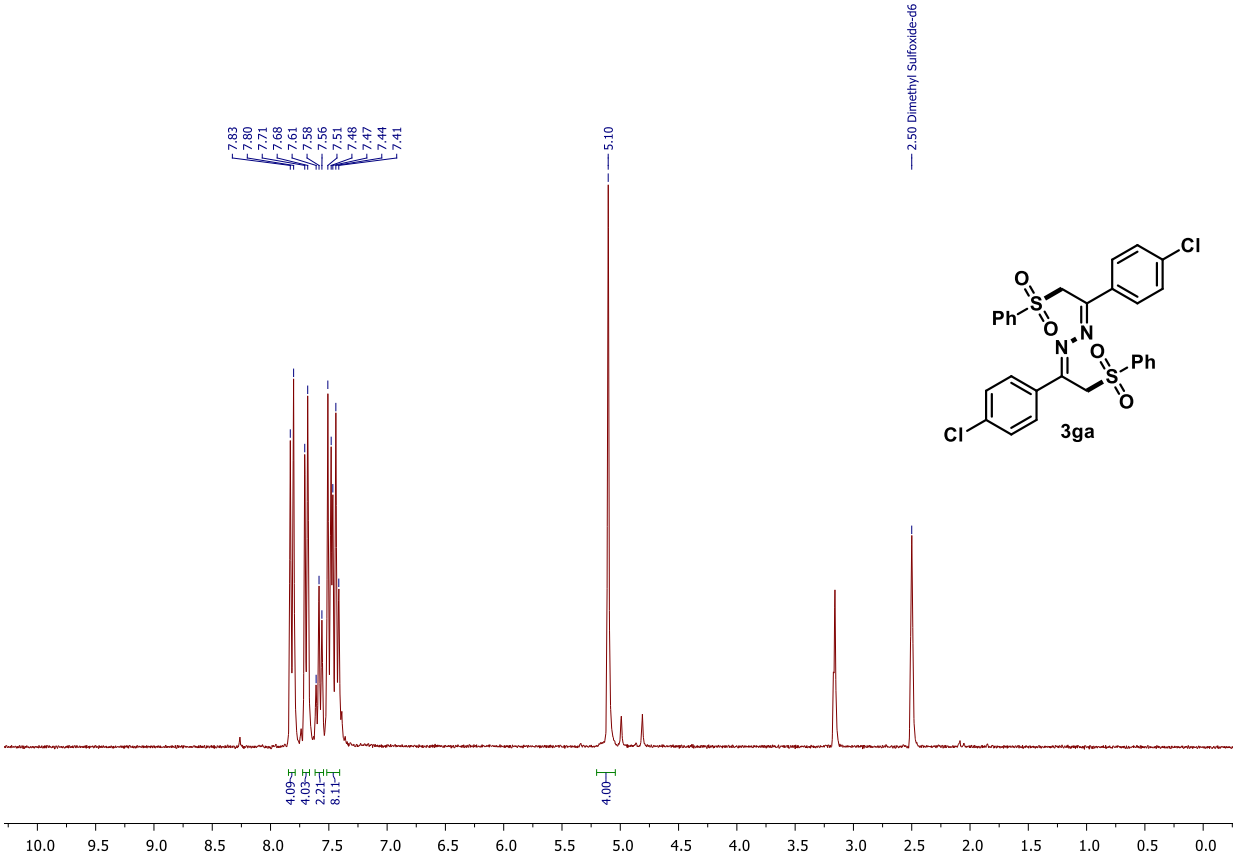
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7.41
5.10
2.50 Dimethyl Sulfoxide-d6
Cl
O
S
Ph
O
N
N
O
Ph
S
O
Cl
3ga
4.09
4.03
2.21
8.11
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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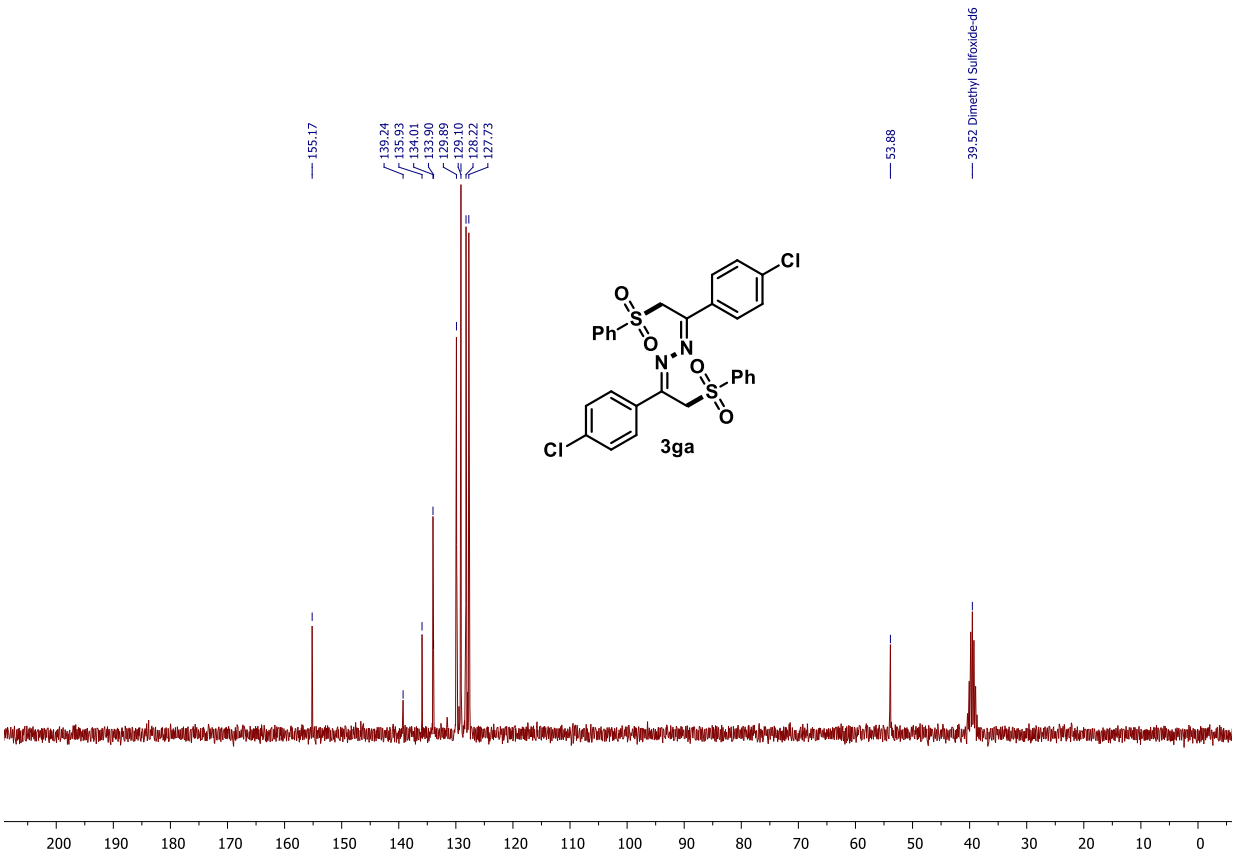
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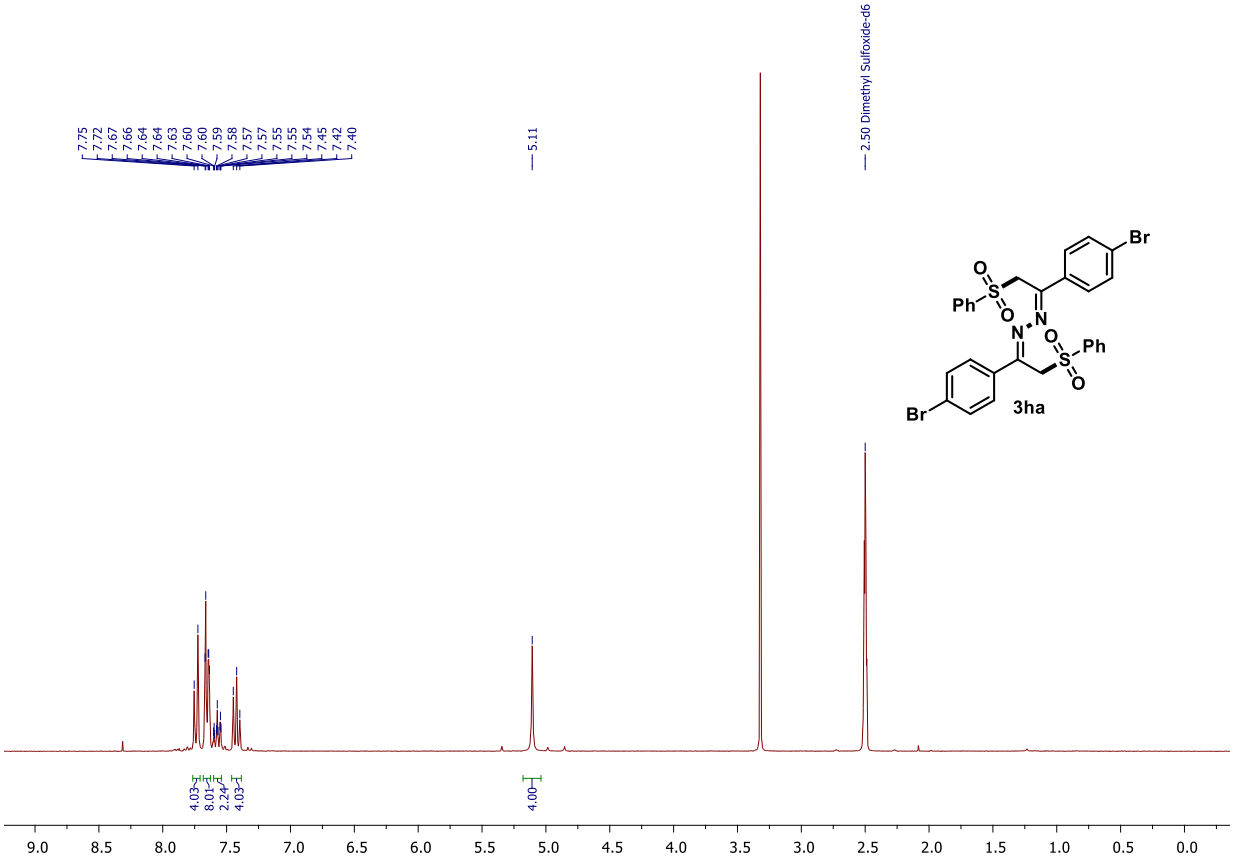
Cl
Ph
Ph
Cl
3ga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7.57
7.55
7.55
7.54
7.45
7.42
7.40
5.11
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Br
Ph
Ph
Br
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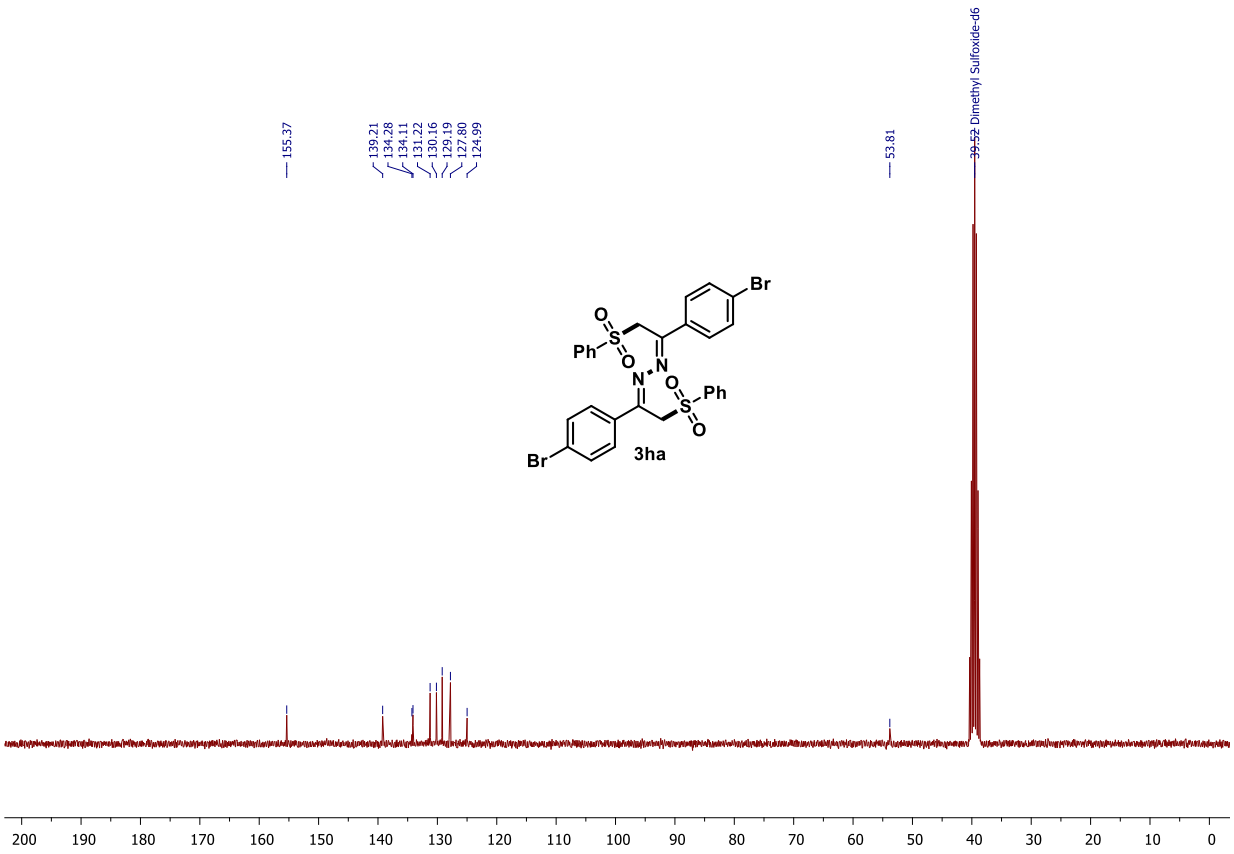
4.03
8.01
2.24
4.03
4.00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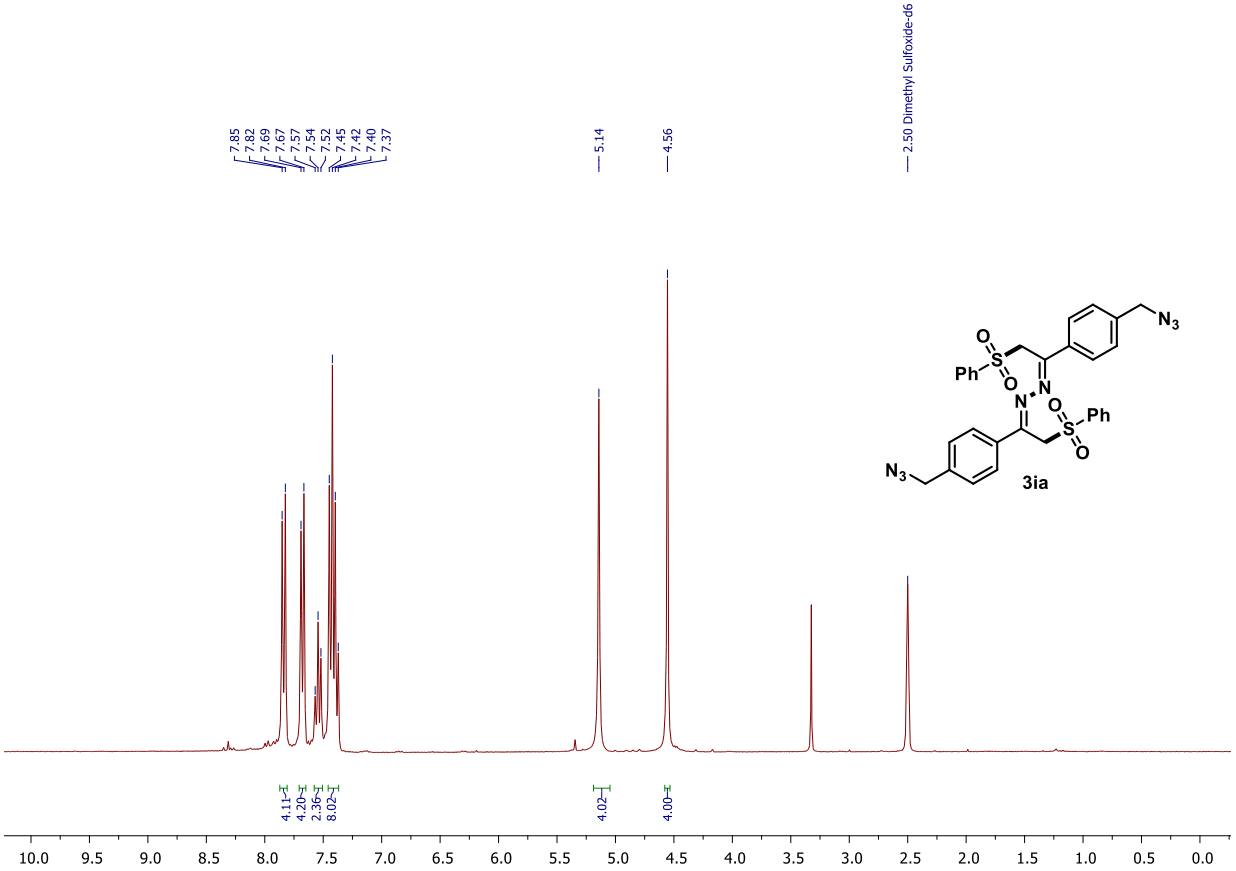
Br
Ph
Ph
Br
3ha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7.52
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5.14
4.56
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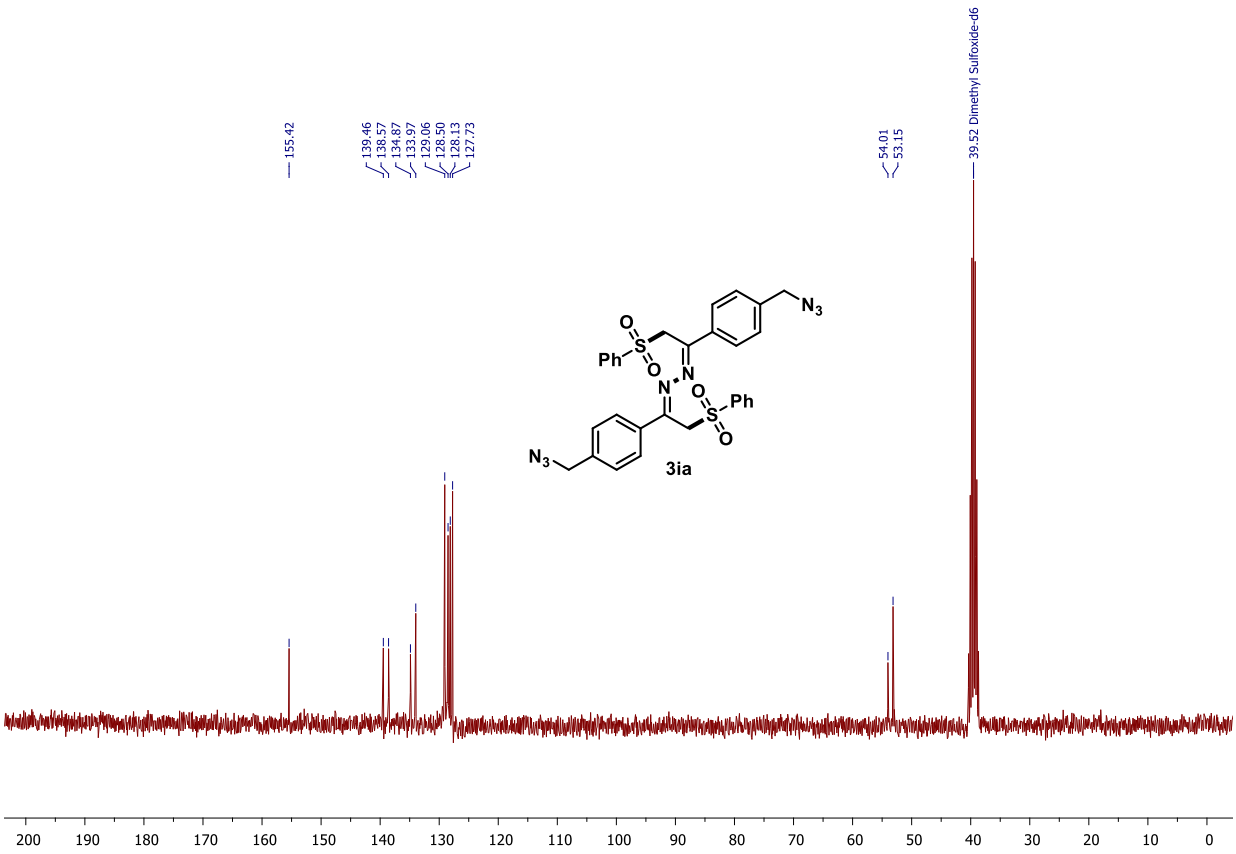
N3
Ph
Ph
N3
3ia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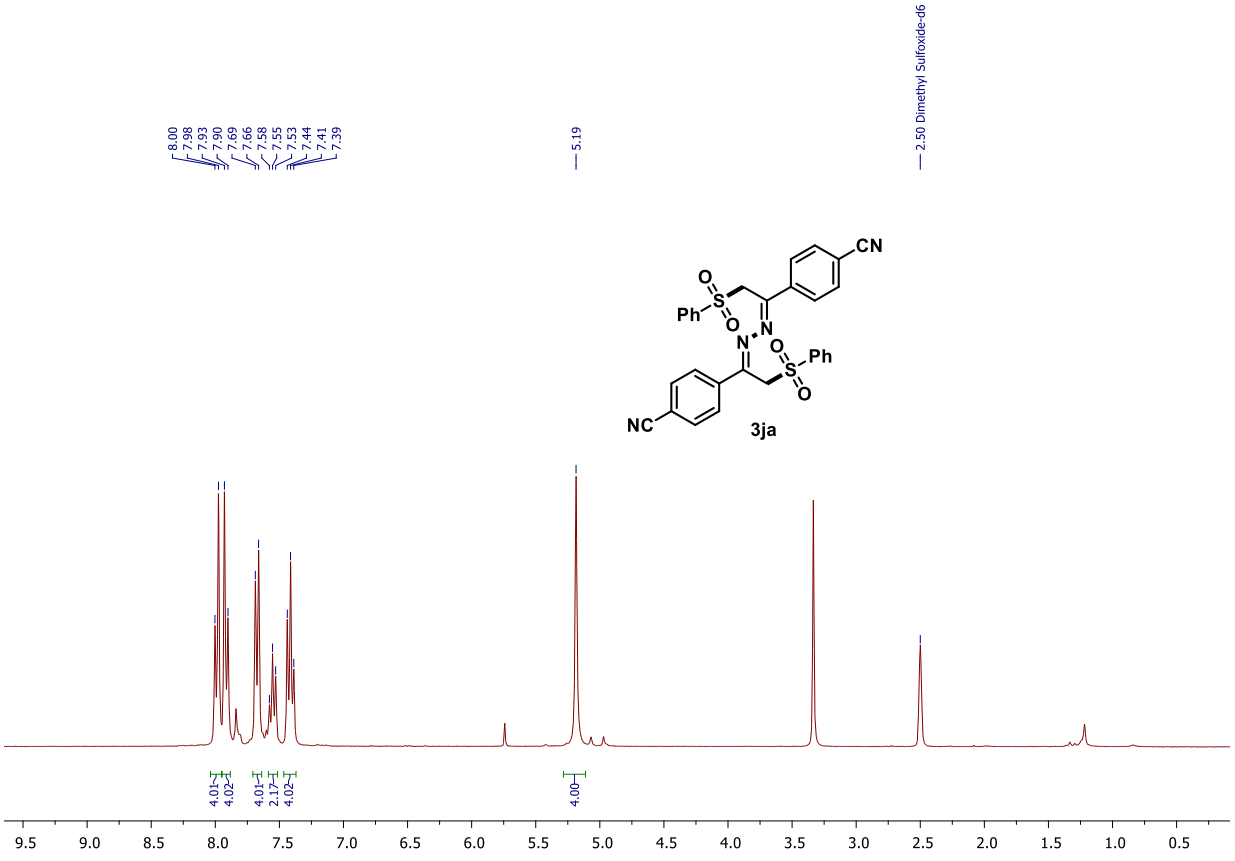
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5.19
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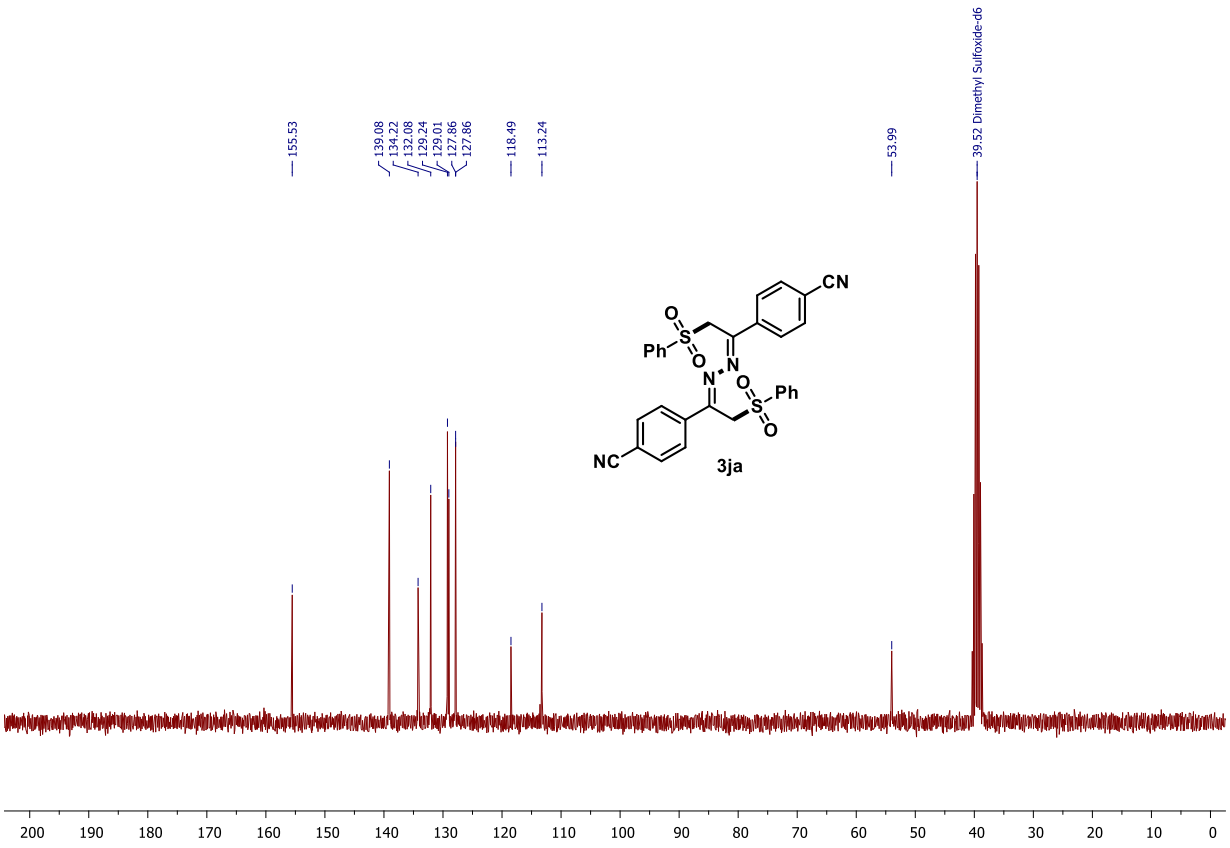
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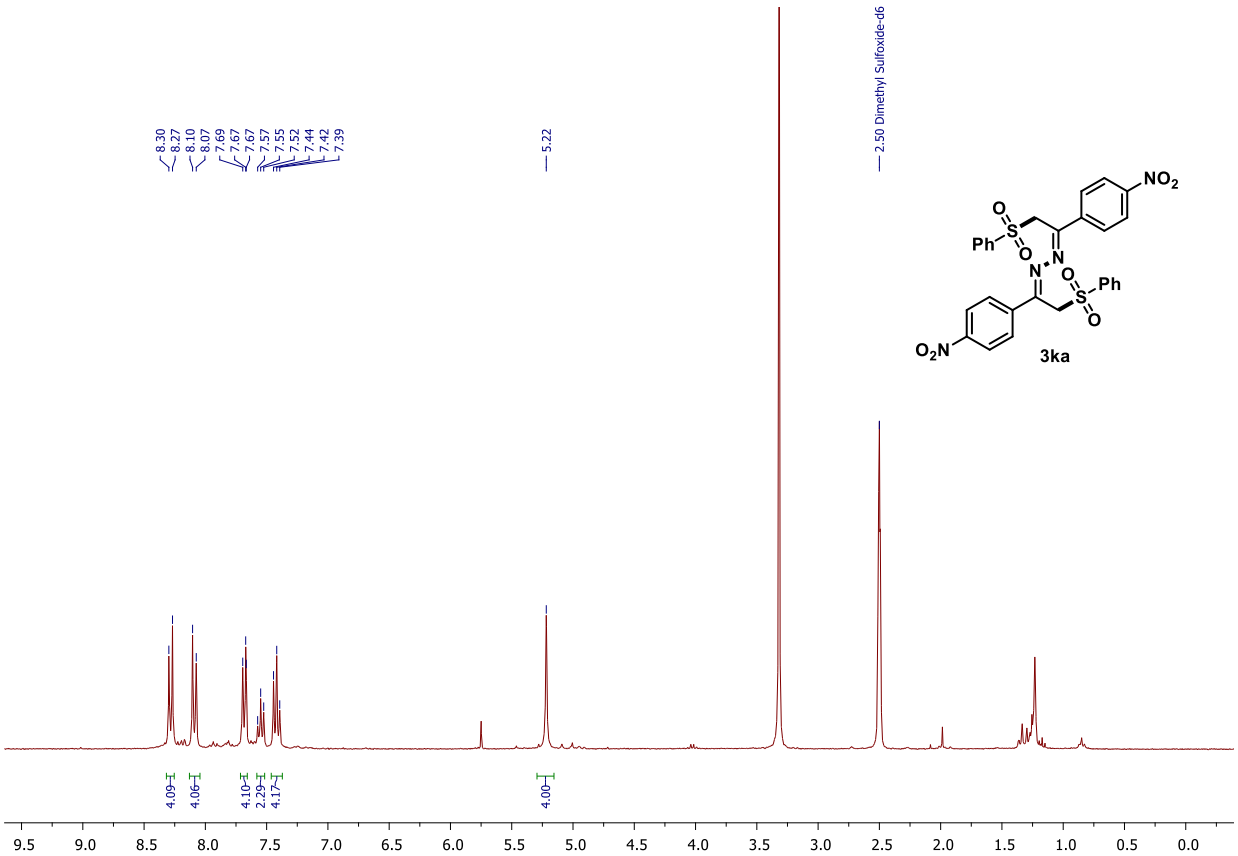
CN
Ph
Ph
NC
3ja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7.57
7.55
7.52
7.44
7.42
7.39
5.22
2.50 Dimethyl Sulfoxide-d6
NO2
Ph
Ph
O2N
3ka
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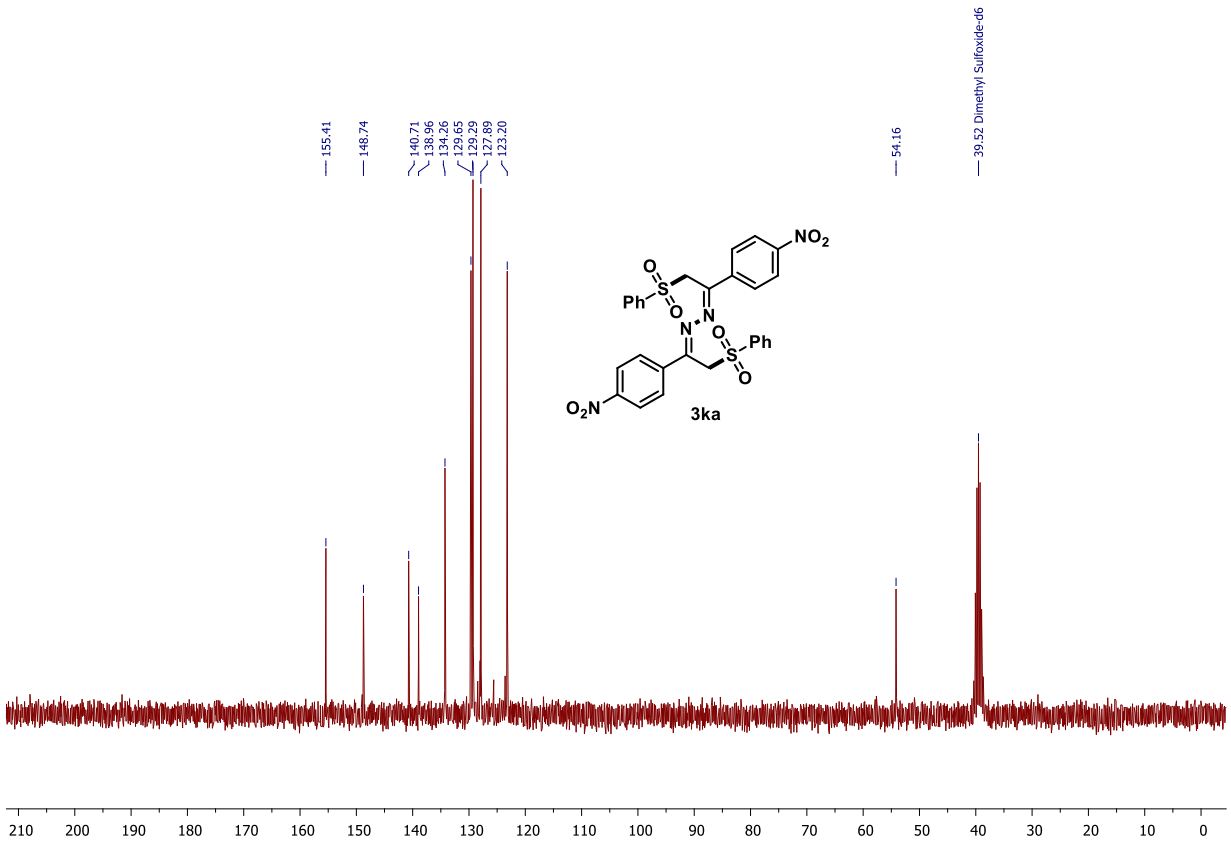
4.06
4.10
2.29
4.17
4.00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NO2
Ph
Ph
O2N
3ka
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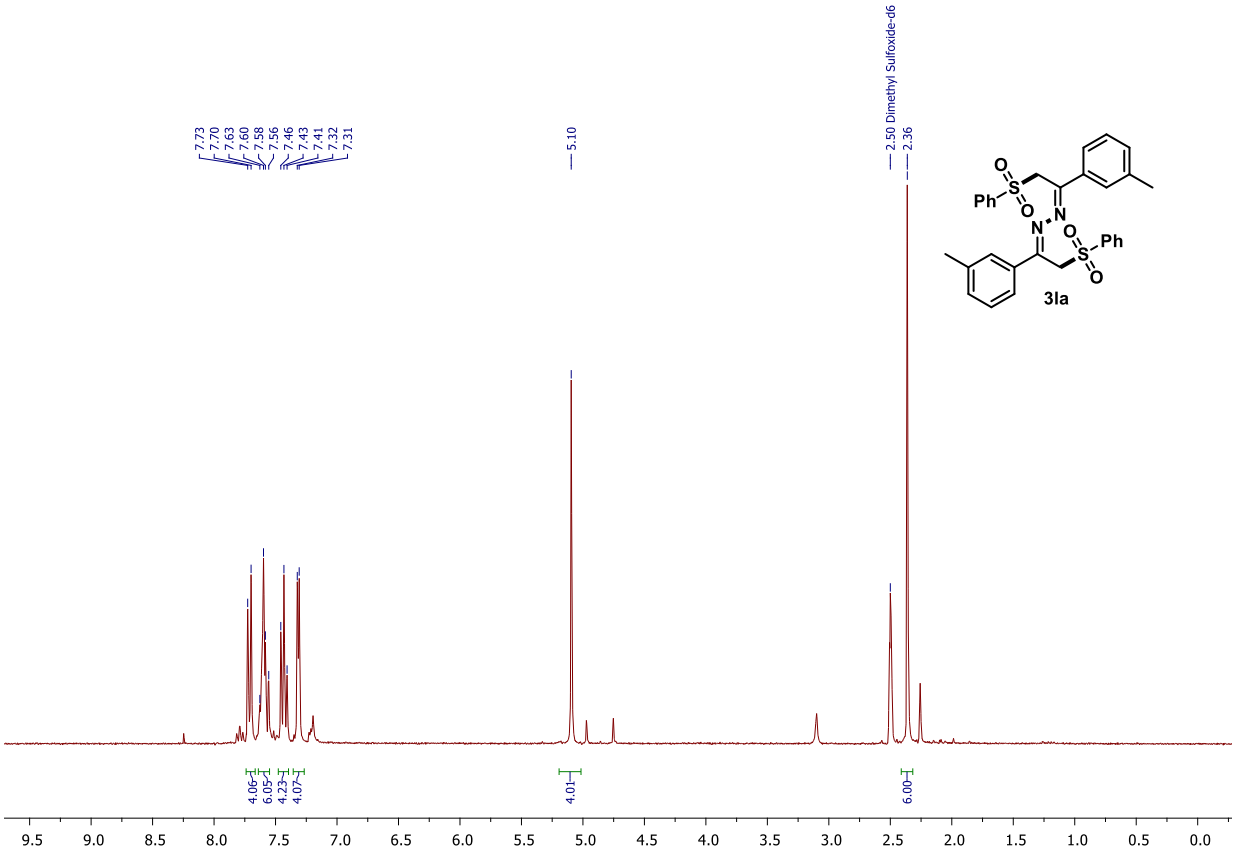
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7.32
7.31
5.10
2.50 Dimethyl Sulfoxide-d6
2.36
Ph
Ph
3la
4.06
6.05
4.23
4.07
4.01
6.00
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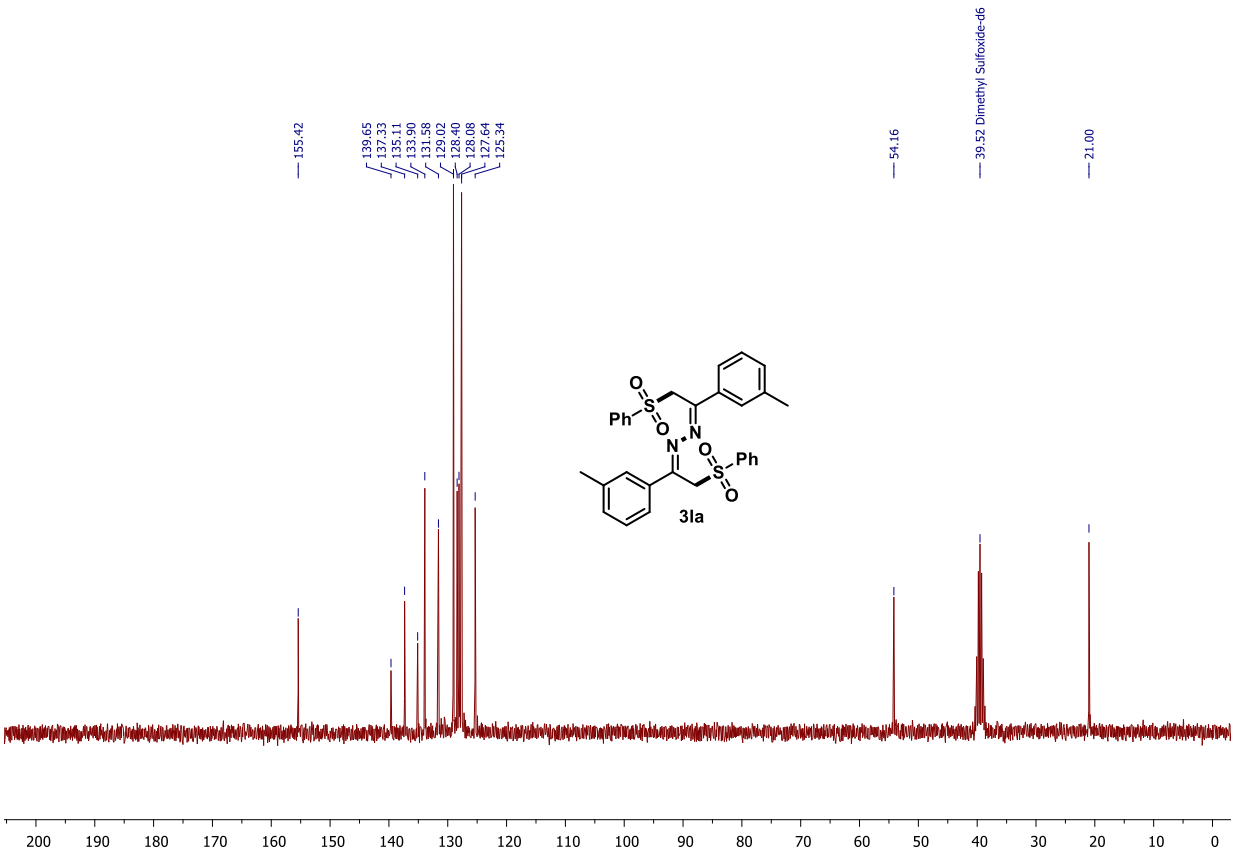
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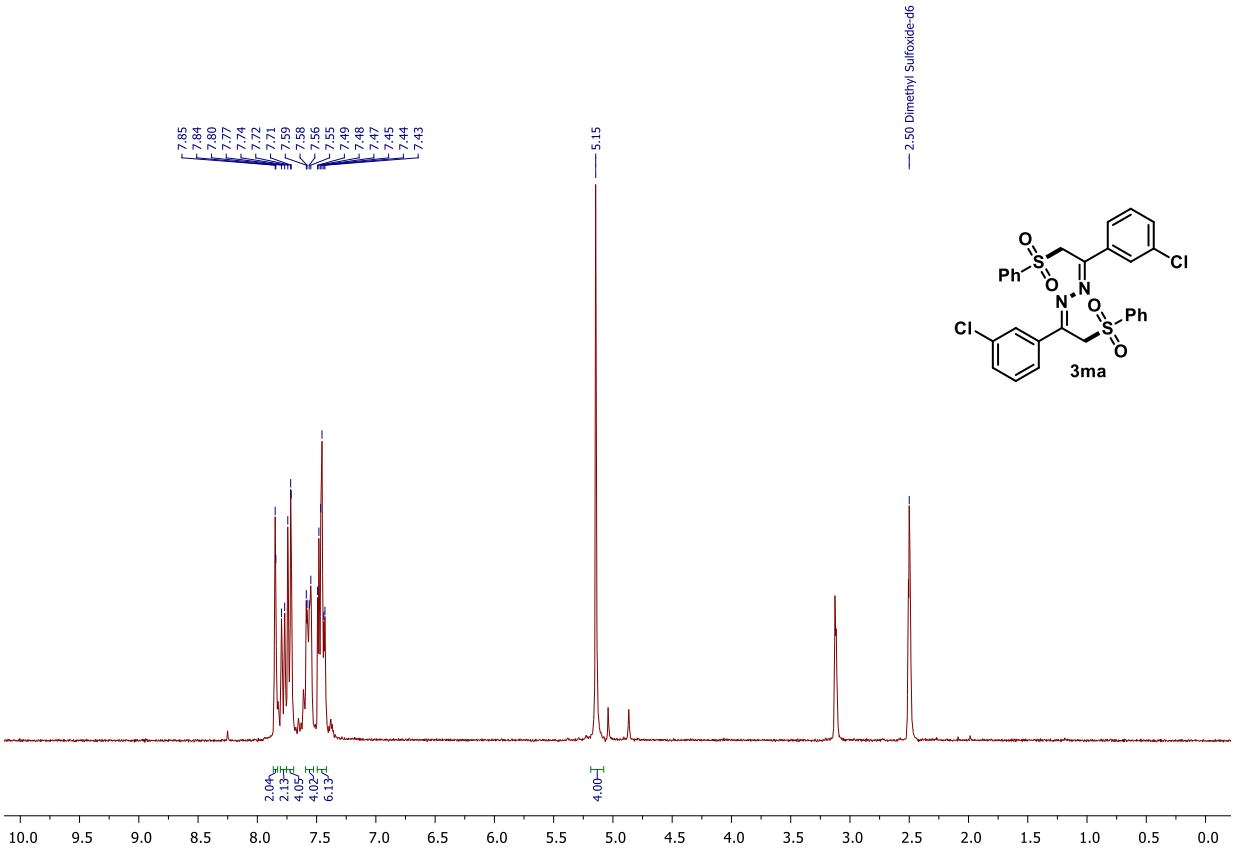
39.52 Dimethyl Sulfoxide-d6
21.00
3la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7.45
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2.50 Dimethyl Sulfoxide-d6
2.04
2.13
4.05
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6.13
4.00
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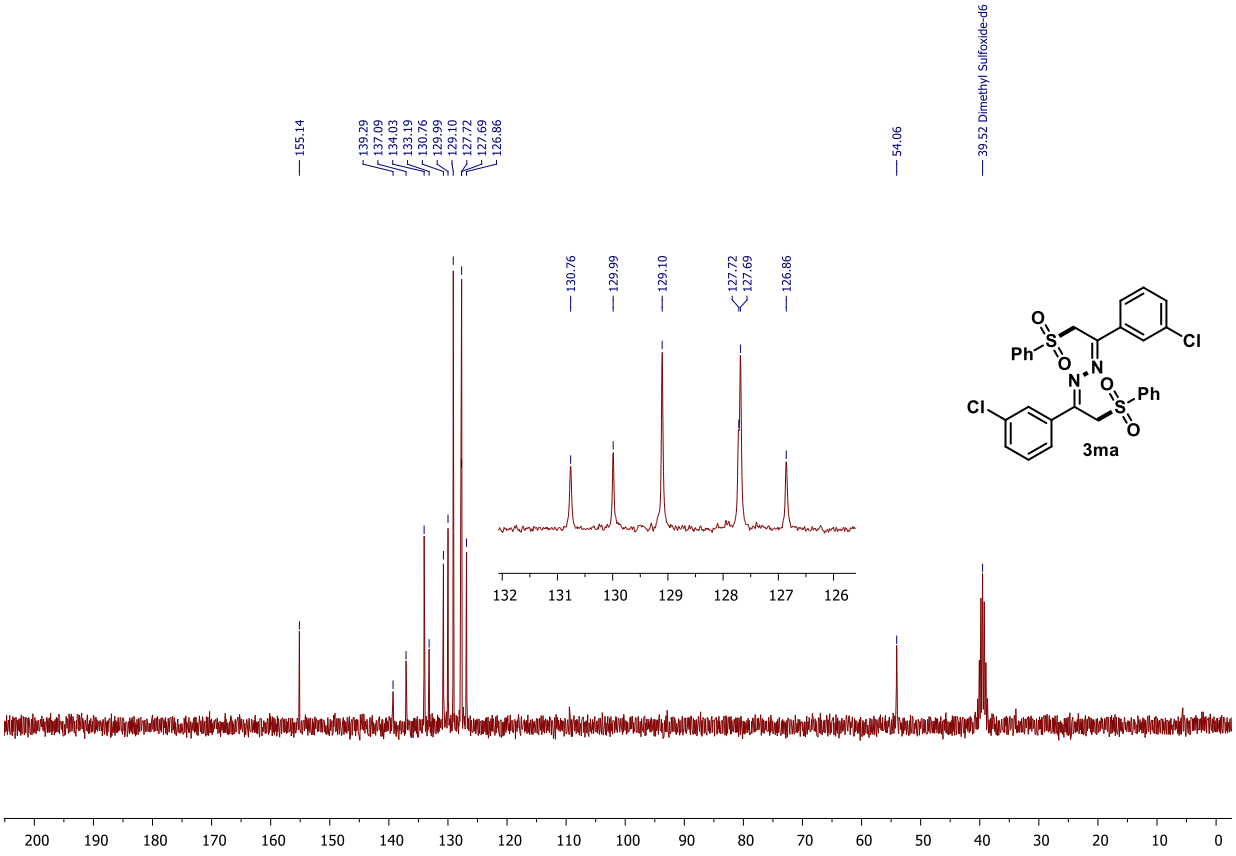
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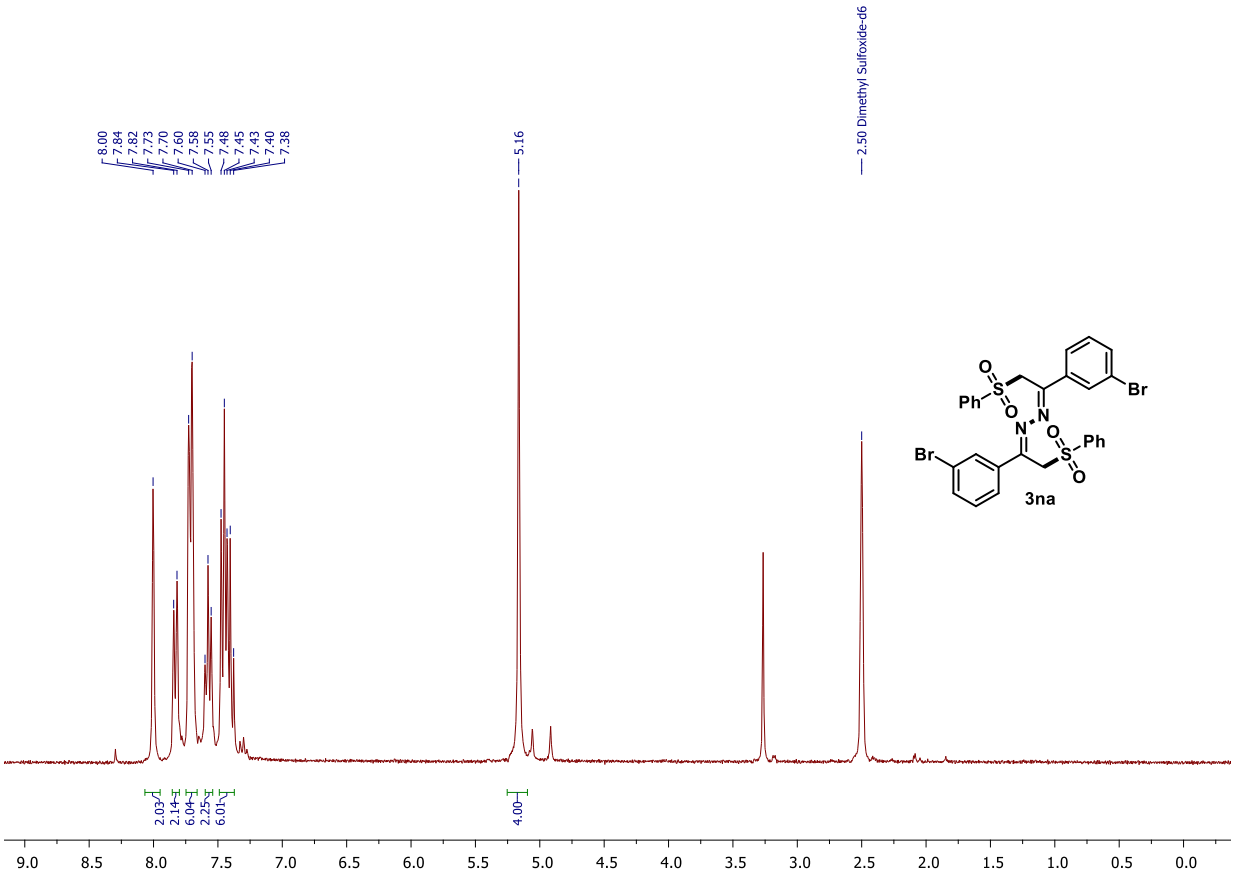
39.52 Dimethyl Sulfoxide-d6
Cl
Ph
Ph
Cl
3ma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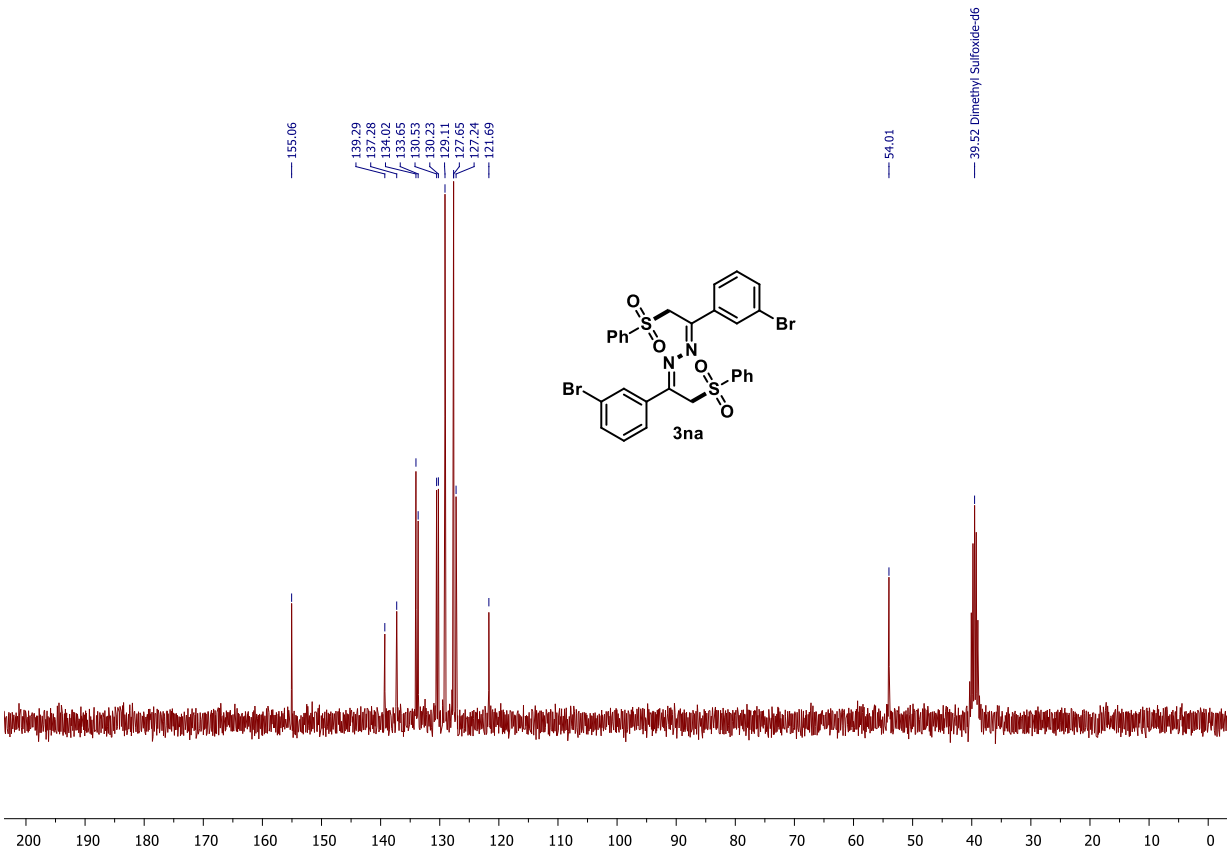
7.38
5.16
2.50 Dimethyl Sulfoxide-d6
Br
Ph
Ph
Br
3na
2.03
2.14
6.04
2.25
6.01
4.00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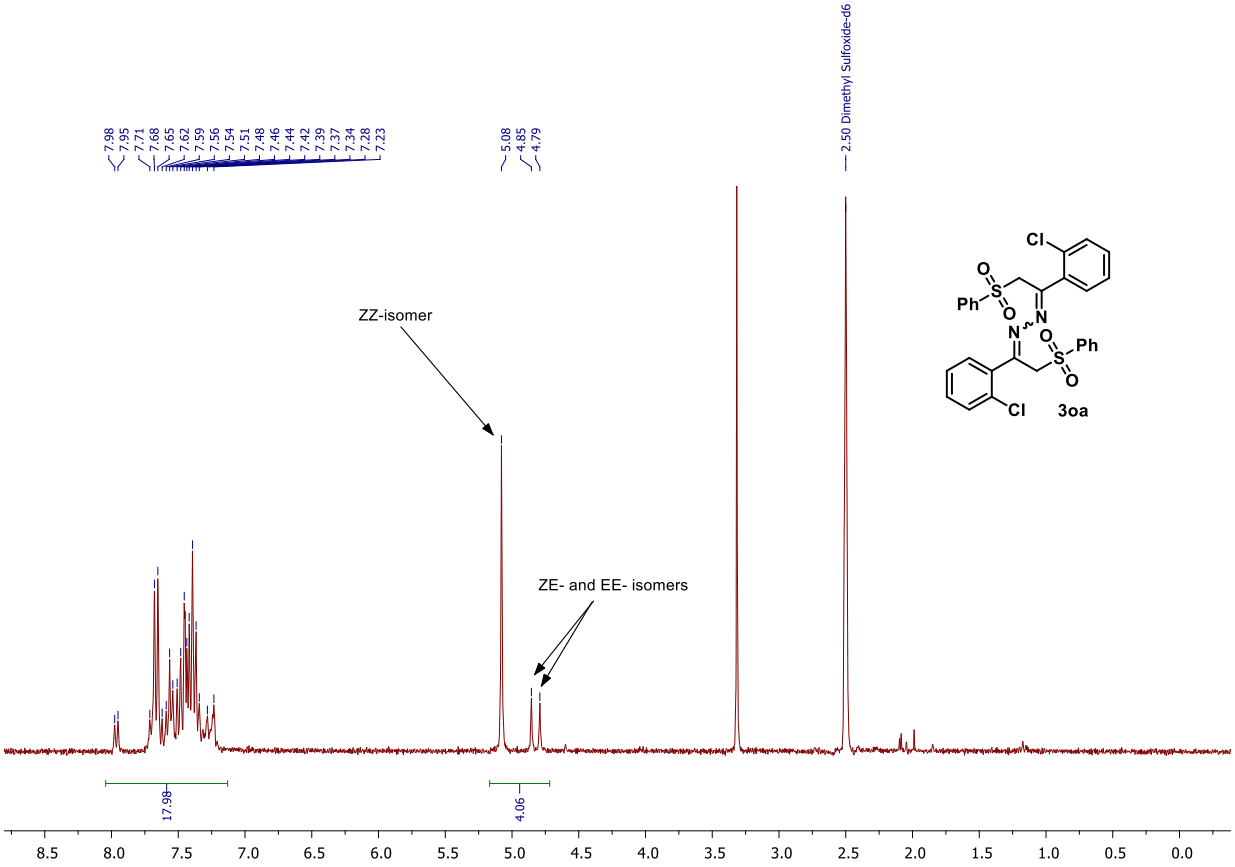
Br
Ph
Br
Ph
3na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7.42
7.39
7.37
7.34
7.28
7.23
5.08
4.85
4.79
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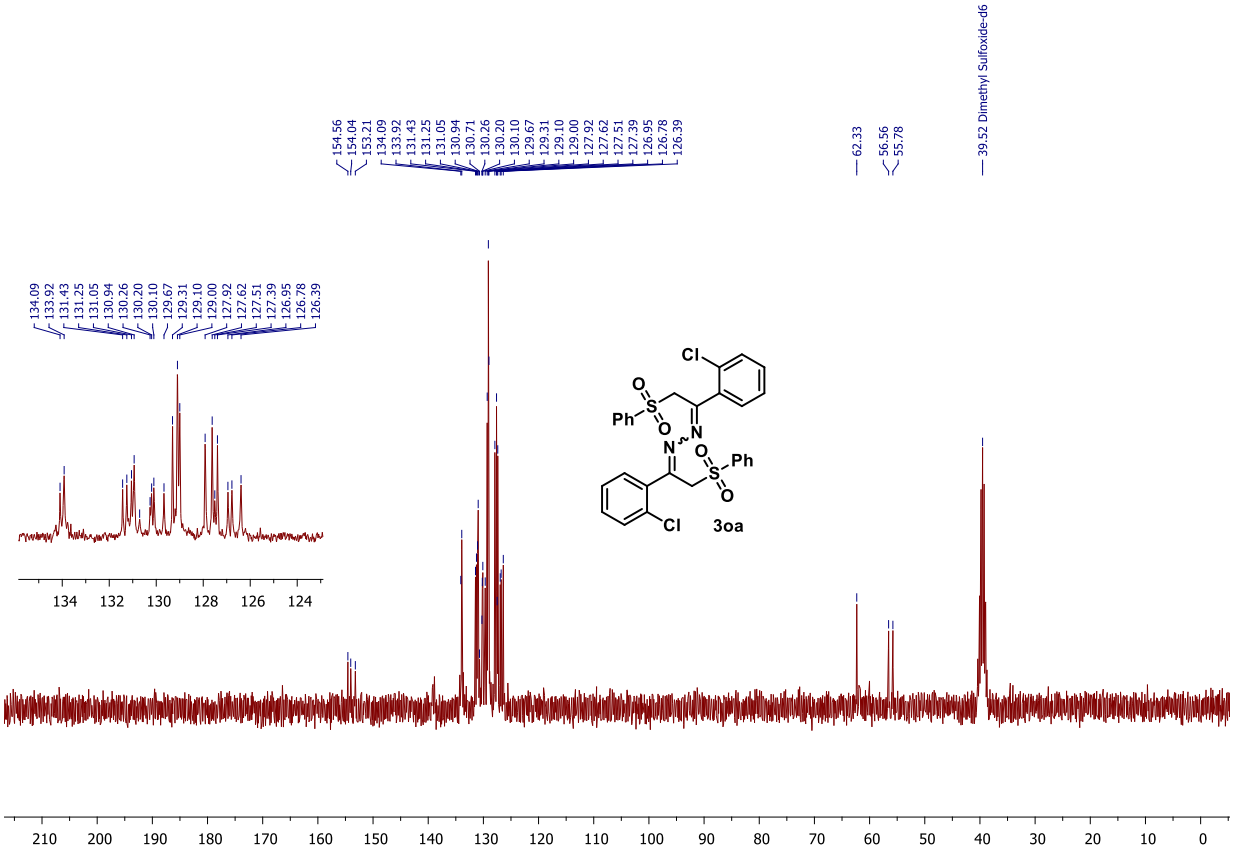
ZZ-isomer
ZE- and EE- isomers
Cl
Ph
Ph
Cl
3oa
17.98
4.06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127.39
126.95
126.78
126.39
62.33
56.56
55.78
39.52 Dimethyl Sulfoxide-d6
Cl
Ph
Ph
Cl
3oa
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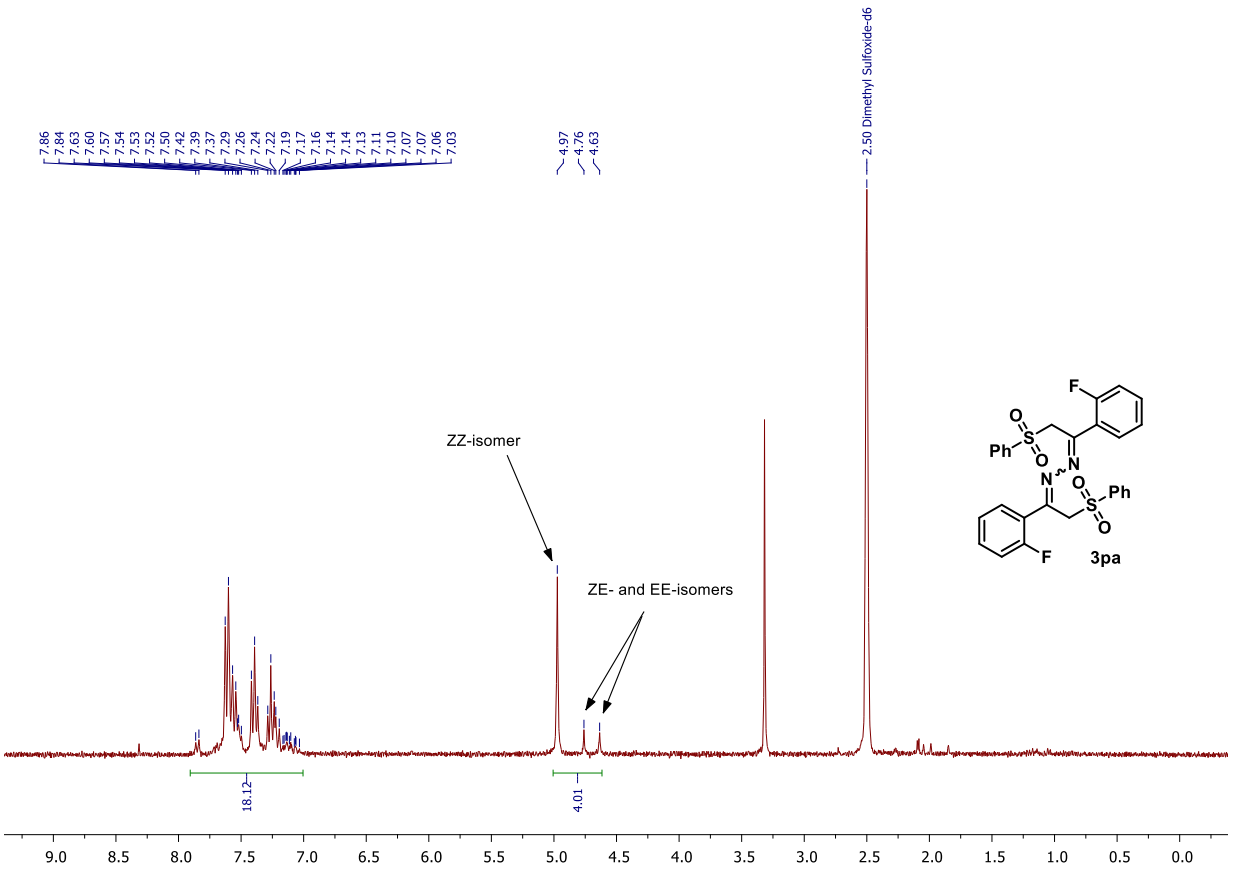
134 132 130 128 126 124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7.06
7.03
4.97
4.76
4.63
2.50 Dimethyl Sulfoxide-d6
ZZ-isomer
ZE- and EE-isomers
F
Ph
Ph
F
3pa
18.12
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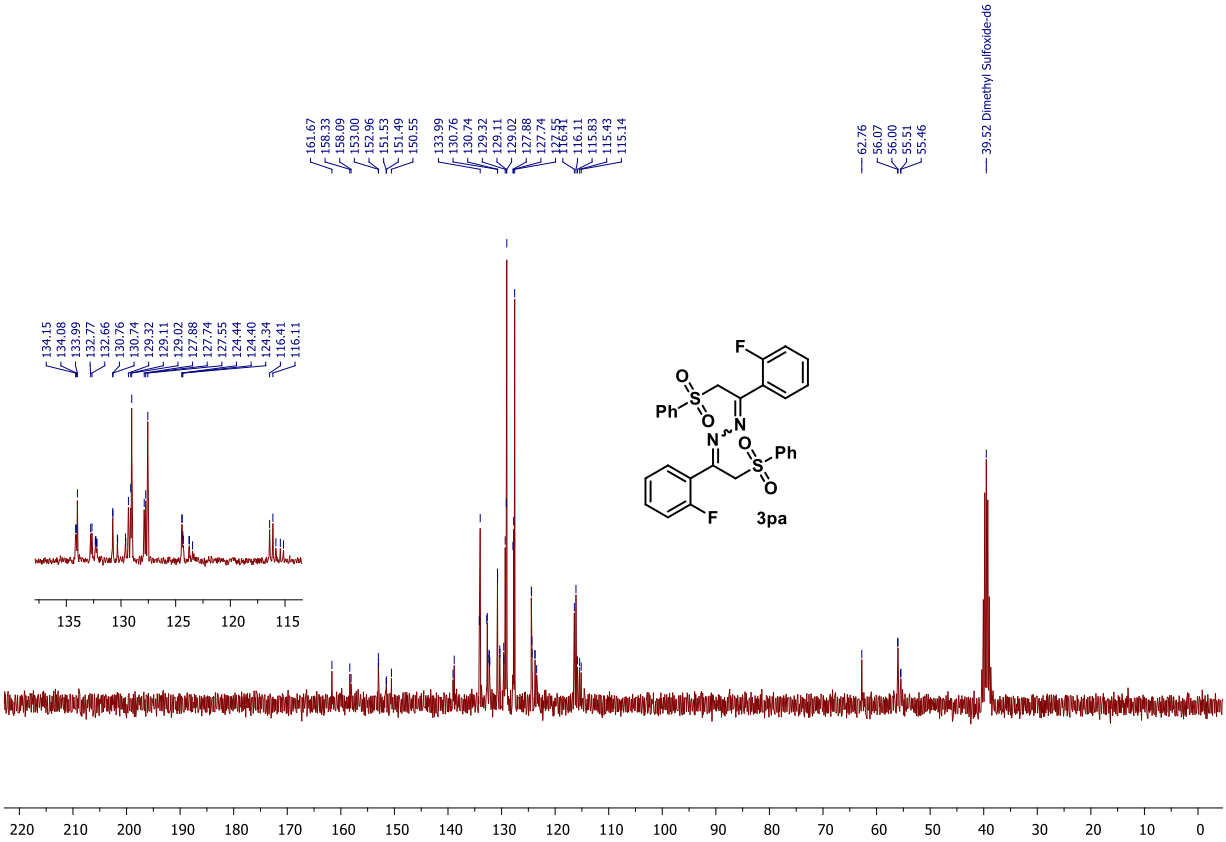
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116.11
115.83
115.43
115.14
62.76
56.07
56.00
55.51
55.46
39.52 Dimethyl Sulfoxide-d6
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S
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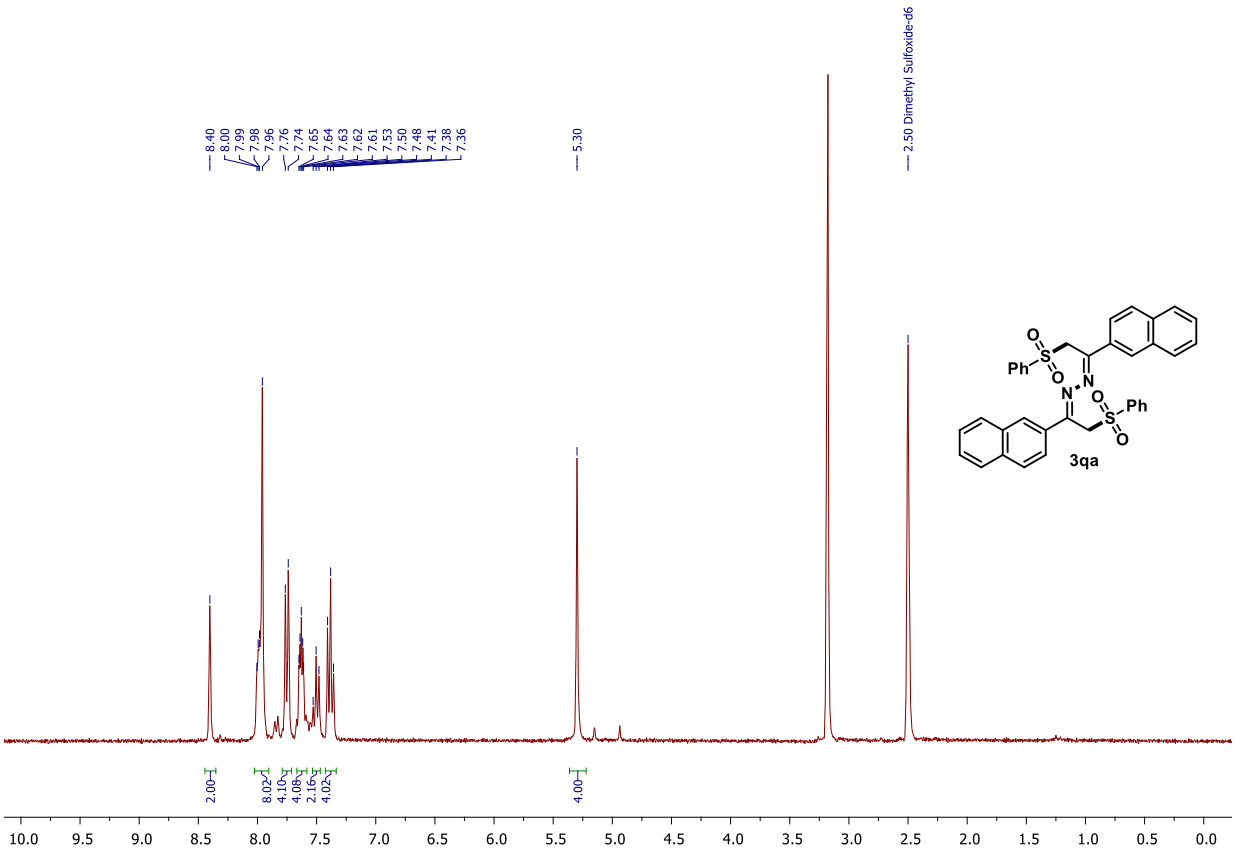
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7.50
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7.38
7.36
5.30
2.50 Dimethyl Sulfoxide-d6
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4.10
4.08
2.16
4.02
4.00
O
S
Ph
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N
N
O
S
Ph
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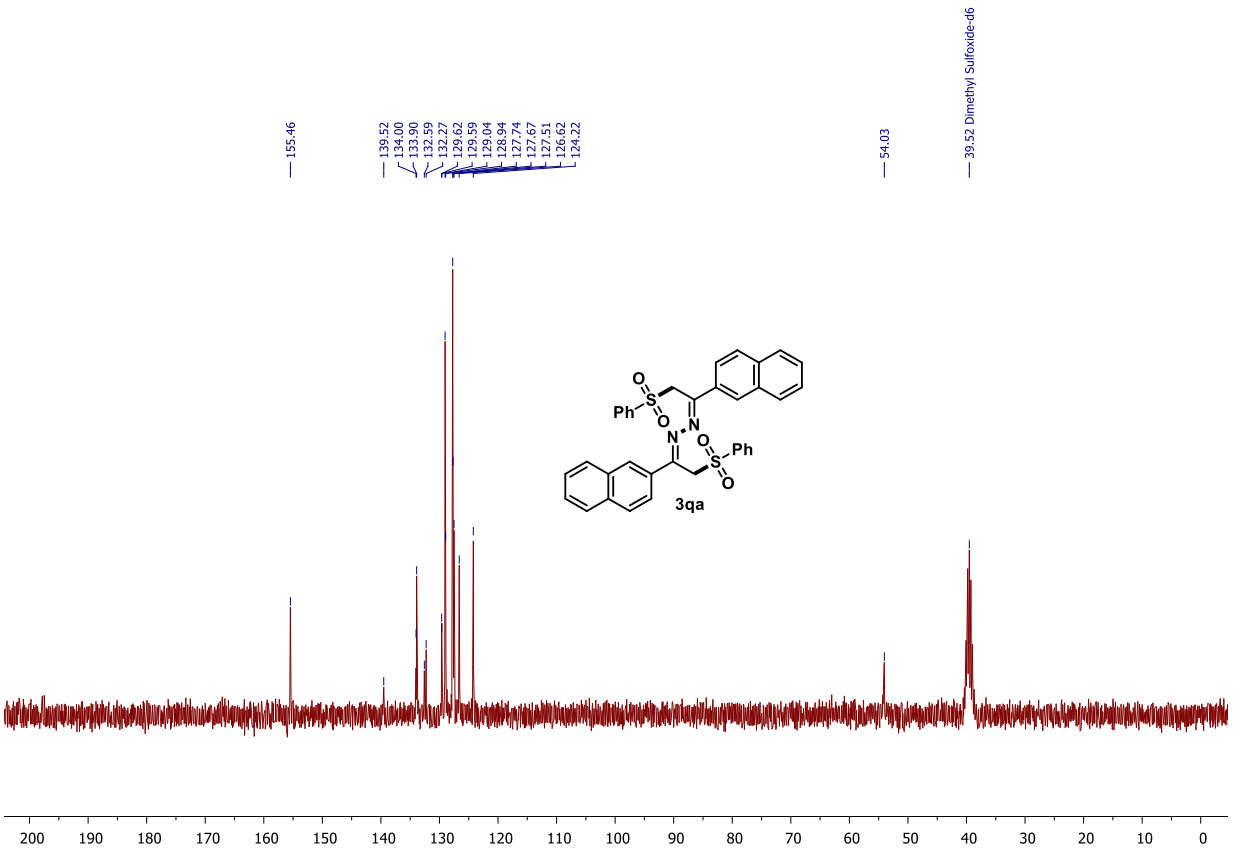
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54.03
39.52 Dimethyl Sulfoxide-d6
Ph
Ph
3qa
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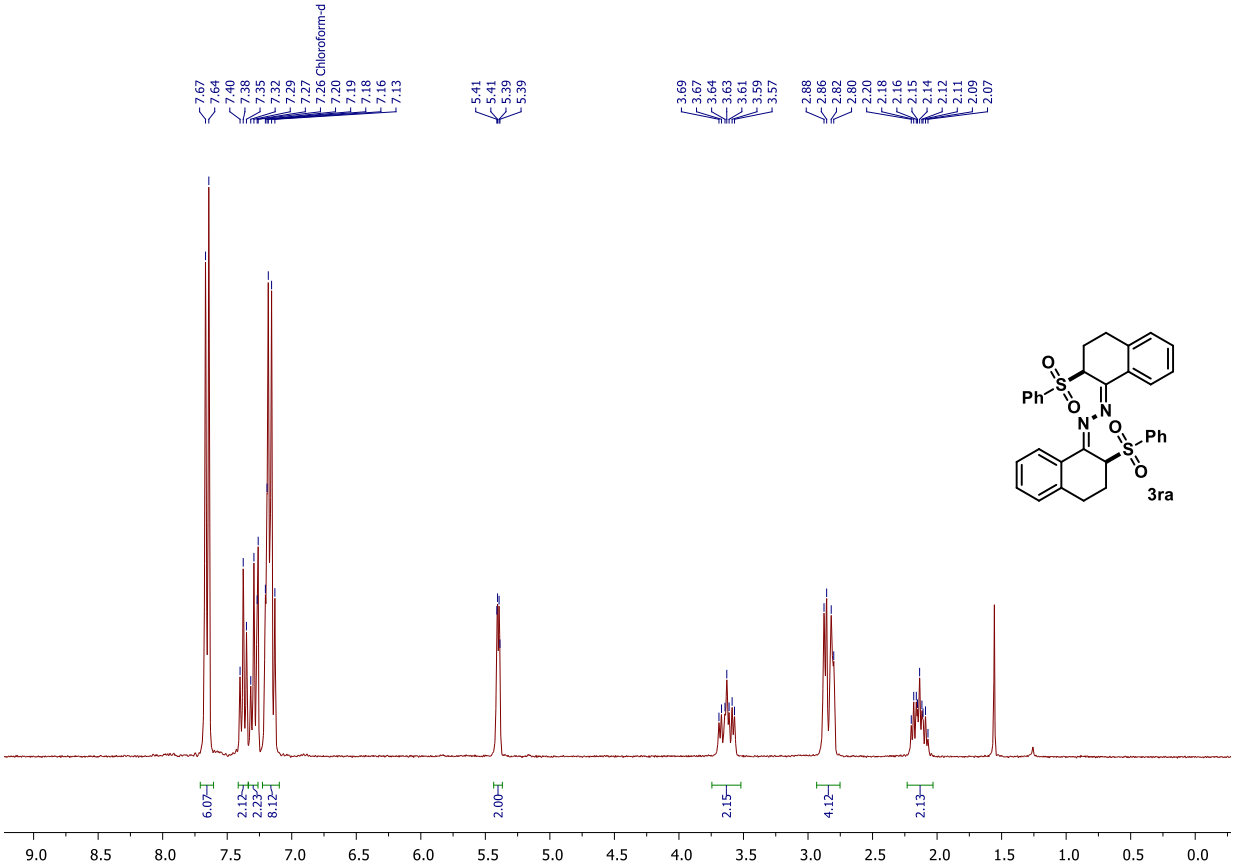
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7.27
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7.18
7.16
7.13
5.41
5.41
5.39
5.39
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3.67
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3.61
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3.57
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2.15
2.14
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Ph
Ph
3ra
6.07
2.12
2.23
8.12
2.00
2.15
4.12
2.13
9.0
8.5
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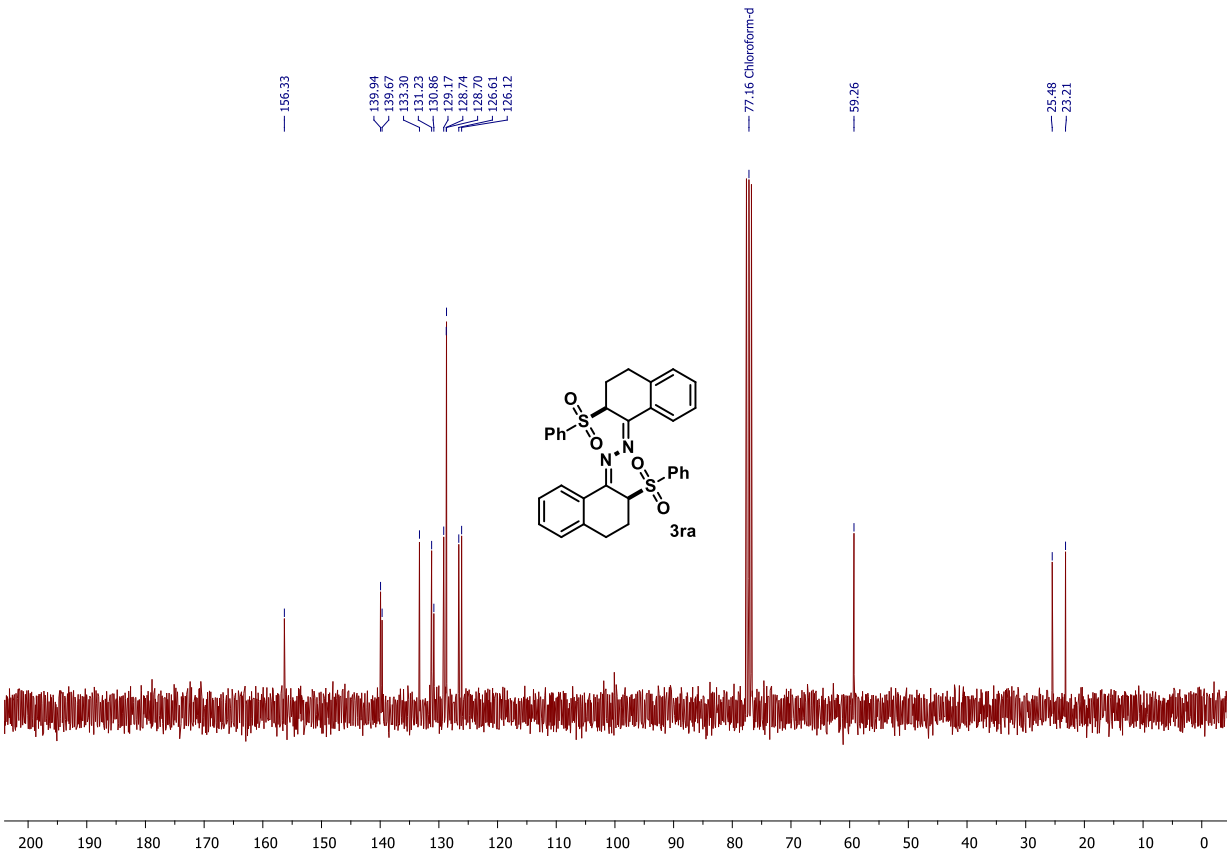
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Ph
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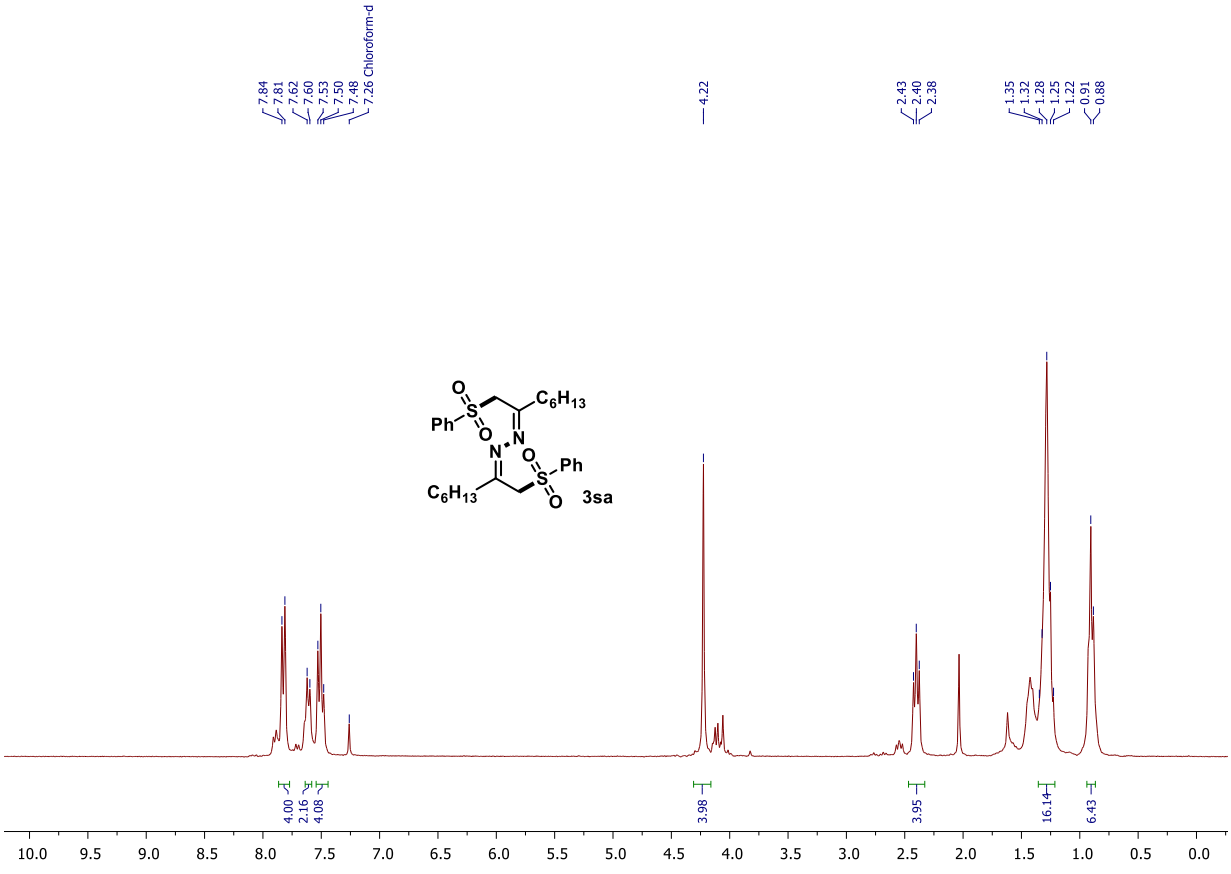
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2.38
1.35
1.32
1.28
1.25
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0.88
Ph
Ph
C6H13
C6H13
3sa
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2.16
4.08
3.98
3.95
16.14
6.43
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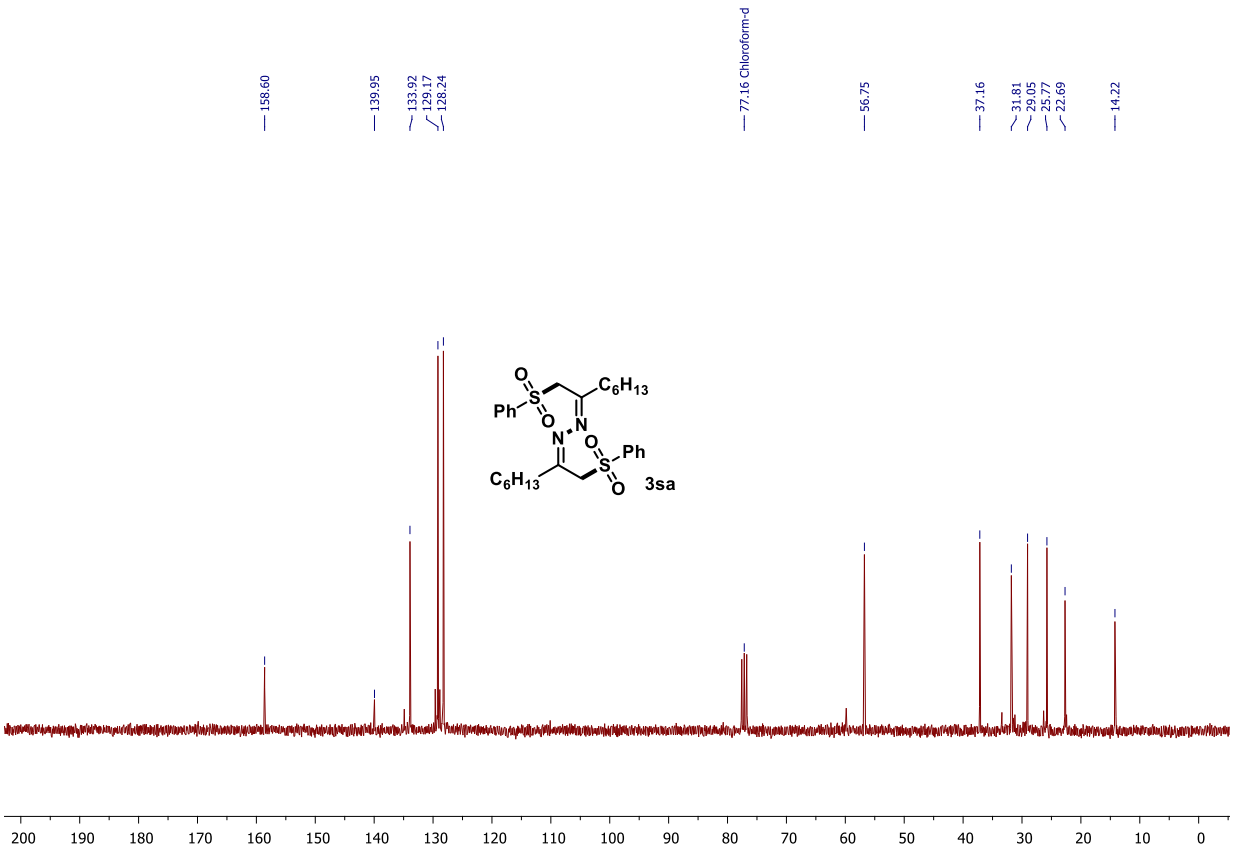
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14.22
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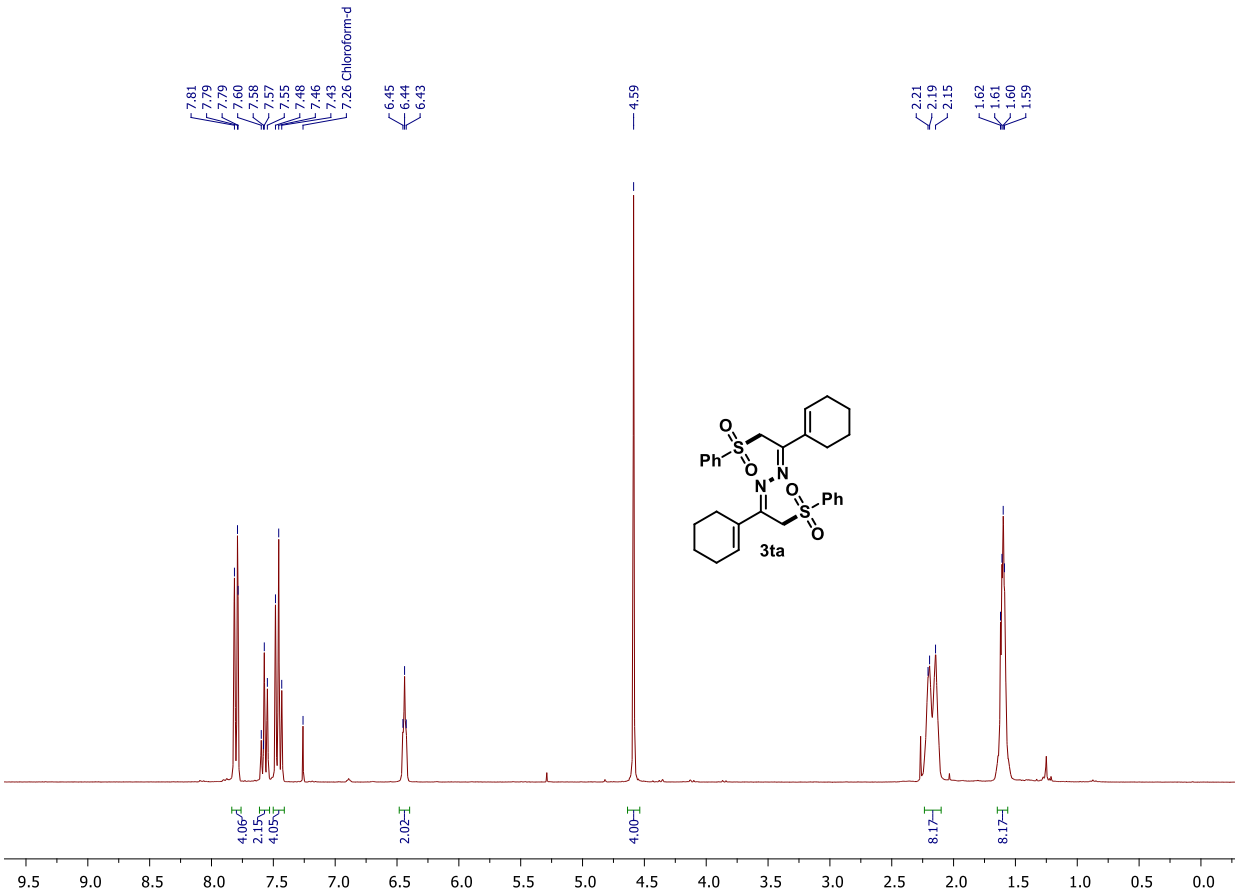
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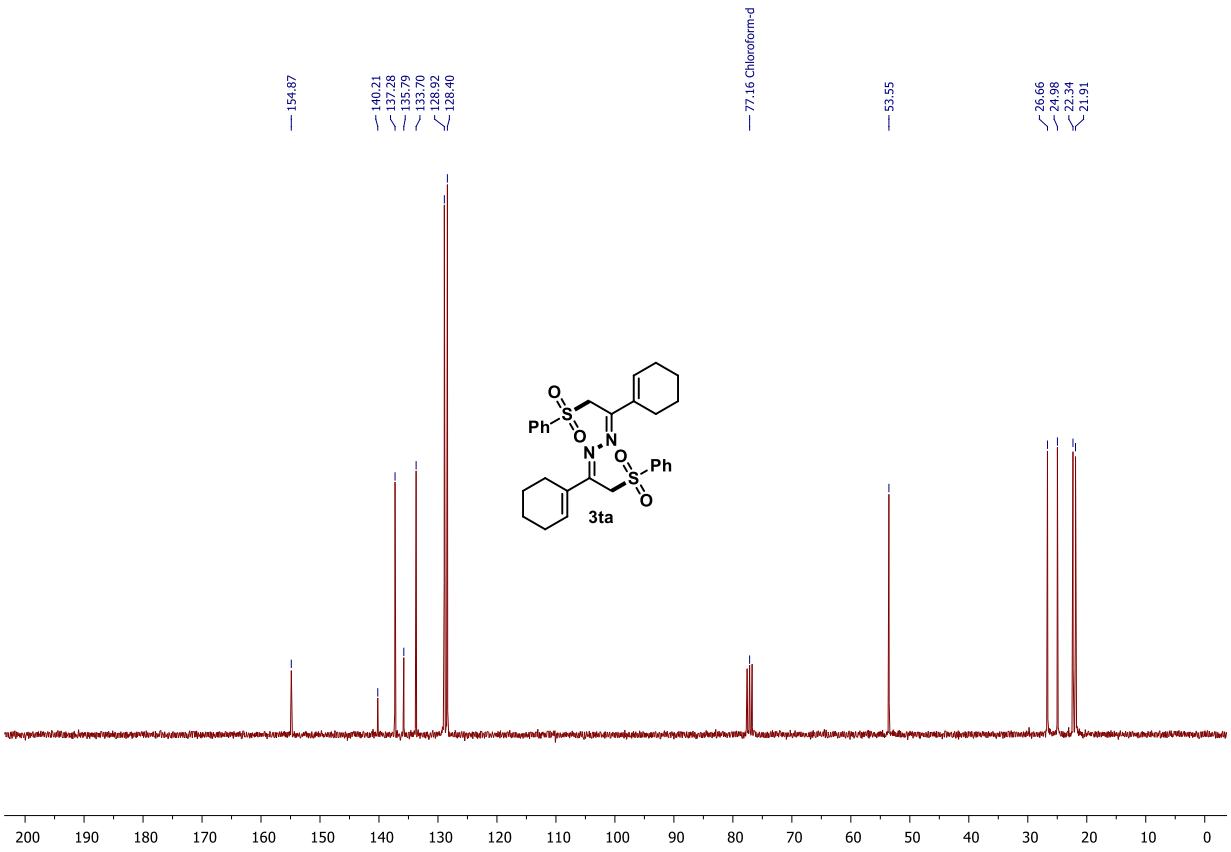
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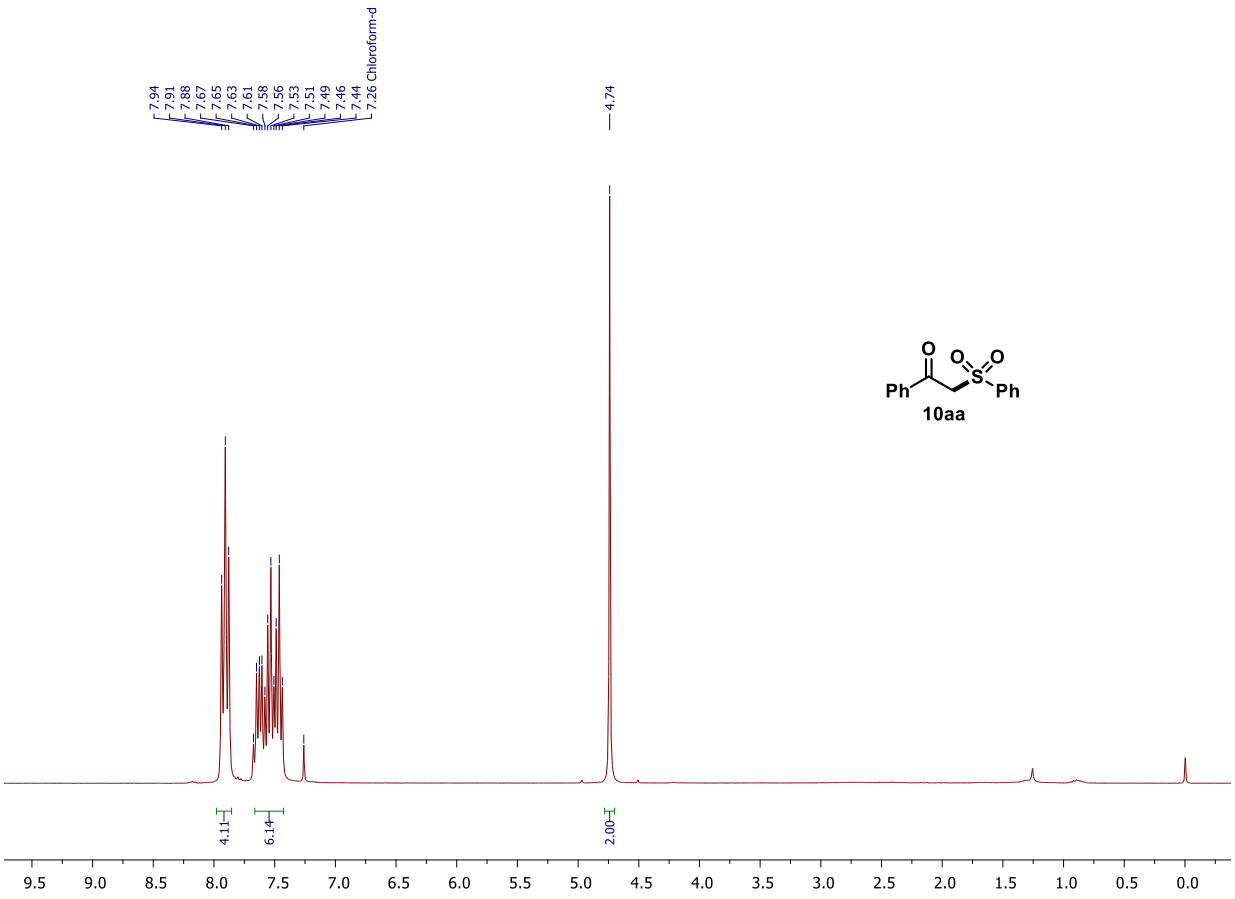
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7.26 Chloroform-d
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6.14
2.00
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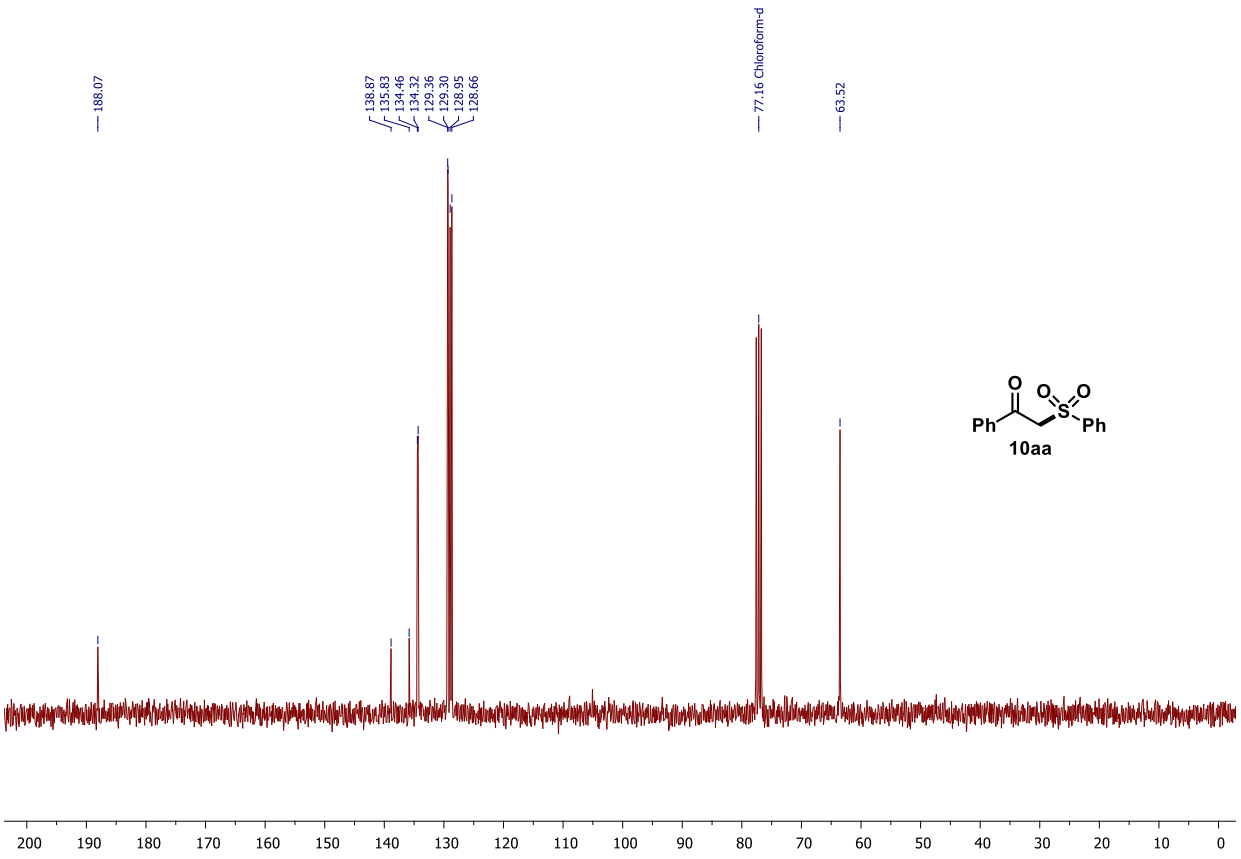
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Ph
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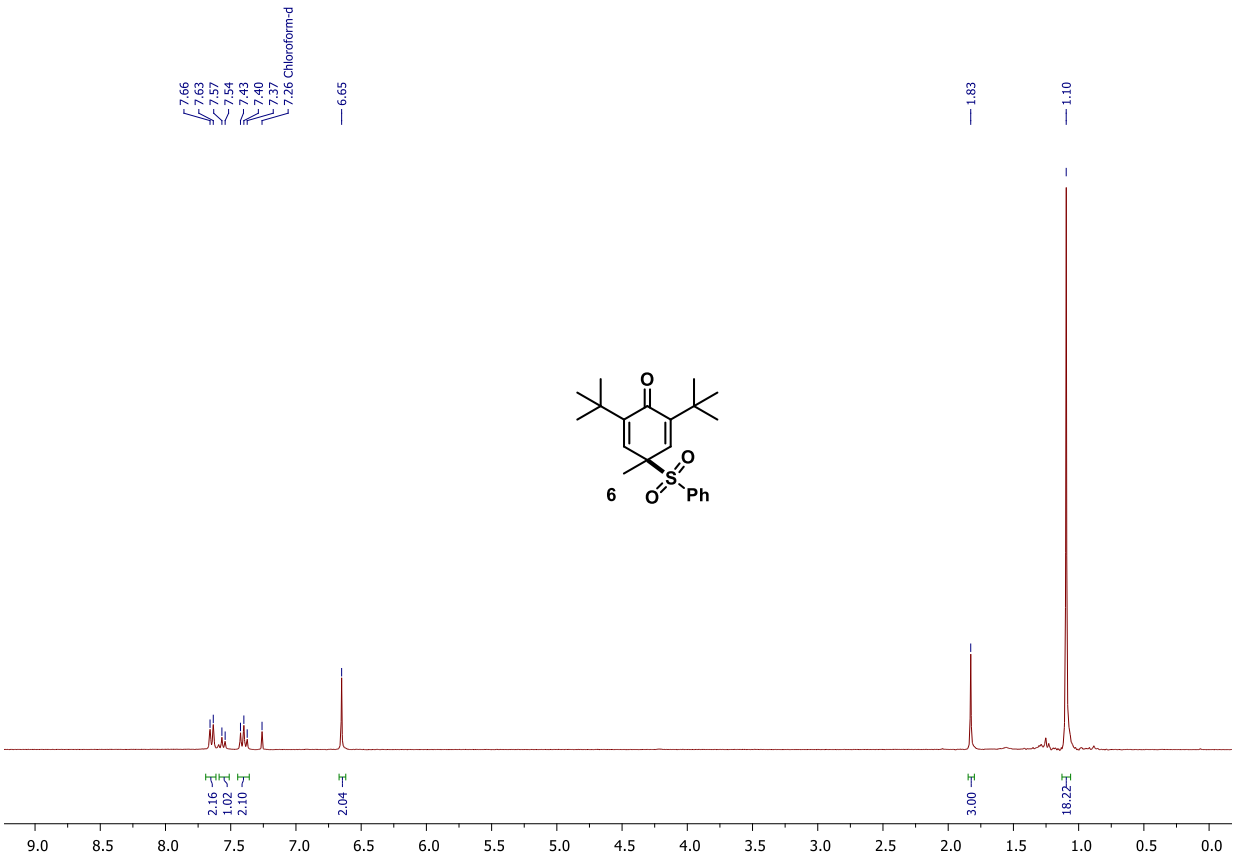
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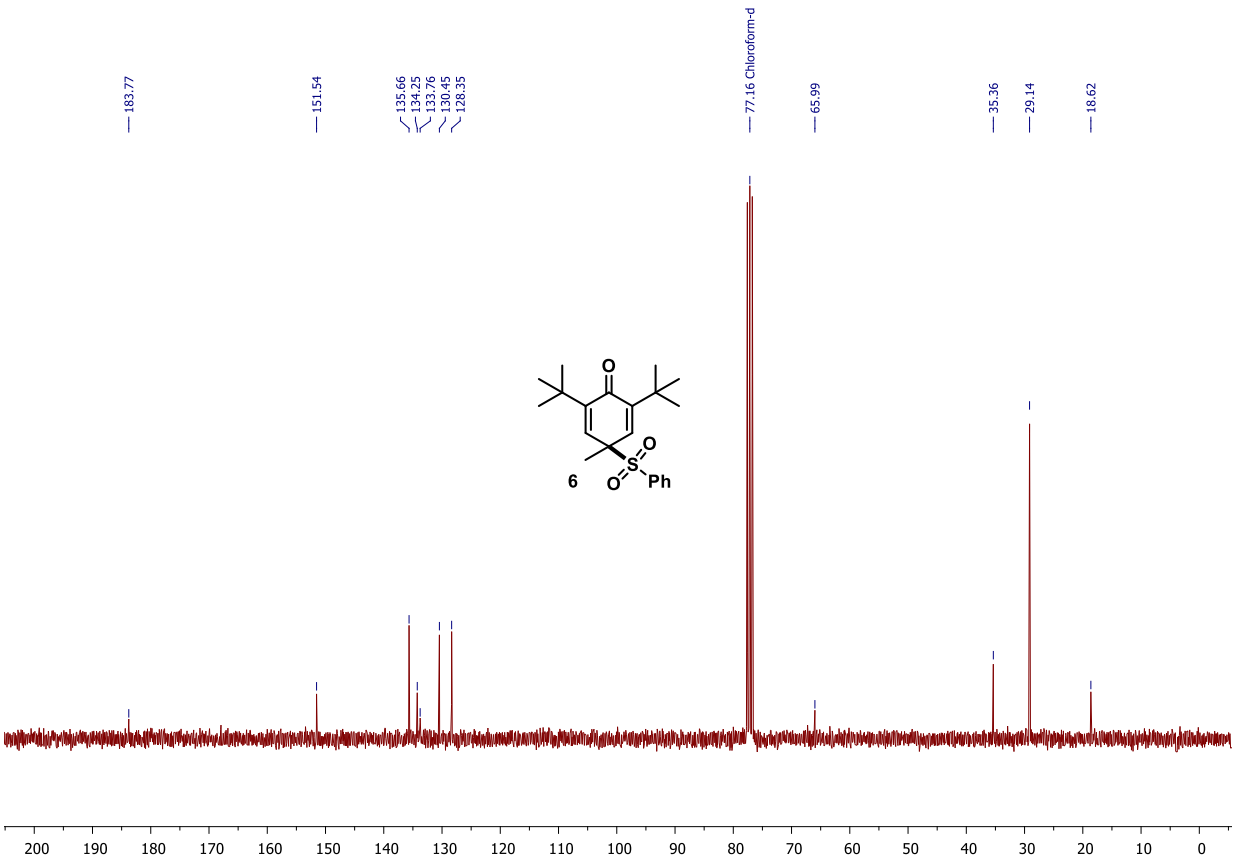


HRMS spectra of the synthesized compounds 3aa – 3ta

HRMS of (1Z,2Z)-1,2-bis(1-phenyl-2-(phenylsulfonyl)ethylidene)hydrazine 3aa

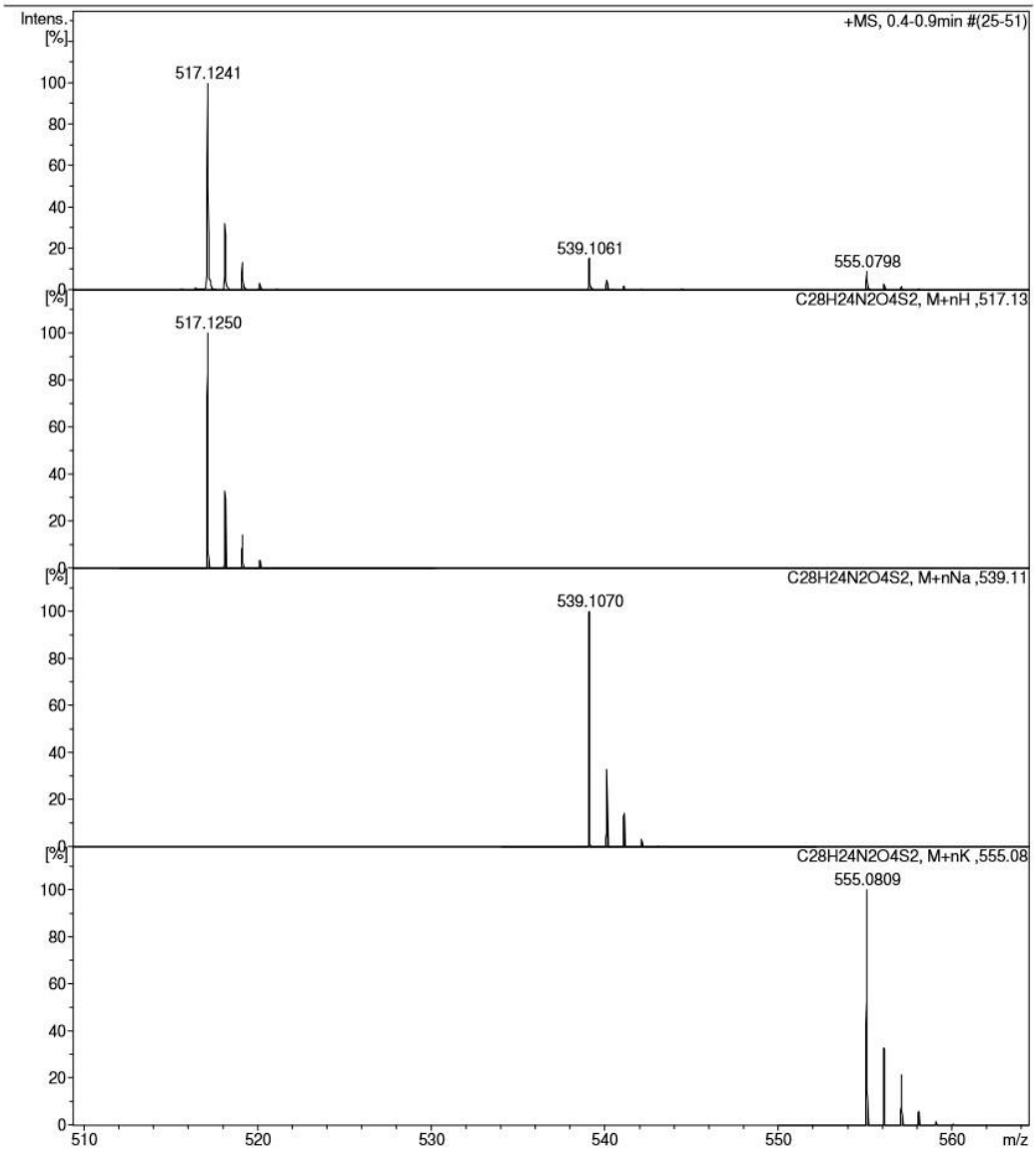
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0722021.d	Acquisition Date	22.07.2020 17:46:54
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN VP-190	Instrument / Ser#	micrOTOF 10248
Comment	C28H24N2O4S2 mH 517.1250 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of (1Z,2Z)-1,2-bis(1-phenyl-2-tosylethylidene)hydrazine 3ab.

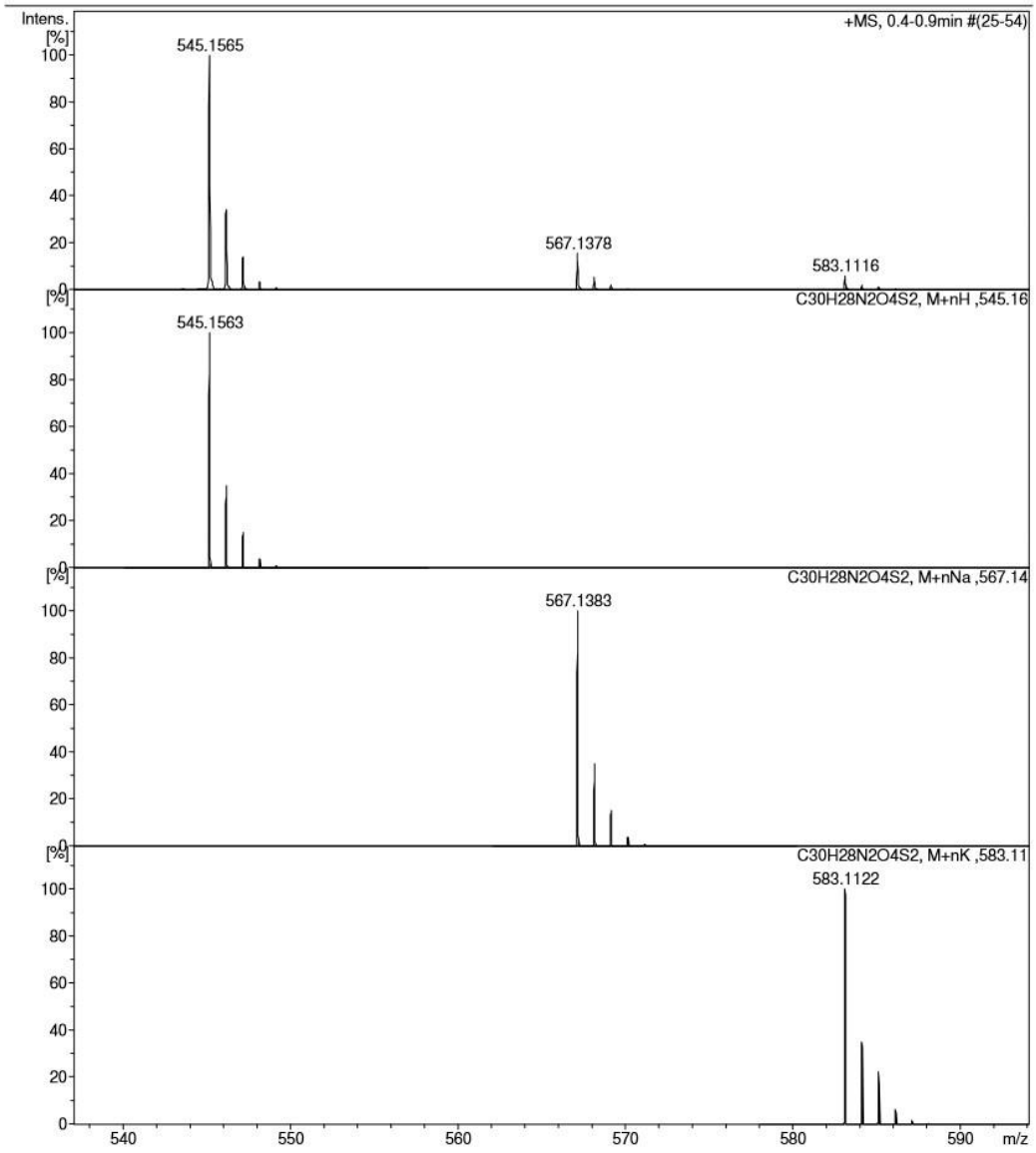
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0722022.d	Acquisition Date	22.07.2020 17:52:01
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN VP-207	Instrument / Ser#	micrOTOF 10248
Comment	C30H28N2O4S2 mH 545.1563 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 22.07.2020 17:54:35 Page 1 of 1

HRMS of (1Z,2Z)-1,2-bis(2-((4-methoxyphenyl)sulfonyl)-1-phenylethylidene)hydrazine 3ac

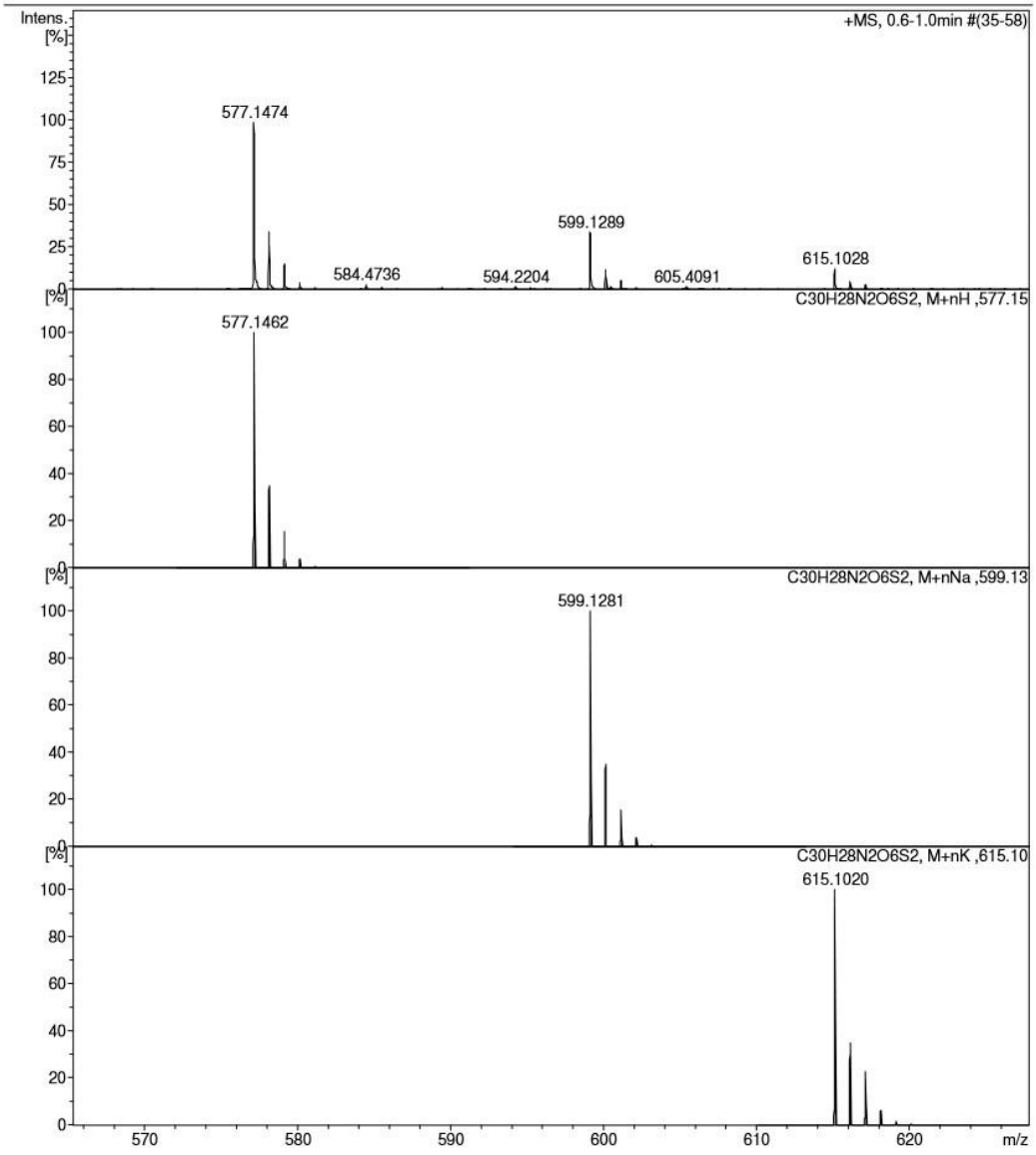
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0722024.d	Acquisition Date	22.07.2020 18:01:36
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN VP-216	Instrument / Ser#	micrOTOF 10248
Comment	C30H28N2O6S2 mH 577.1461 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 22.07.2020 18:06:30 Page 1 of 1

HRMS of N,N'-(((2Z,2'Z)-hydrazine-1,2-diylidenebis(2-phenylethan-1-yl-2 ylidenesulfonyl))bis(4,1-phenylene))diacetamide 3ad

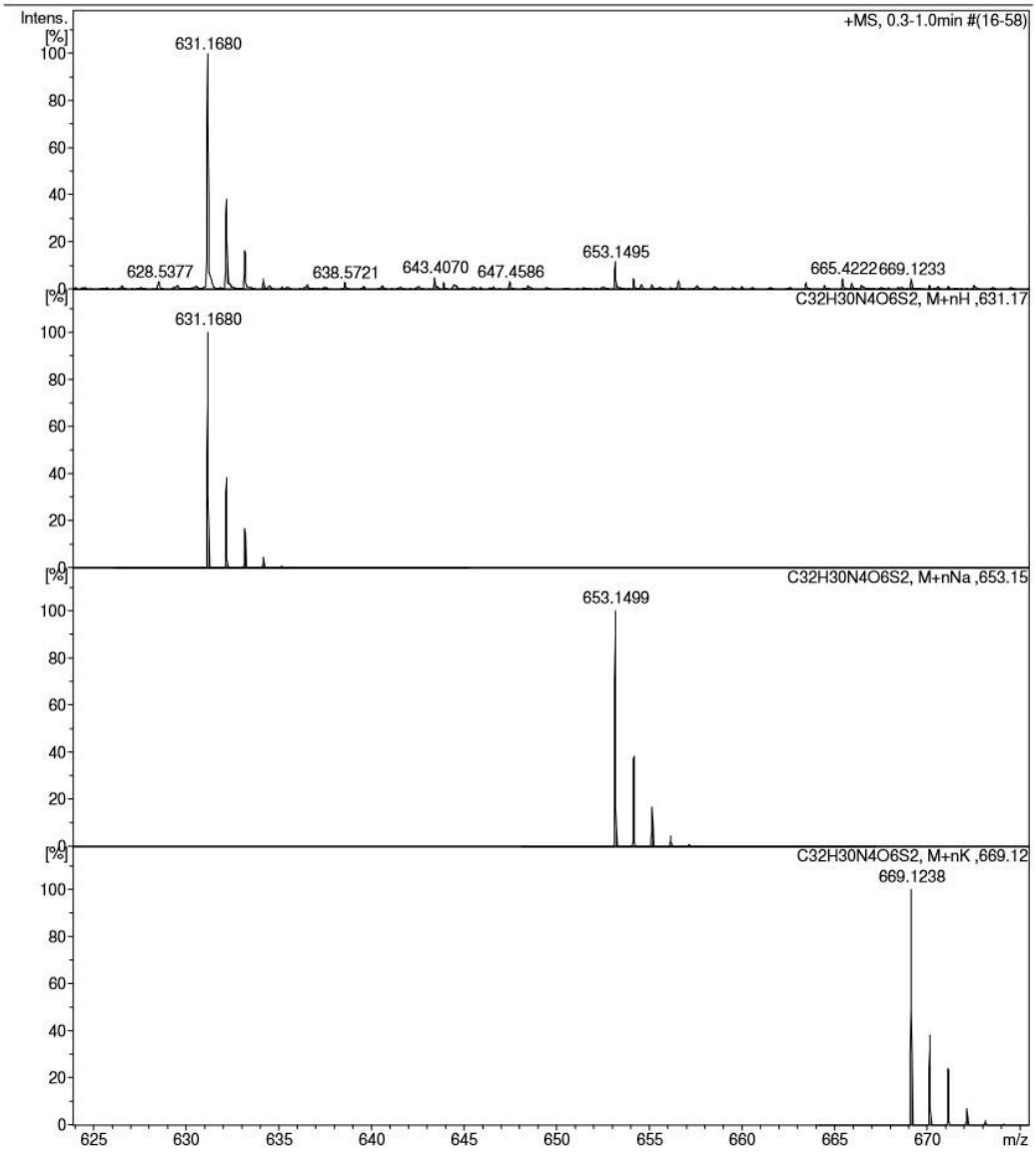
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0929008.d	Acquisition Date	29.09.2020 10:50:02
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-233	Instrument / Ser#	micrOTOF 10248
Comment	C32H30N4O6S2 mH 631.1679 calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 29.09.2020 10:55:04 Page 1 of 1

HRMS of (1Z,2Z)-1,2-bis(2-((4-fluorophenyl)sulfonyl)-1-phenylethylidene)hydrazine 3ae

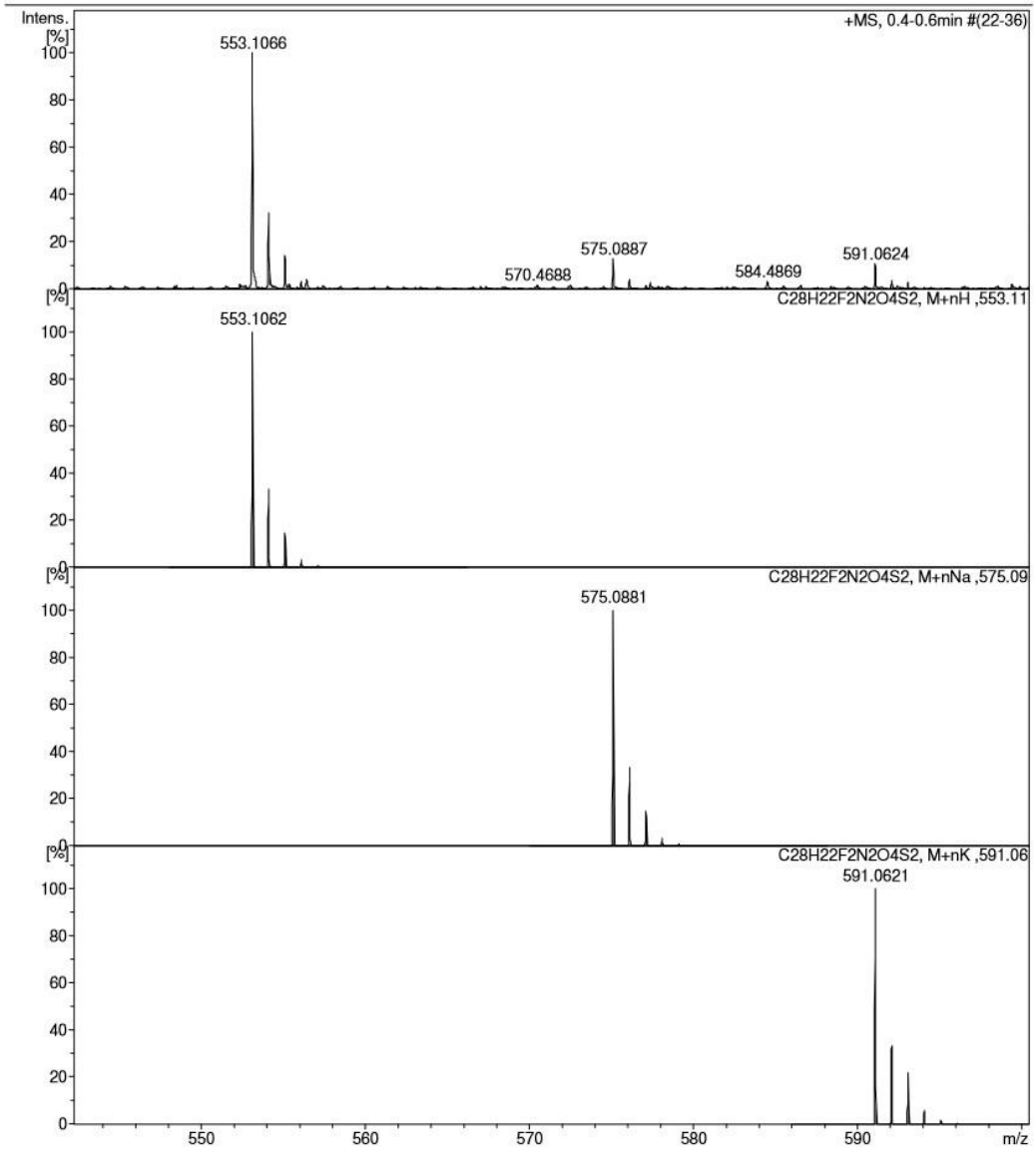
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0929007.d	Acquisition Date	29.09.2020 10:43:23
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-229	Instrument / Ser#	micrOTOF 10248
Comment	C28H22F2O4S2 mH 553.1061 calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of (1Z,2Z)-1,2-bis(2-((4-chlorophenyl)sulfonyl)-1-phenylethylidene)hydrazine 3af

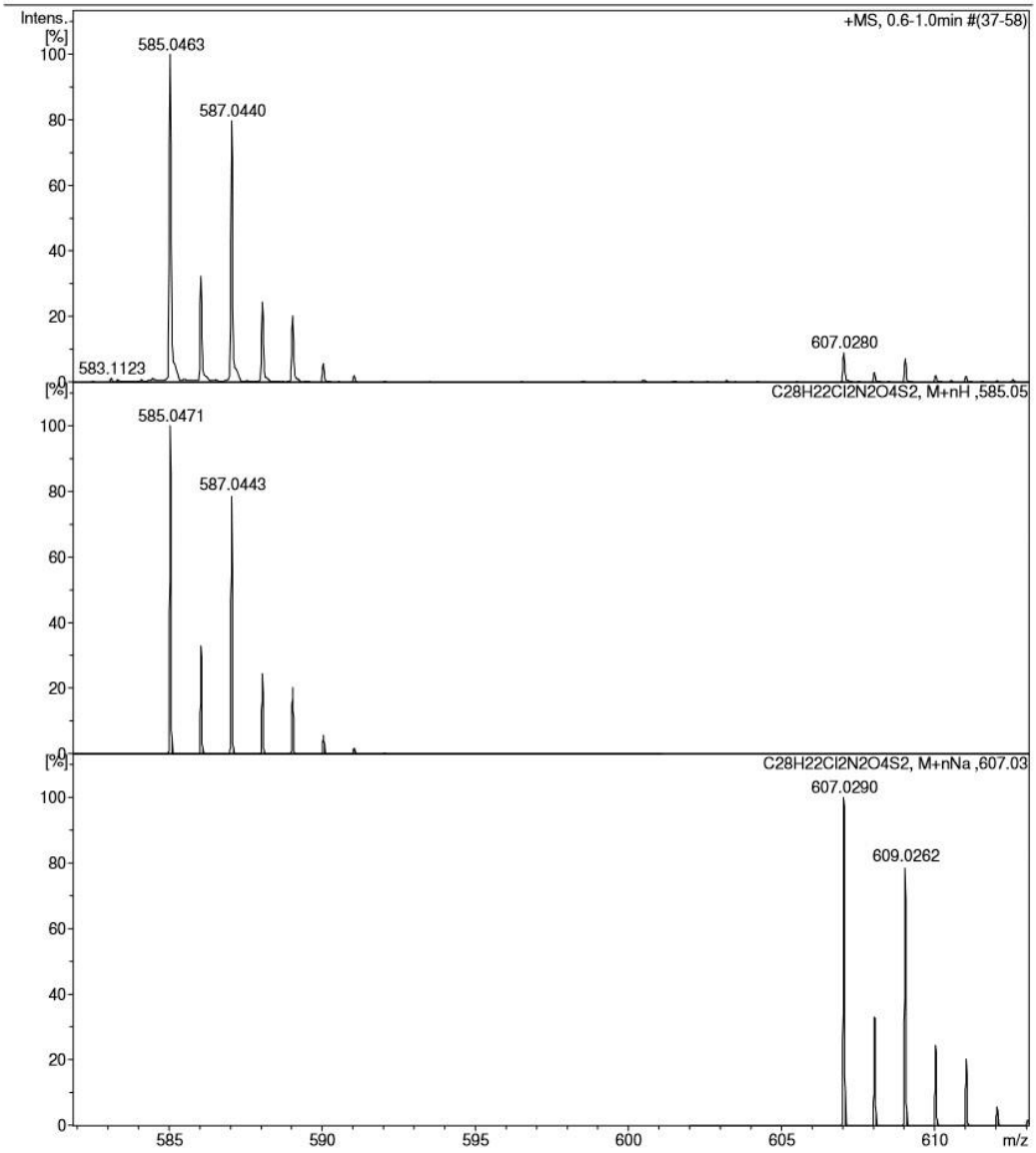
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0722023.d	Acquisition Date	22.07.2020 17:56:19
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN VP-209	Instrument / Ser#	micrOTOF 10248
Comment	C28H22Cl2N2O4S2 mH 585.0470 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 22.07.2020 17:59:41 Page 1 of 1

HRMS of (1Z,2Z)-1,2-bis(2-(naphthalen-2-ylsulfonyl)-1-phenylethylidene)hydrazine 3ag

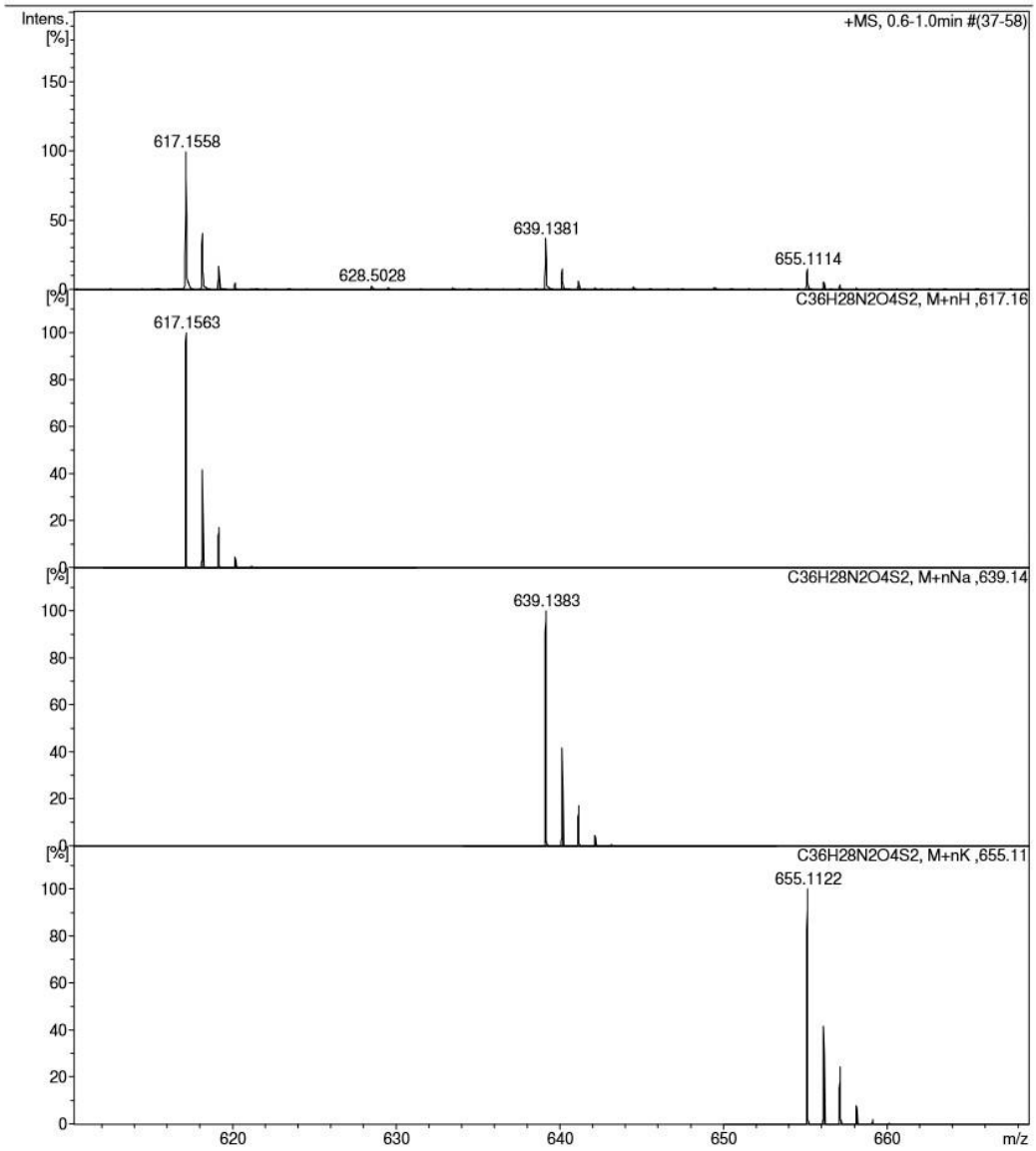
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0722025.d	Acquisition Date	22.07.2020 18:08:22
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN VP-221	Instrument / Ser#	micrOTOF 10248
Comment	C36H28N2O4S2 mH 617.1563 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 22.07.2020 18:13:41 Page 1 of 1

HRMS of (1Z,2Z)-1,2-bis(1-phenyl-2-(thiophen-2-ylsulfonyl)ethylidene)hydrazine 3ah

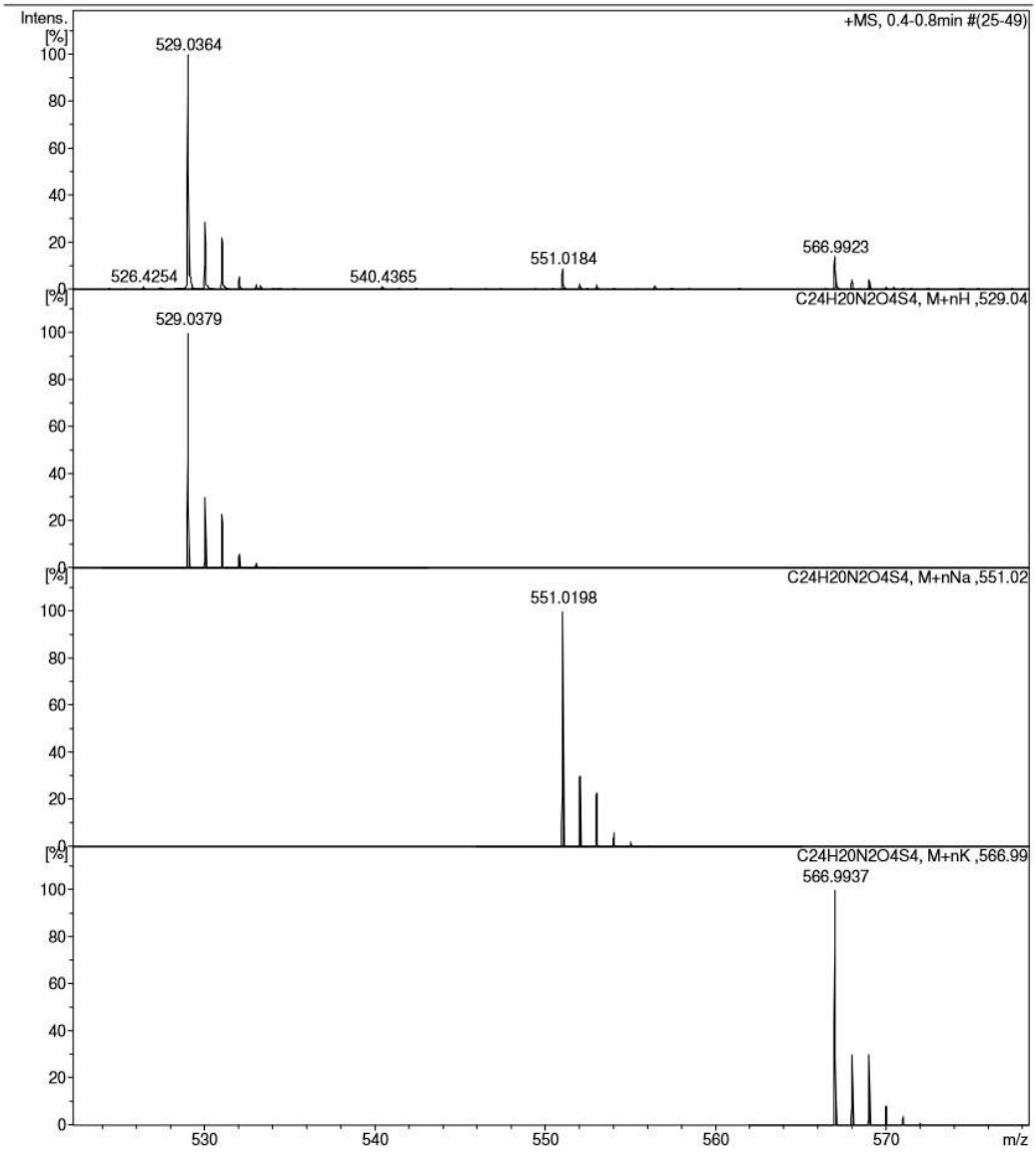
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2021\Mulina\0128040.d	Acquisition Date	28.01.2021 18:05:21
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN VP-253	Instrument / Ser#	micrOTOF 10248
Comment	C24H20N2O4S4 mH 529.0378 calibrant added, CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 28.01.2021 18:08:40 Page 1 of 1

HRMS of (1Z,2Z)-1,2-bis(2-(methylsulfonyl)-1-phenylethylidene)hydrazine 3ai

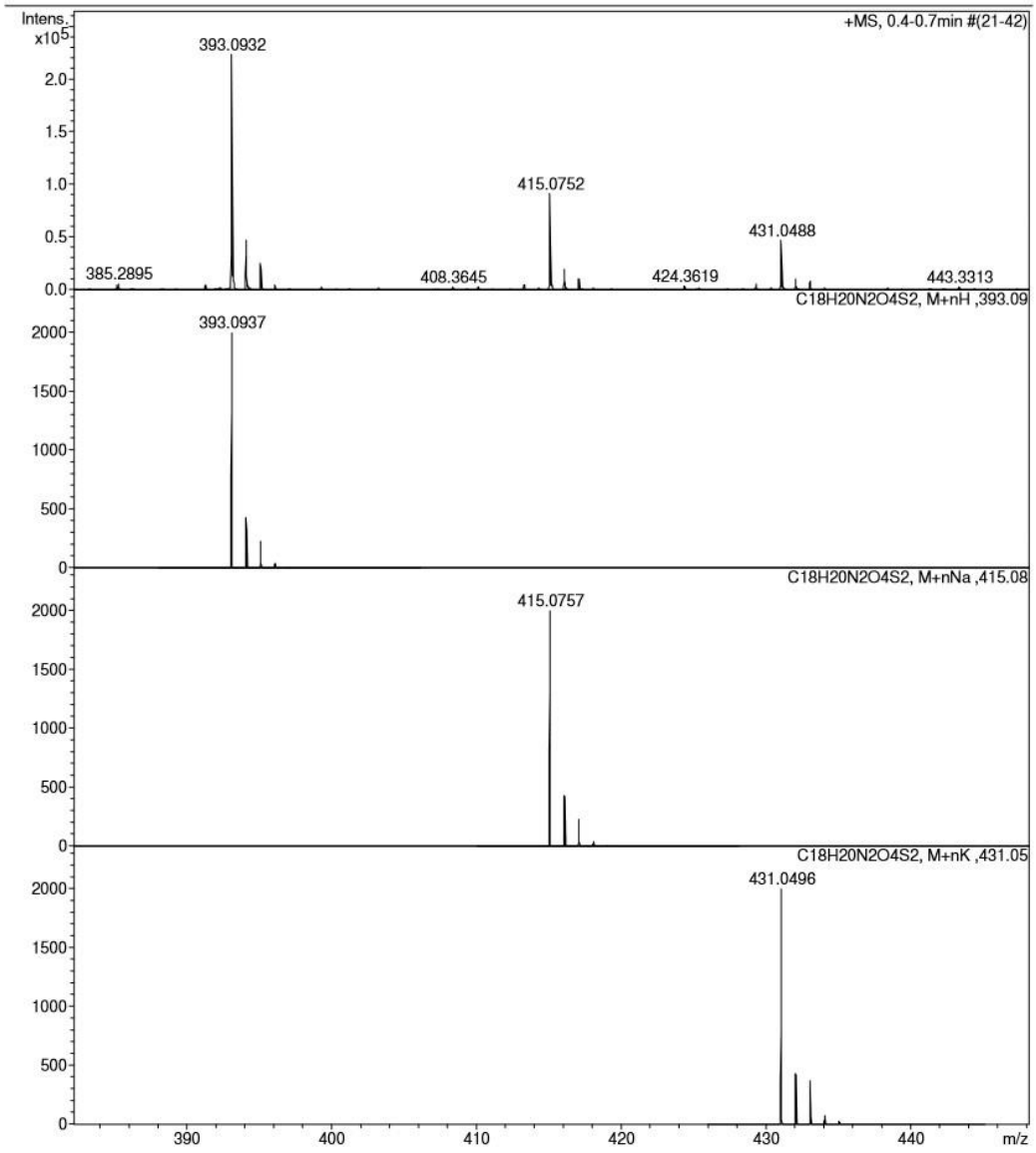
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\1202044.d	Acquisition Date	02.12.2020 18:37:49
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-245	Instrument / Ser#	micrOTOF 10248
Comment	C18H20N2O4S2 mH 393.0937 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 02.12.2020 18:40:08 Page 1 of 1

HRMS of (1Z,2Z)-1,2-bis(2-(ethylsulfonyl)-1-phenylethylidene)hydrazine 3aj

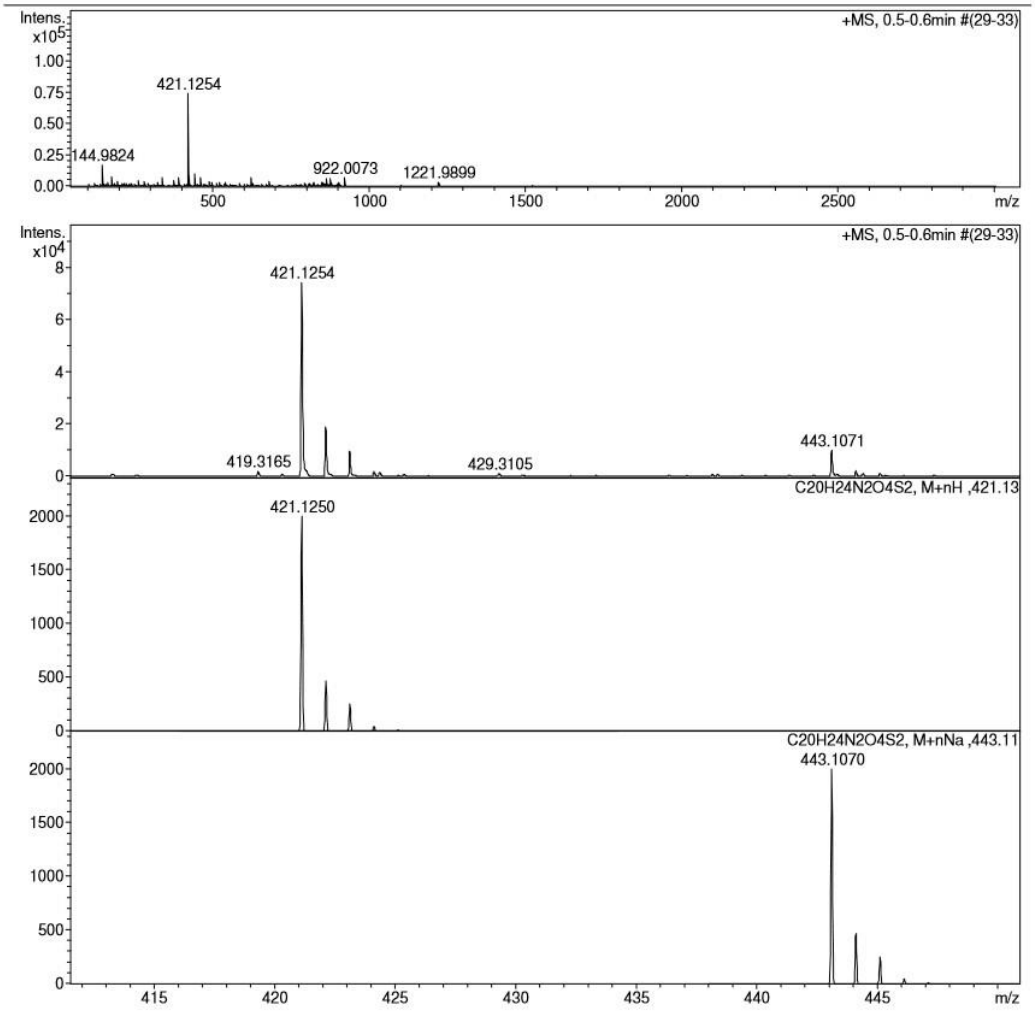
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2025\Doronin\0423012.d	Acquisition Date	23.04.2025 13:15:09
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN M-1237	Instrument / Ser#	micrOTOF 10248
Comment	C20H24N2O4S2 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(2-(isopropylsulfonyl)-1-phenylethylidene)hydrazine 3ak

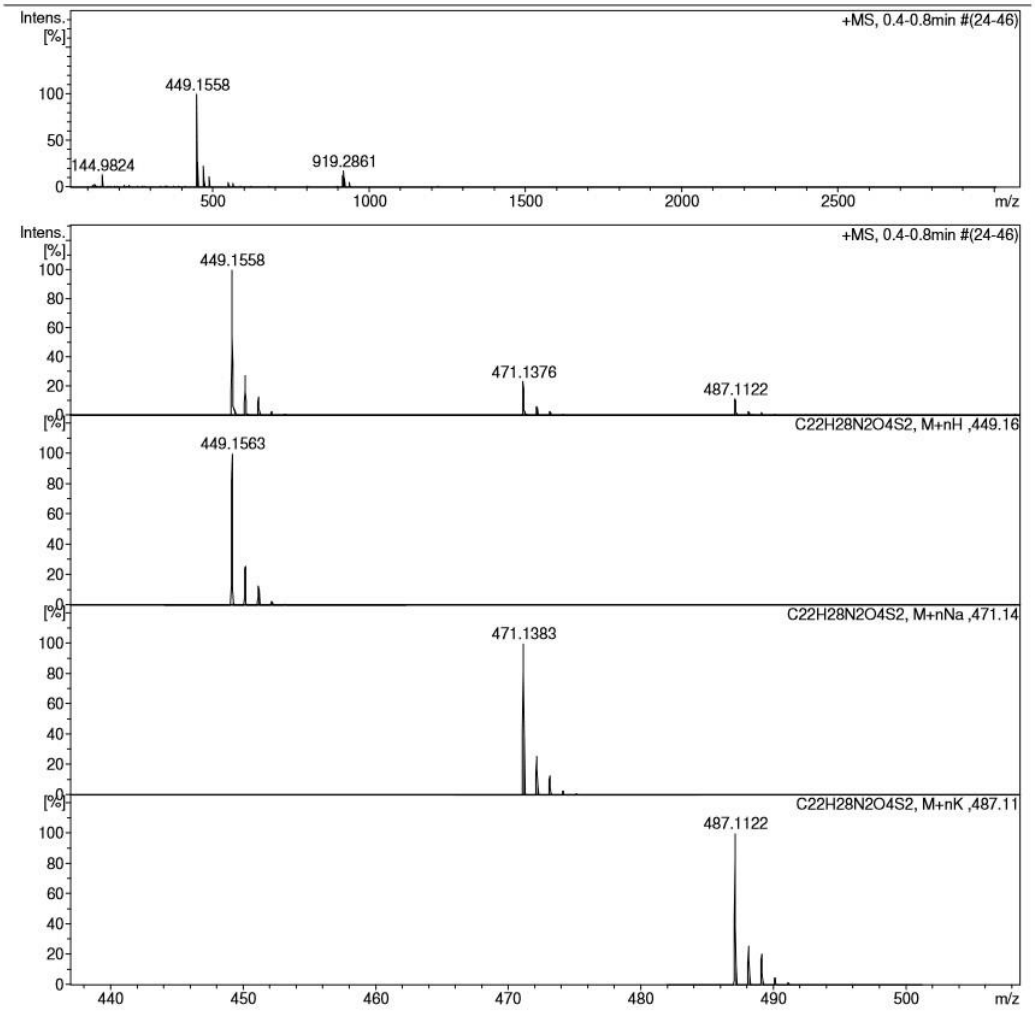
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2025\Doronin\0424004.d	Acquisition Date	24.04.2025 10:34:16
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN M-1238	Instrument / Ser#	micrOTOF 10248
Comment	C22H28N2O4s2 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(2-(cyclopropylsulfonyl)-1-phenylethylidene)hydrazine 3al

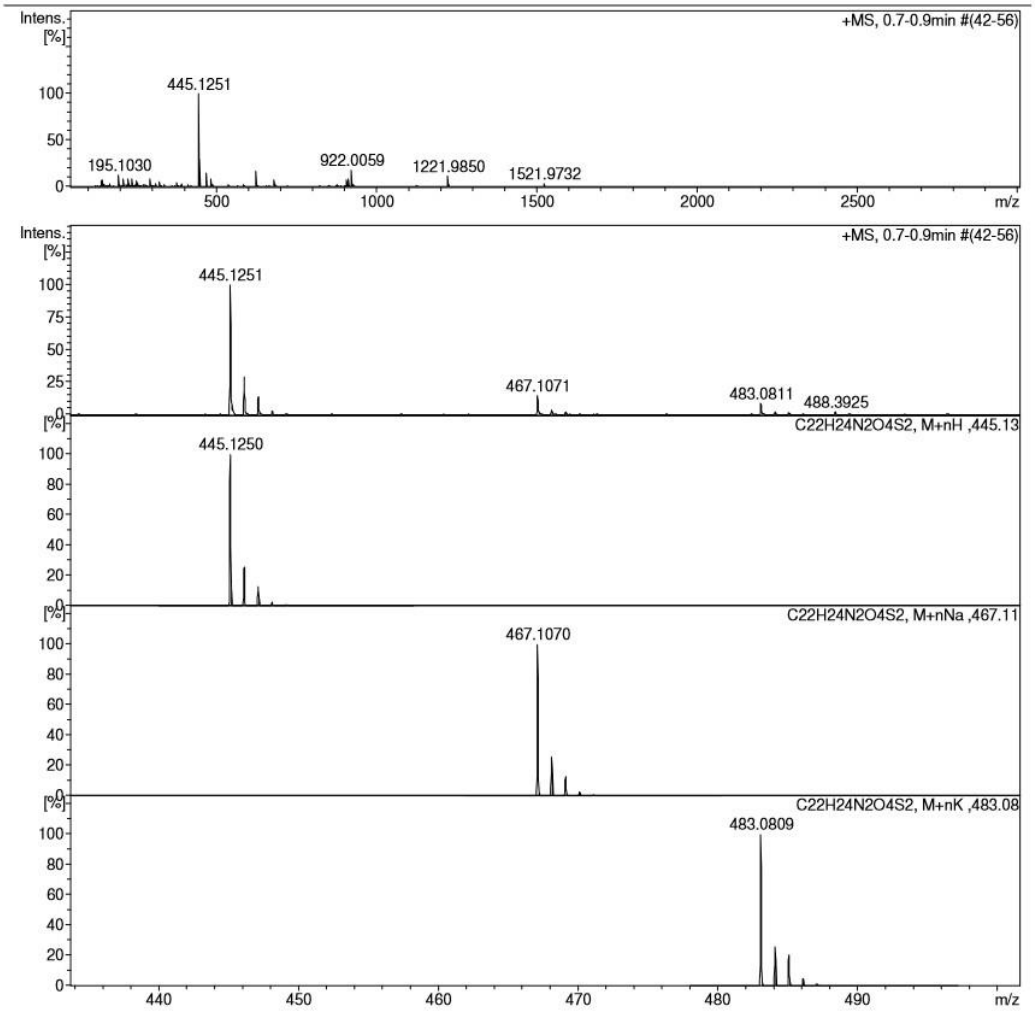
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2025\Doronin\0422009.d	Acquisition Date	22.04.2025 10:56:44
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN M-1236	Instrument / Ser#	micrOTOF 10248
Comment	C22H24N2O4S2 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(2-(phenylsulfonyl)-1-(p-tolyl)ethylidene)hydrazine 3ba

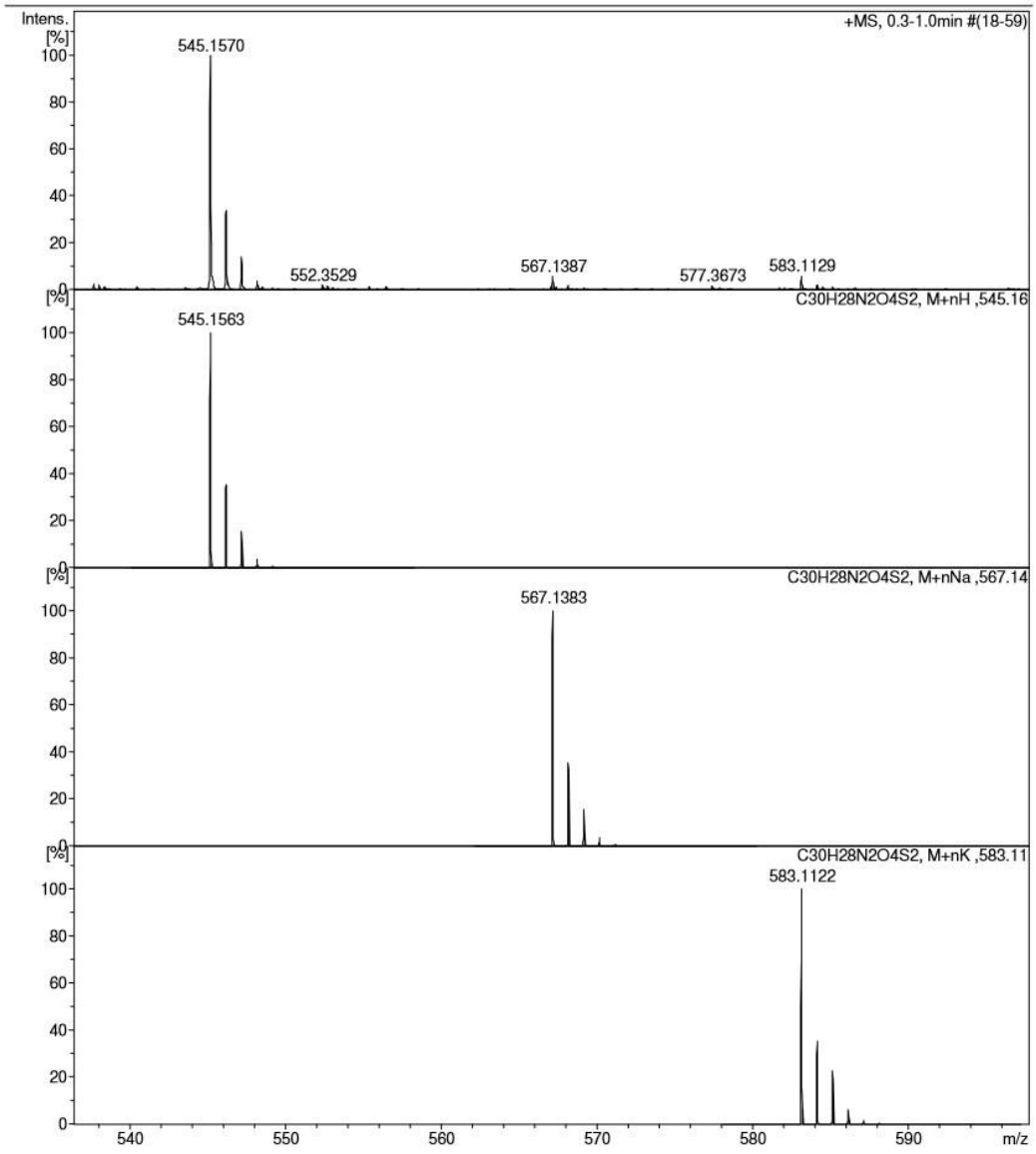
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0929009.d	Acquisition Date	29.09.2020 10:57:03
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-236	Instrument / Ser#	micrOTOF 10248
Comment	C30H28N2O4S2 mH 545.1563 calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(4-isopropylphenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3ca

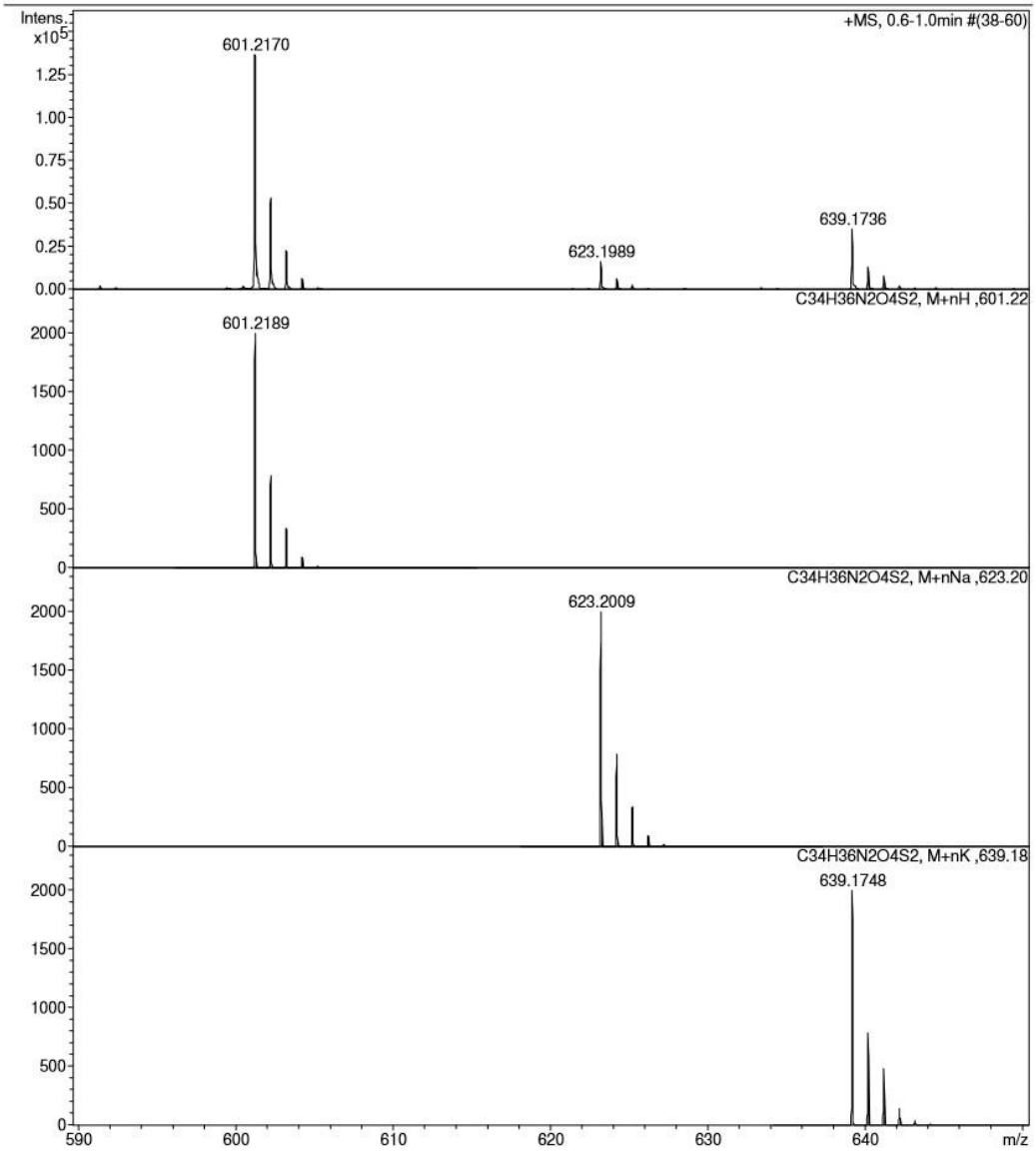
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2021\Mulina\031037.d	Acquisition Date	10.03.2021 17:21:06
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-237	Instrument / Ser#	micrOTOF 10248
Comment	C34H36N2O4S2 mH 601.2189 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of (1Z,2Z)-1,2-bis(1-(4-(tert-butyl)phenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3da

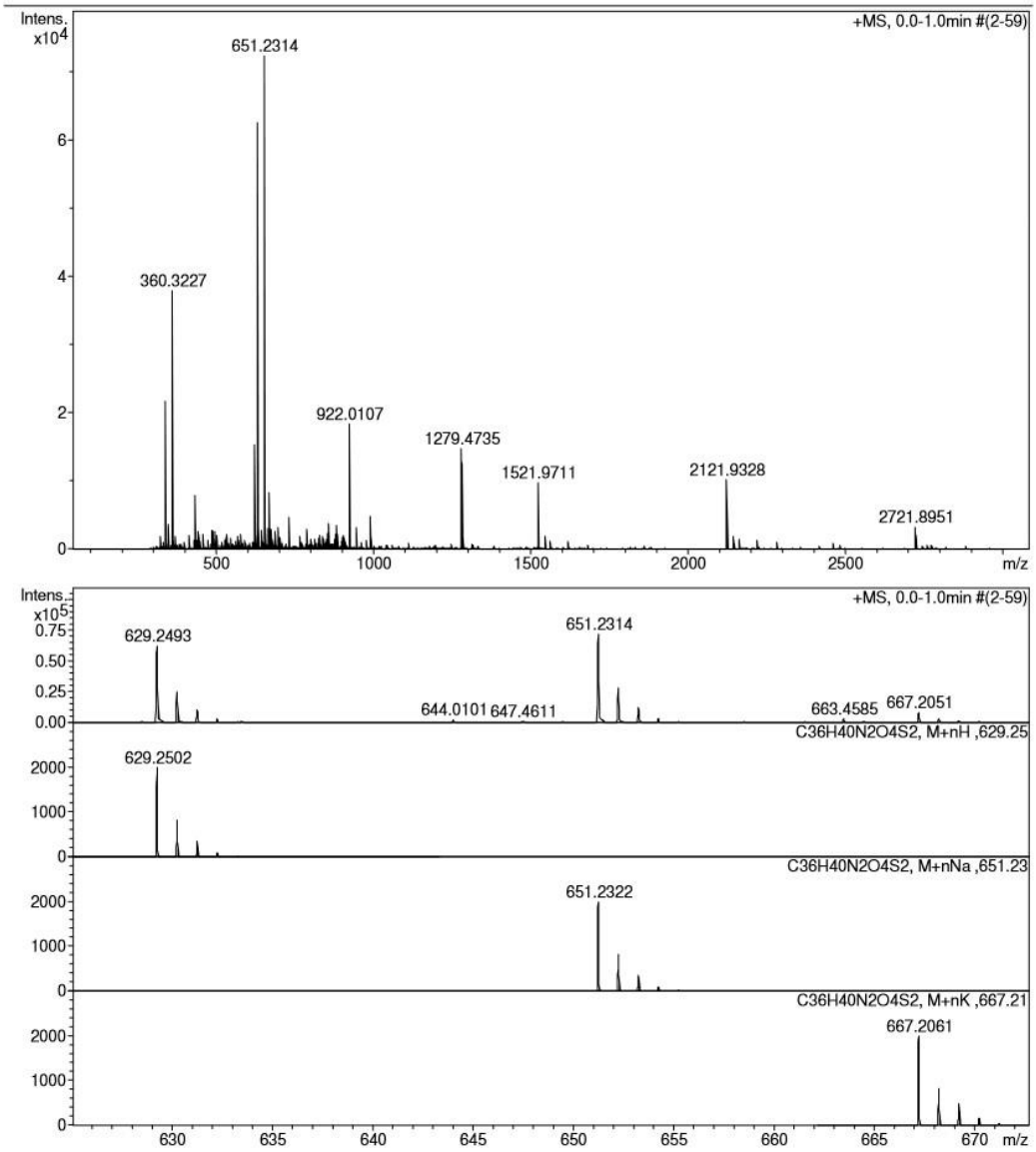
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Mulina\bp-239_&clb.d	Acquisition Date	19.10.2020 17:40:37
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	/TERN BP-239	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 200, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3ea

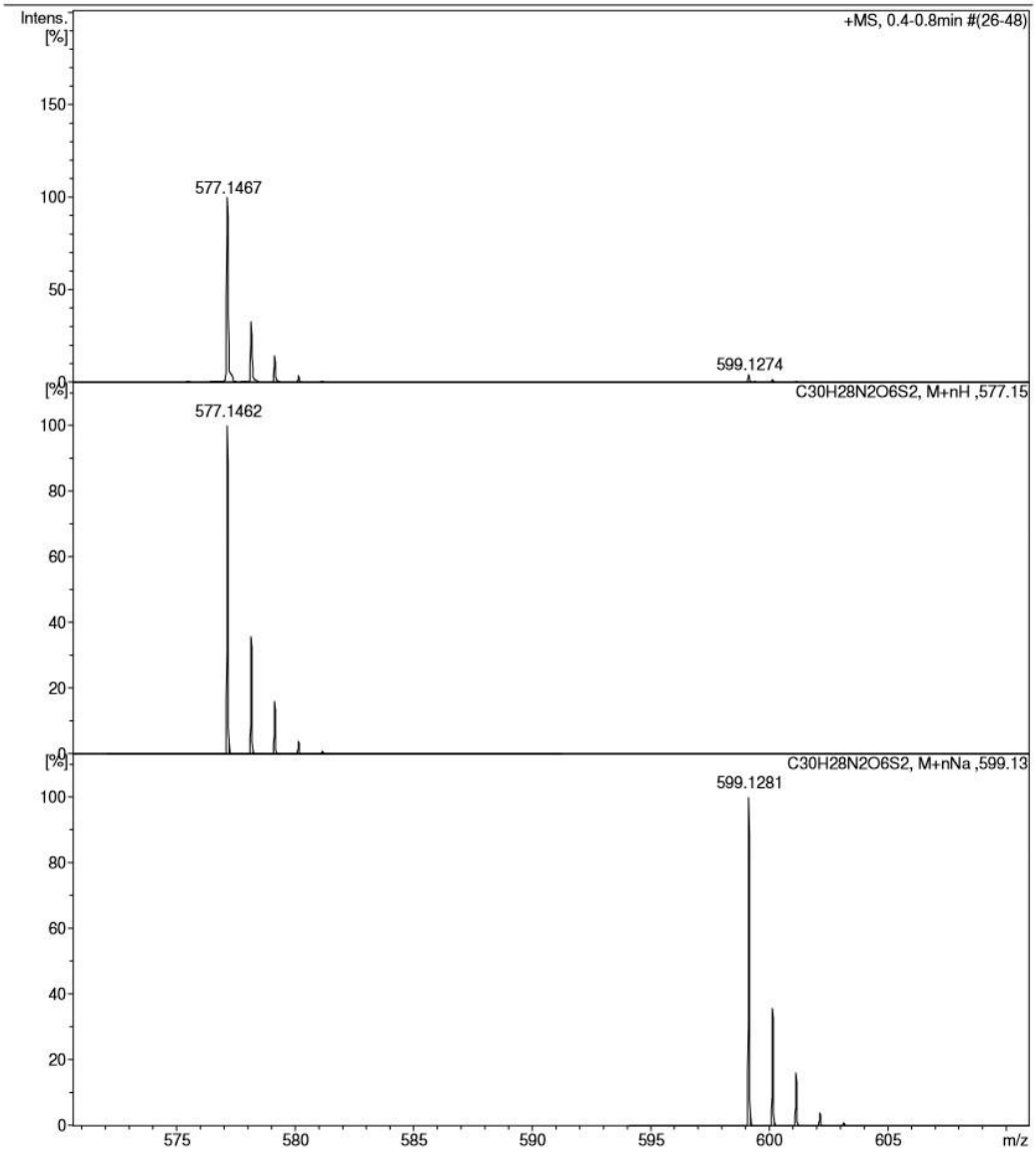
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0929010.d	Acquisition Date	29.09.2020 11:02:16
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-238	Instrument / Ser#	micrOTOF 10248
Comment	C30H28N2O6S2 mH 577.1461 calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(4-fluorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3fa

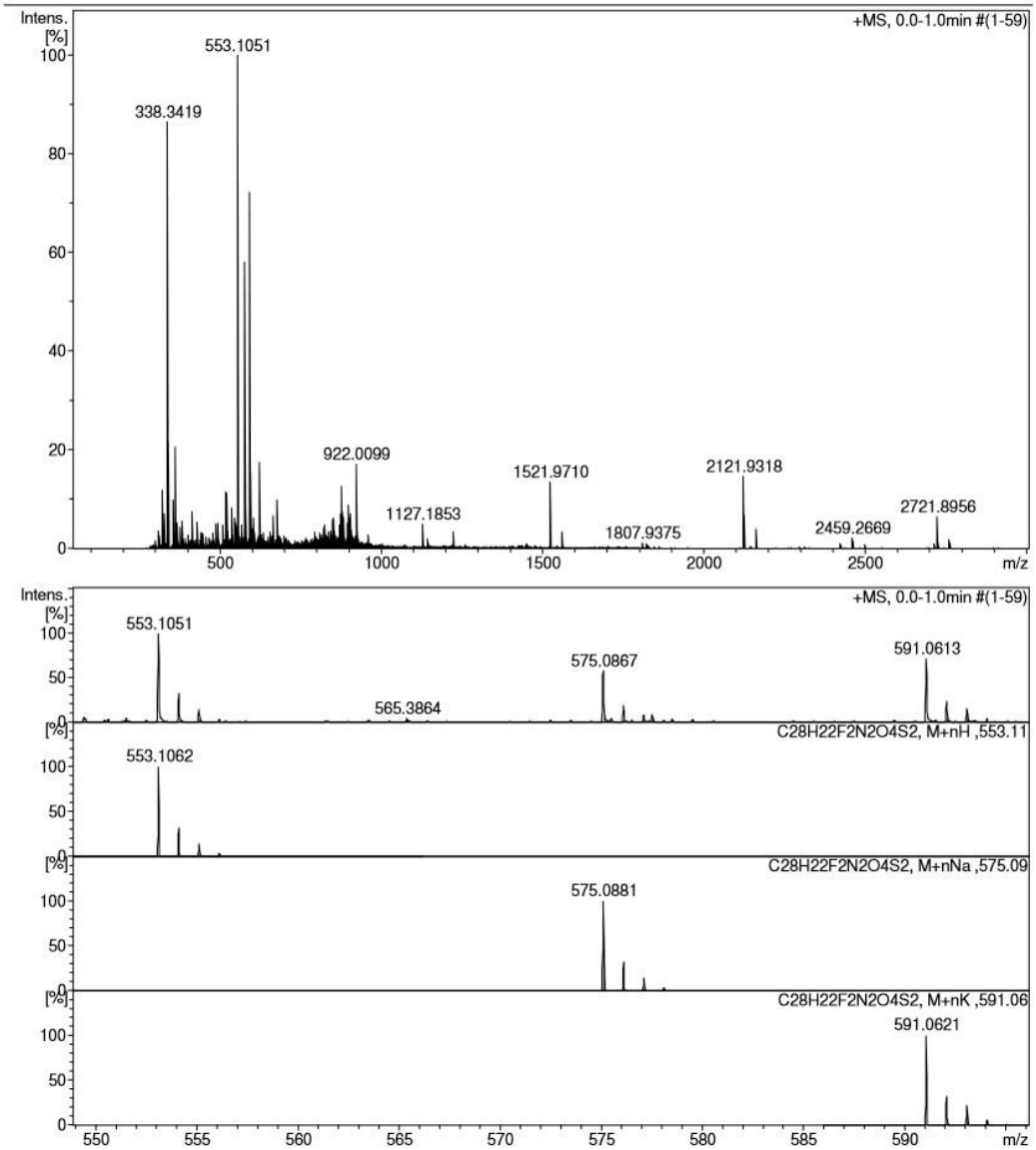
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Mulina\bp-251_&clb.d	Acquisition Date	22.01.2021 11:12:04
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	/TERN BP-251	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(4-chlorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3ga

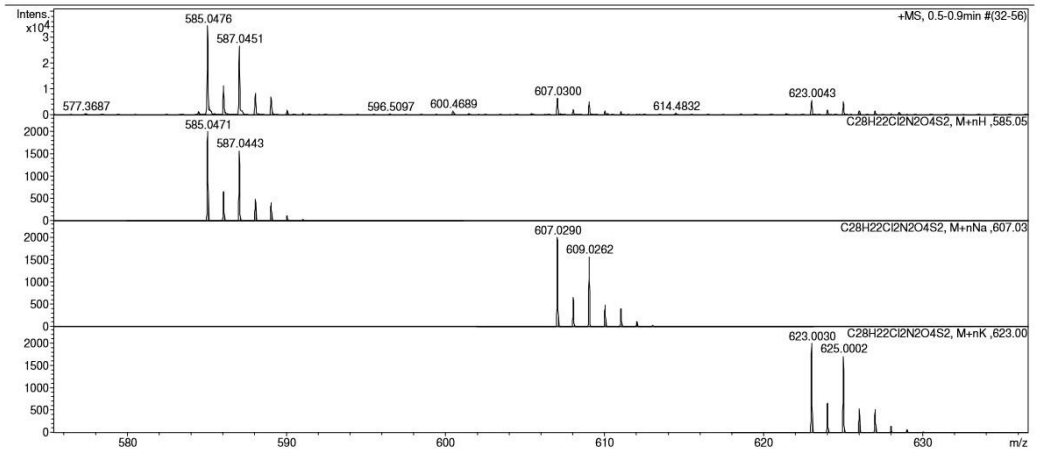
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2021\Mulina\0317001.d	Acquisition Date	17.03.2021 9:38:05
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-267	Instrument / Ser#	micrOTOF 10248
Comment	C28H22Cl2N2O4S2 mH 585.0470 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(4-bromophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3ha

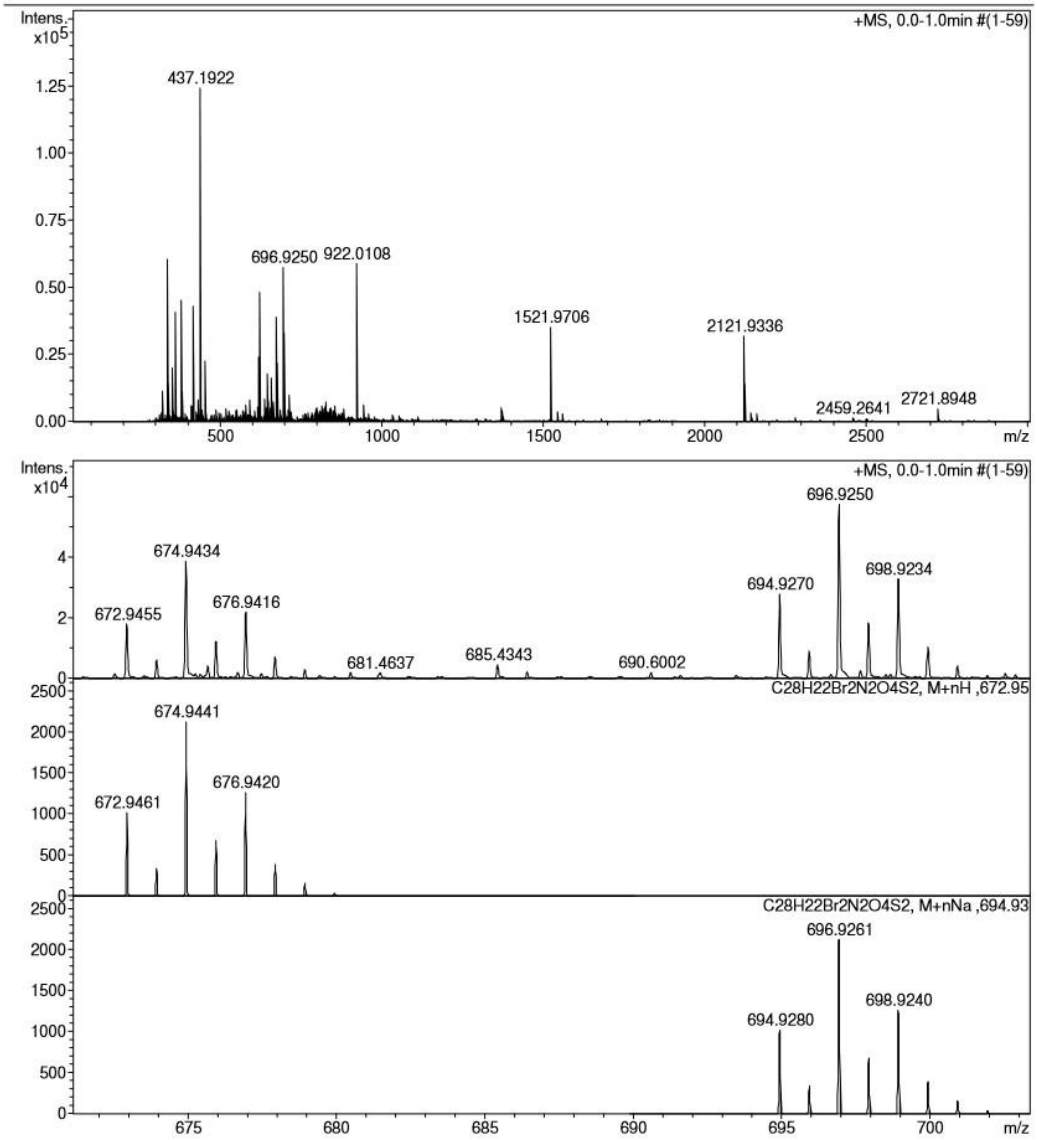
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Mulina\bp-242_&clb.d	Acquisition Date	16.11.2020 17:07:44
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	/TERN BP-242	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 200, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(4-(azidomethyl)phenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3ia

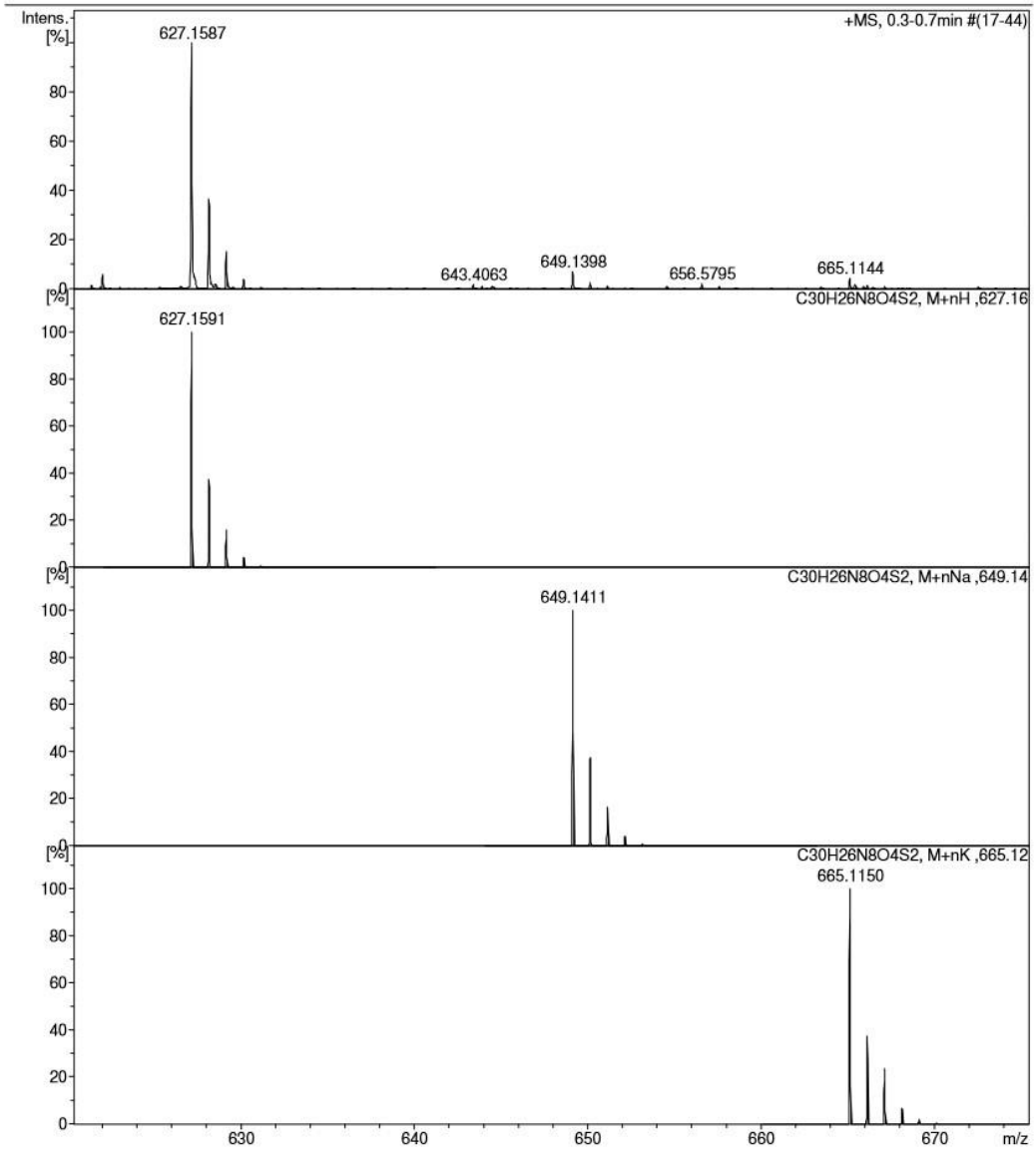
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2020\Mulina\0929011.d	Acquisition Date	29.09.2020 11:07:41
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-240	Instrument / Ser#	micrOTOF 10248
Comment	C30H26N8O4S2 mH 627.1591 calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of 4,4'-((1Z,1'Z)-hydrazine-1,2-diylidenebis(2-(phenylsulfonyl)ethan-1-yl-1-ylidene))dibenzonitrile 3ja

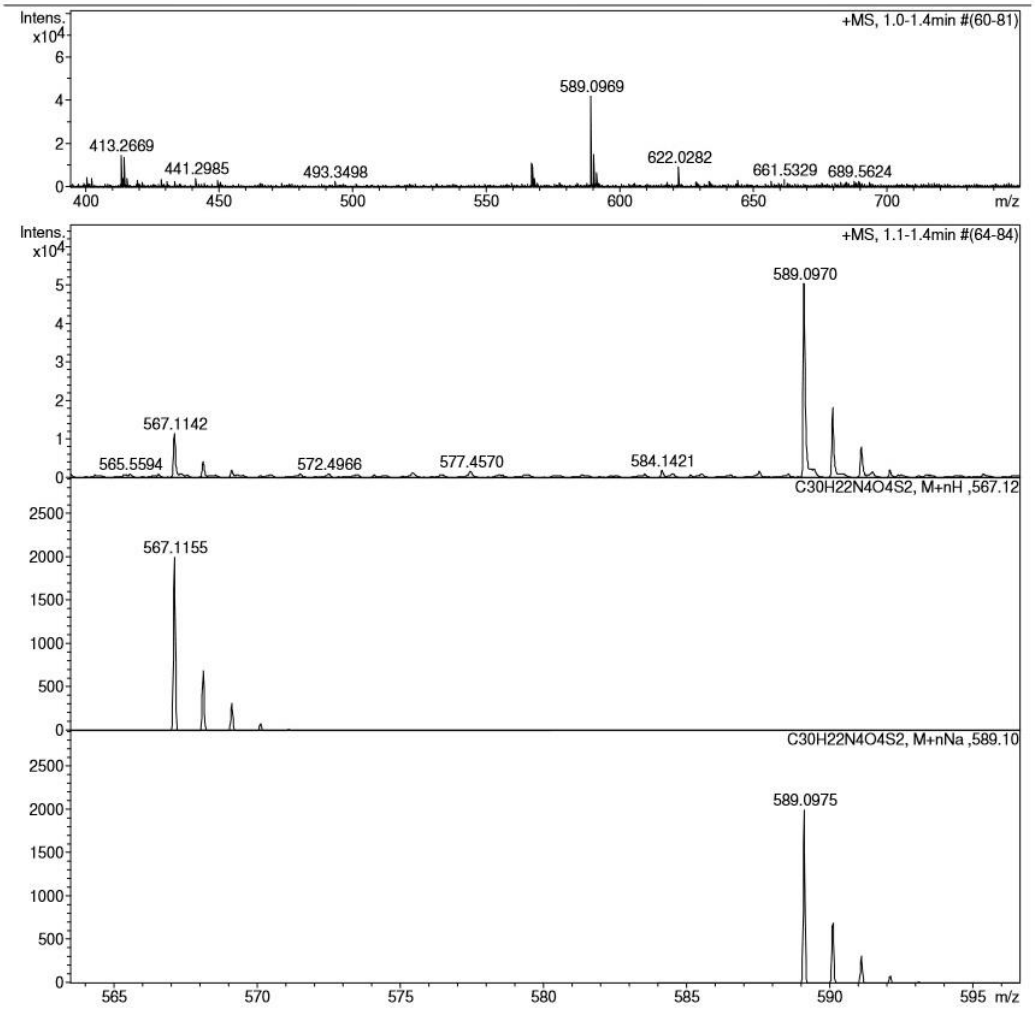
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2025\Doronin\0423017.d	Acquisition Date	23.04.2025 15:21:08
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN M-1241	Instrument / Ser#	micrOTOF 10248
Comment	C30H22N4O4S2 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(4-nitrophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3ka

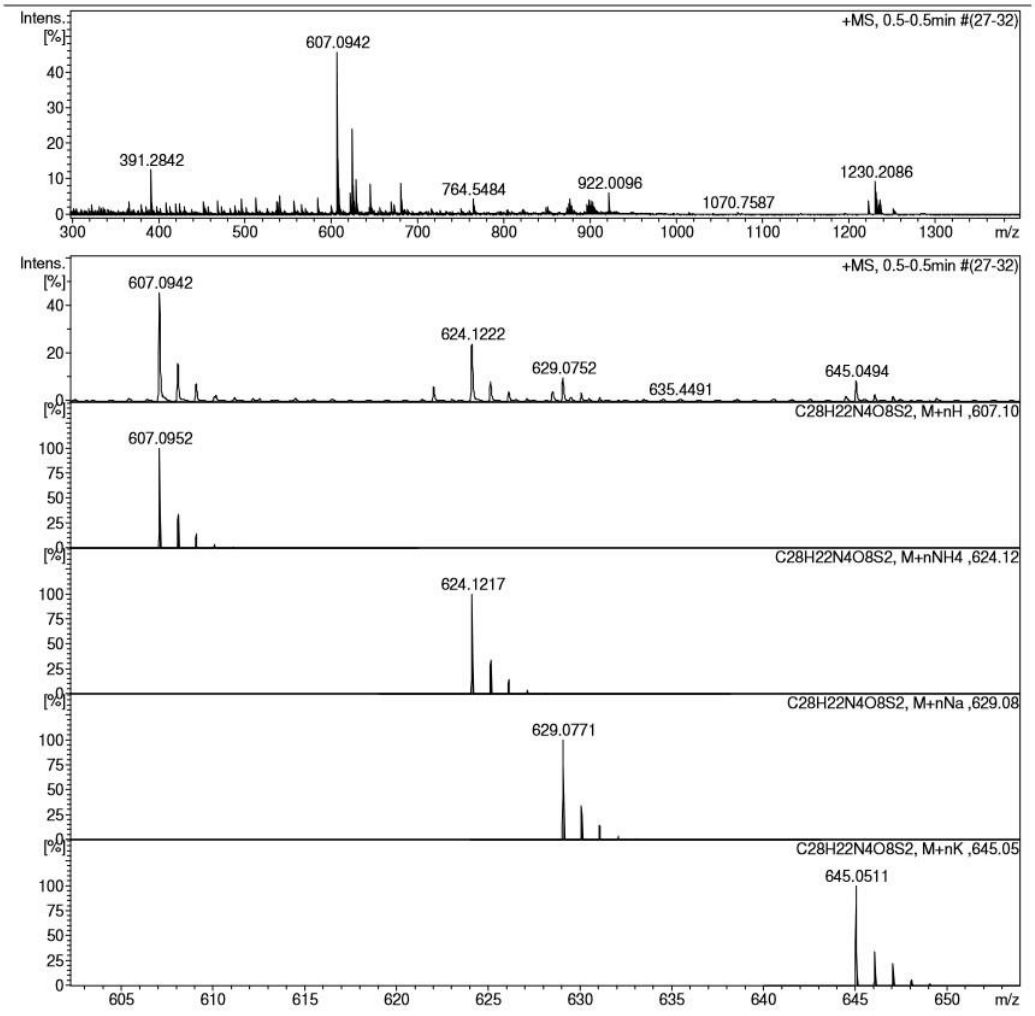
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2025\Doronin\0424015.d	Acquisition Date	24.04.2025 15:58:54
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN M-1242	Instrument / Ser#	micrOTOF 10248
Comment	C28H22N4O8S2 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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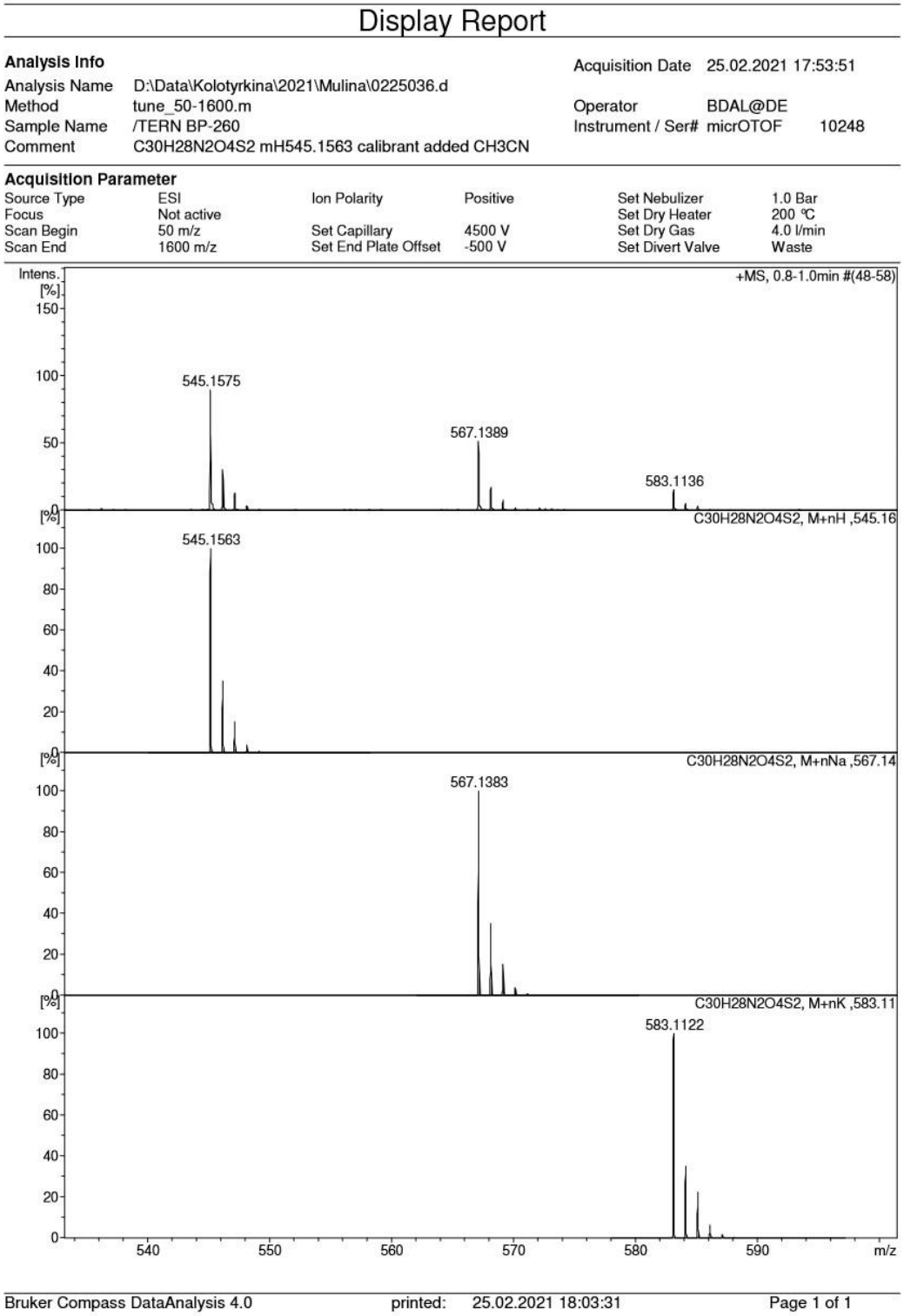
HRMS of (1Z,2Z)-1,2-bis(2-(phenylsulfonyl)-1-(m-tolyl)ethylidene)hydrazine 3la



HRMS of (1Z,2Z)-1,2-bis(1-(3-chlorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3ma

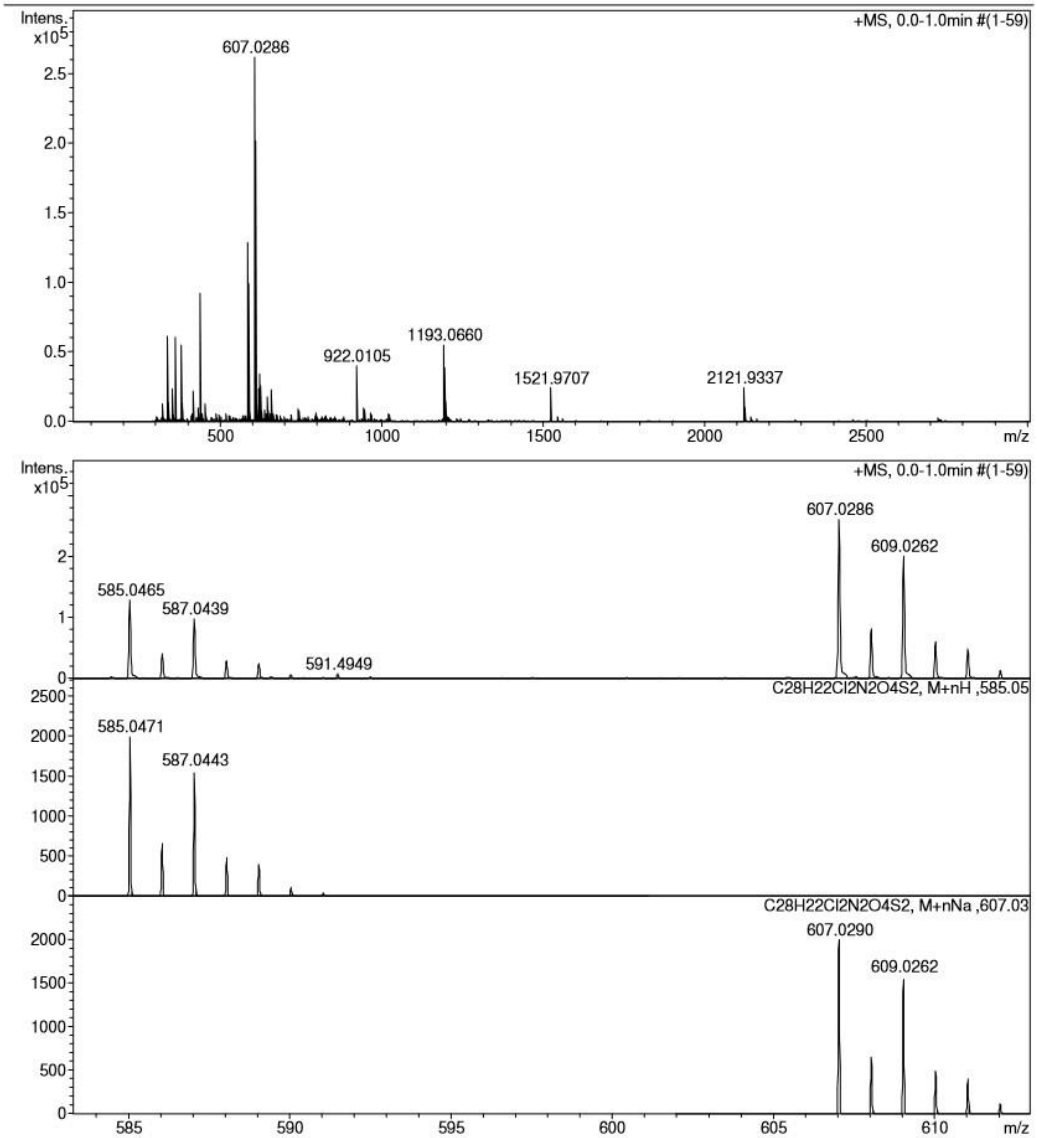
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Mulina\bp-241_&clb.d	Acquisition Date	16.11.2020 17:03:45
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	/TERN BP-241	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 200, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of (1Z,2Z)-1,2-bis(1-(3-bromophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3na

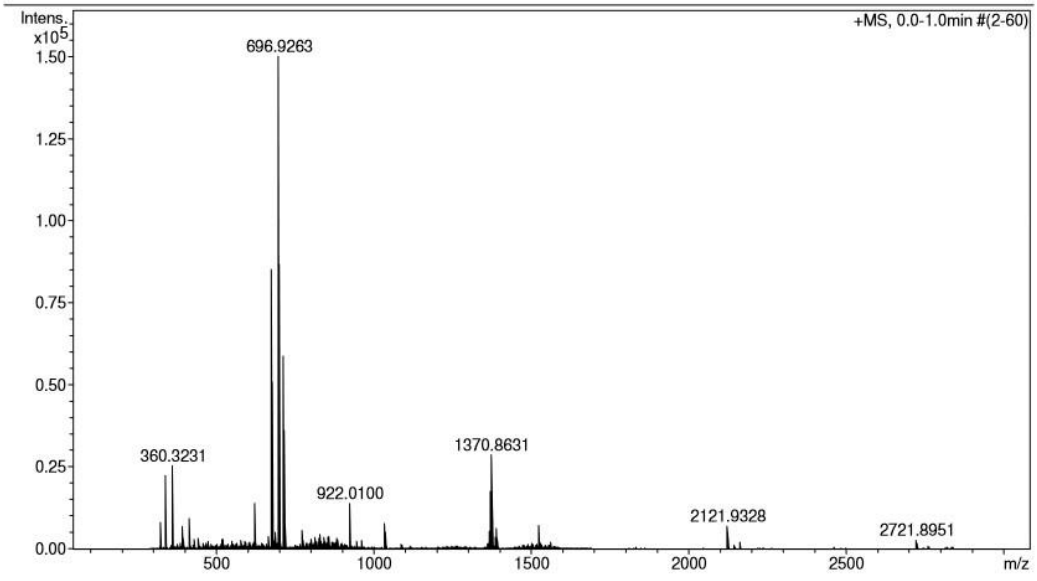
Display Report

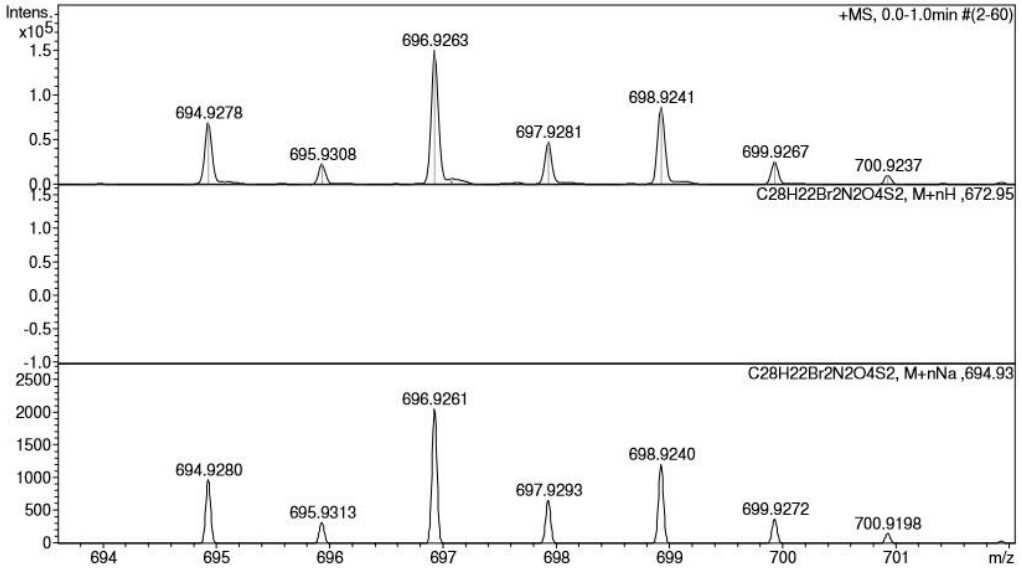
Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Mulina\bp-247_&clb.d	Acquisition Date	21.12.2020 17:34:46
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	/TERN BP-247	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 200, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





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HRMS of (1Z,2Z)-1,2-bis(1-(2-chlorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3oa

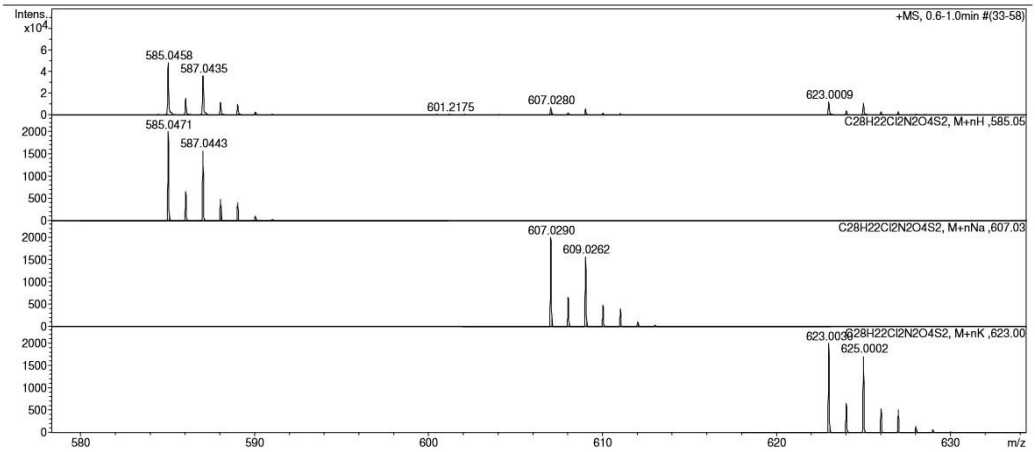
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2021\Mulina\031038.d	Acquisition Date	10.03.2021 17:26:06
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-261	Instrument / Ser#	micrOTOF 10248
Comment	C28H22Cl2N2O4S2 mH 585.0470 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(2-fluorophenyl)-2-(phenylsulfonyl)ethylidene)hydrazine 3pa

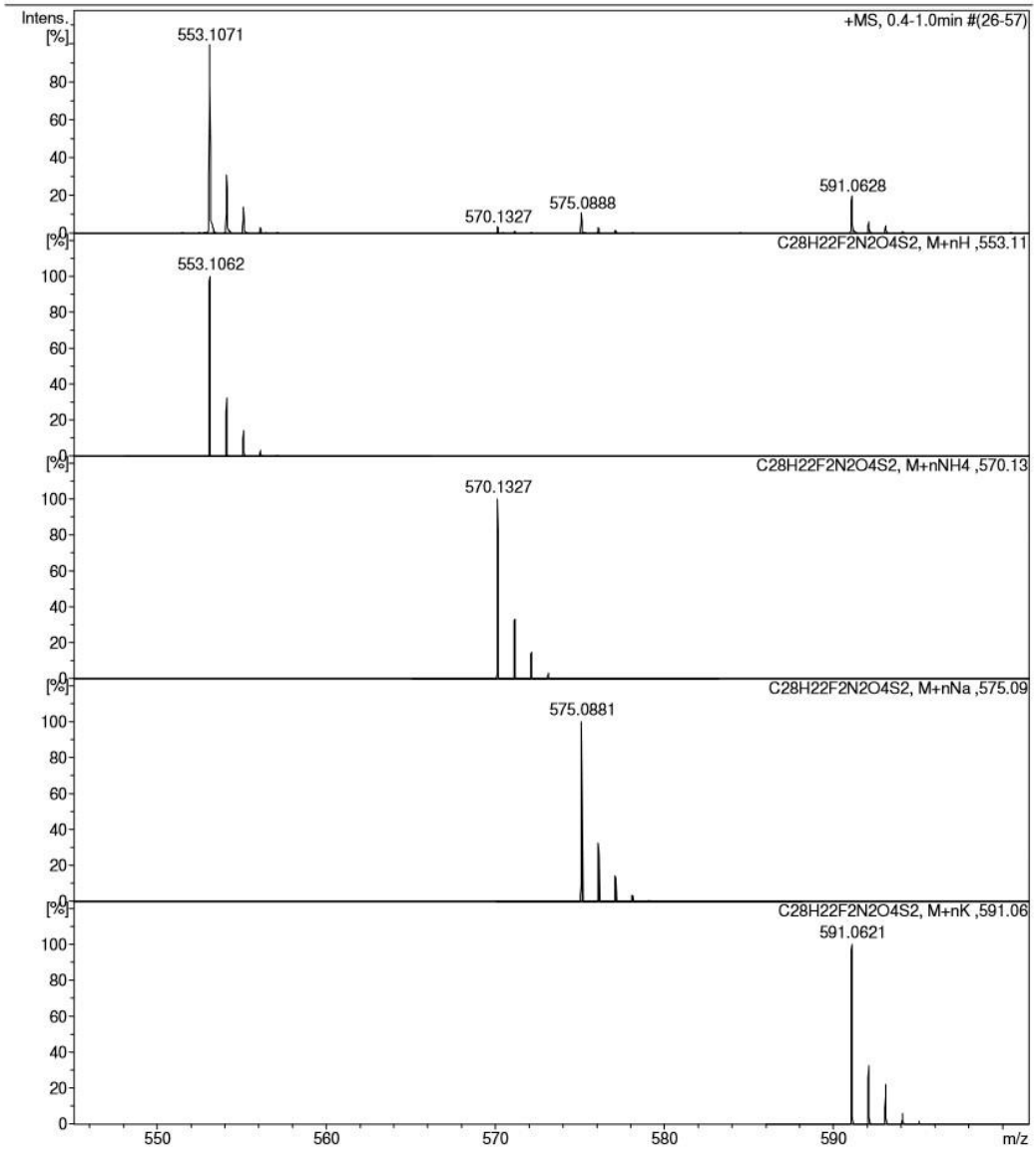
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2021\Mulina\0210001.d	Acquisition Date	10.02.2021 15:54:58
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN VP-256	Instrument / Ser#	micrOTOF 10248
Comment	C28H22F2N3O4S2 mH549.1225 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of (1Z,2Z)-1,2-bis(1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethylidene)hydrazine 3qa

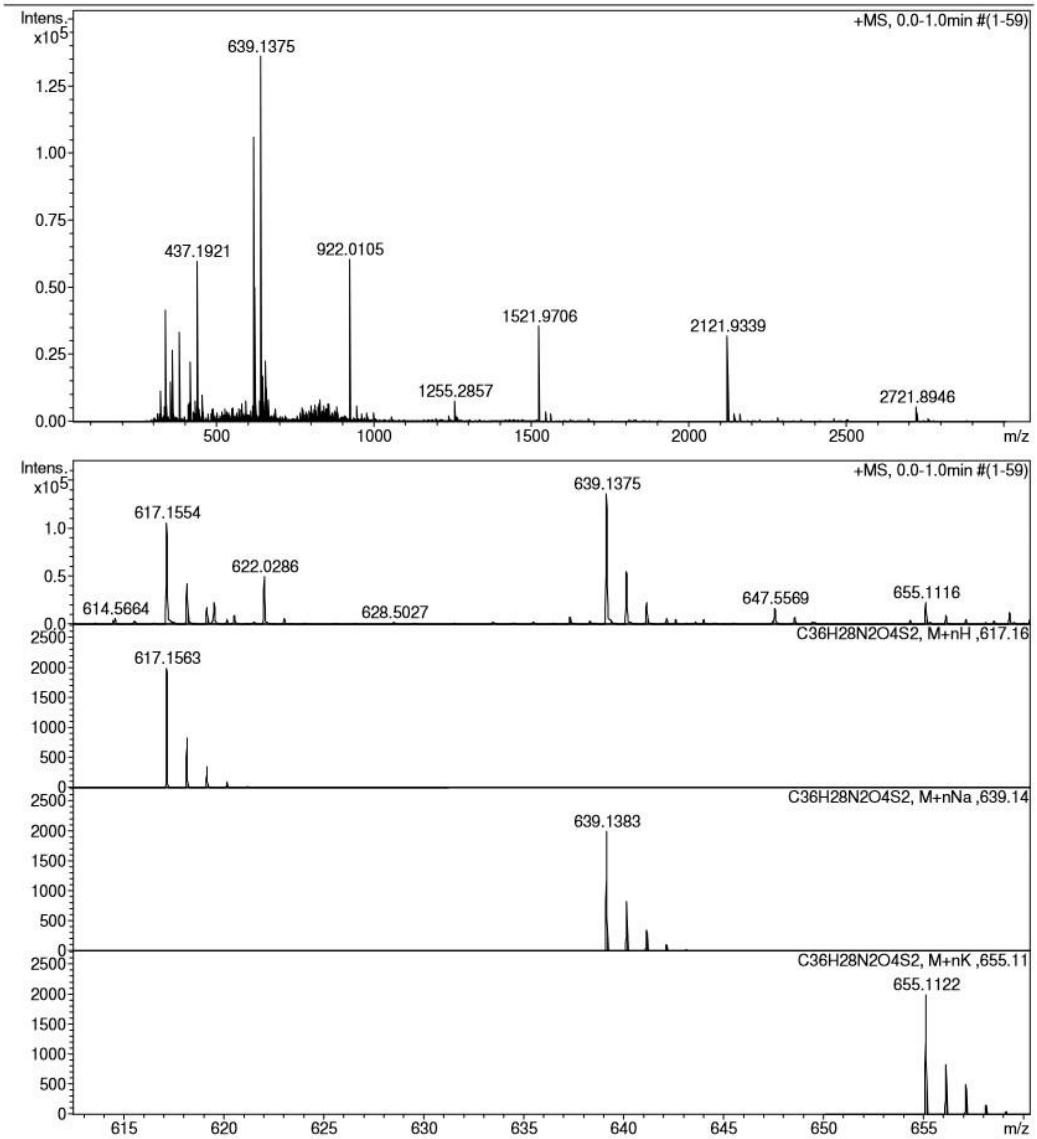
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Terentiev\Mulina\bp-243_&clb.d	Acquisition Date	16.11.2020 17:15:09
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	/TERN BP-243	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 200, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS of 1,2-bis((S,Z)-2-(phenylsulfonyl)-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine 3ra

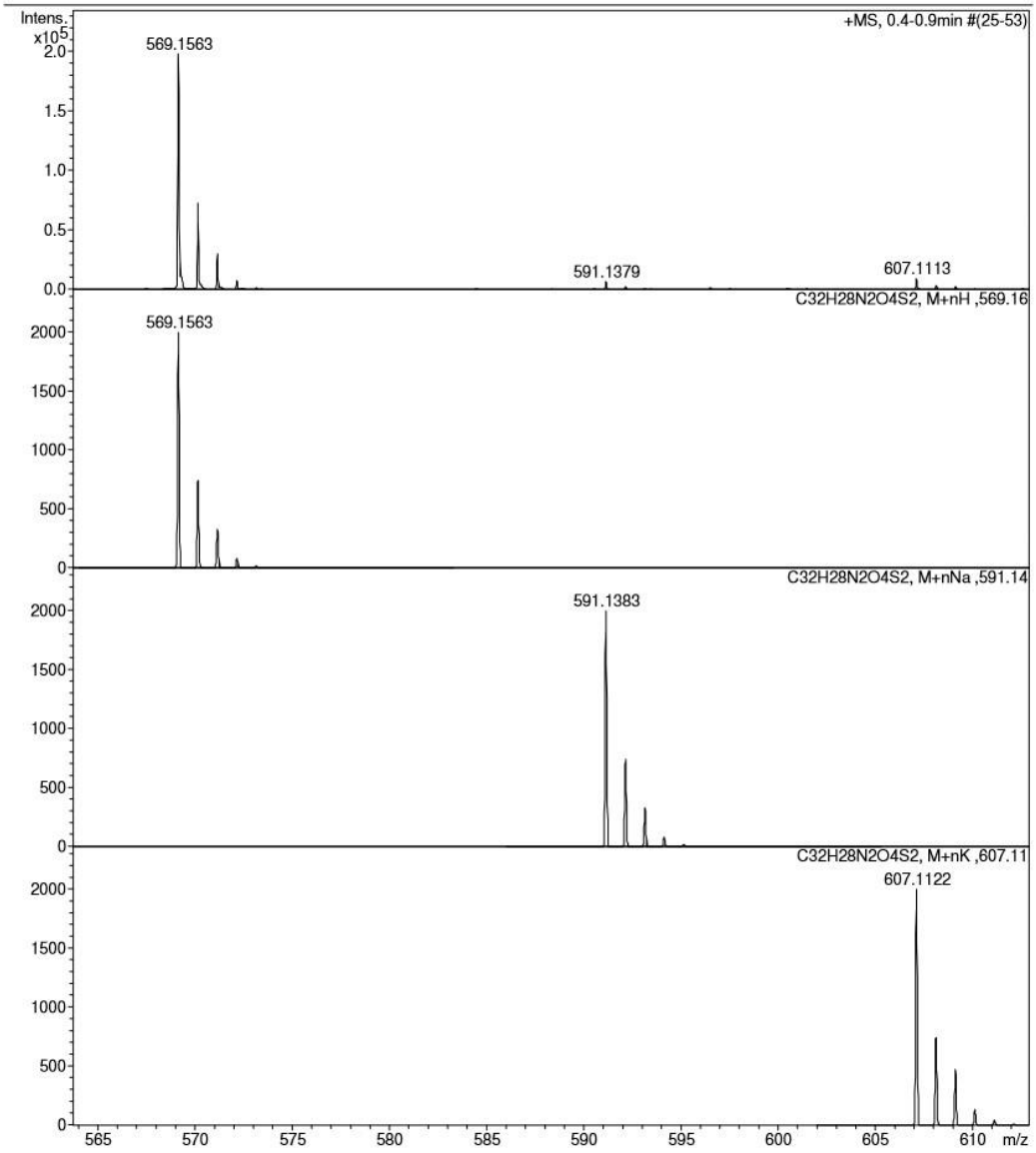
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2021\Mulina\0112024.d	Acquisition Date	12.01.2021 16:56:22
Method	tune_50-1600.m	Operator	BDAL@DE
Sample Name	/TERN BP-248	Instrument / Ser#	micrOTOF 10248
Comment	C32H28N2O4S2 mH 569.1563 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(phenylsulfonyl)octan-2-ylidene)hydrazine 3sa

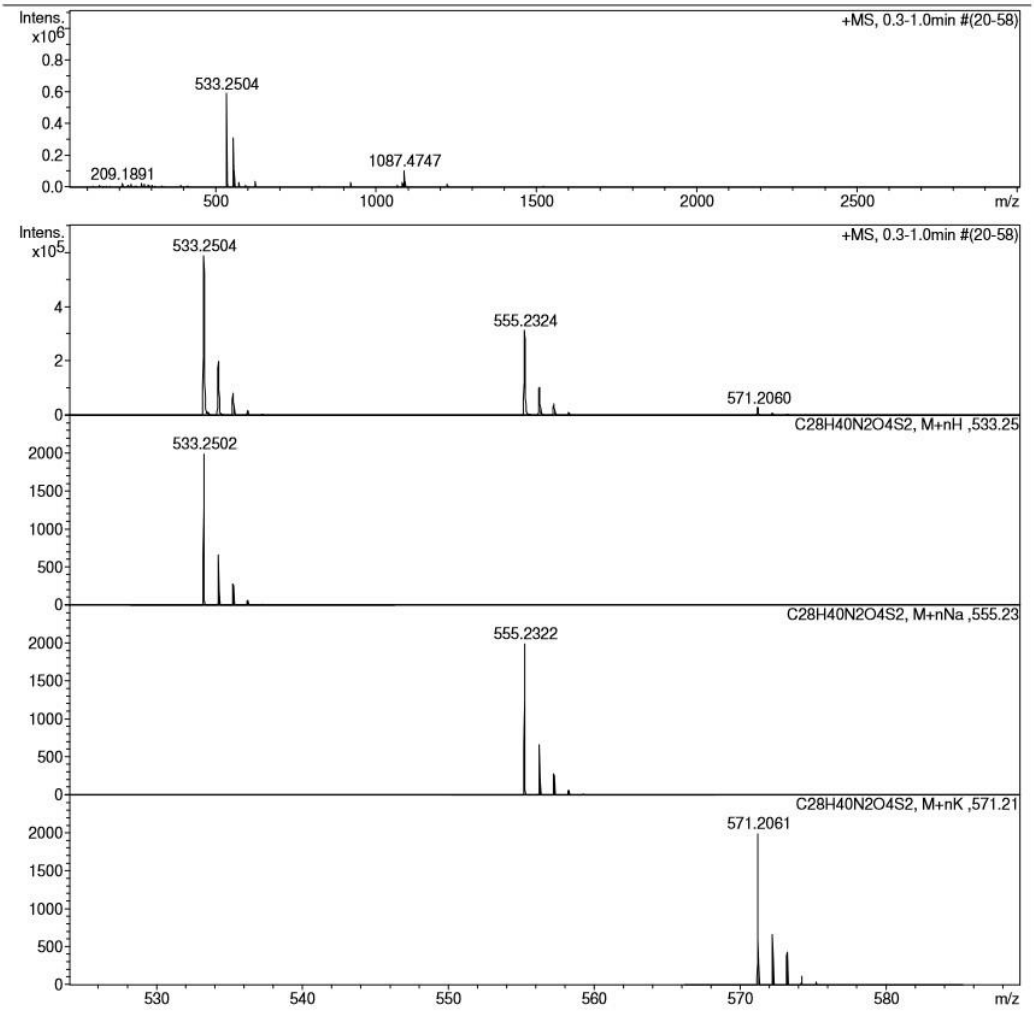
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2024\Doronin\0409022.d	Acquisition Date	09.04.2024 13:33:31
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN M-1162	Instrument / Ser#	micrOTOF 10248
Comment	C28H40N2O4S2 mH 533.2502 calibrant added CH3OH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of (1Z,2Z)-1,2-bis(1-(cyclohex-1-en-1-yl)-2-(phenylsulfonyl)ethylidene)hydrazine 3ta

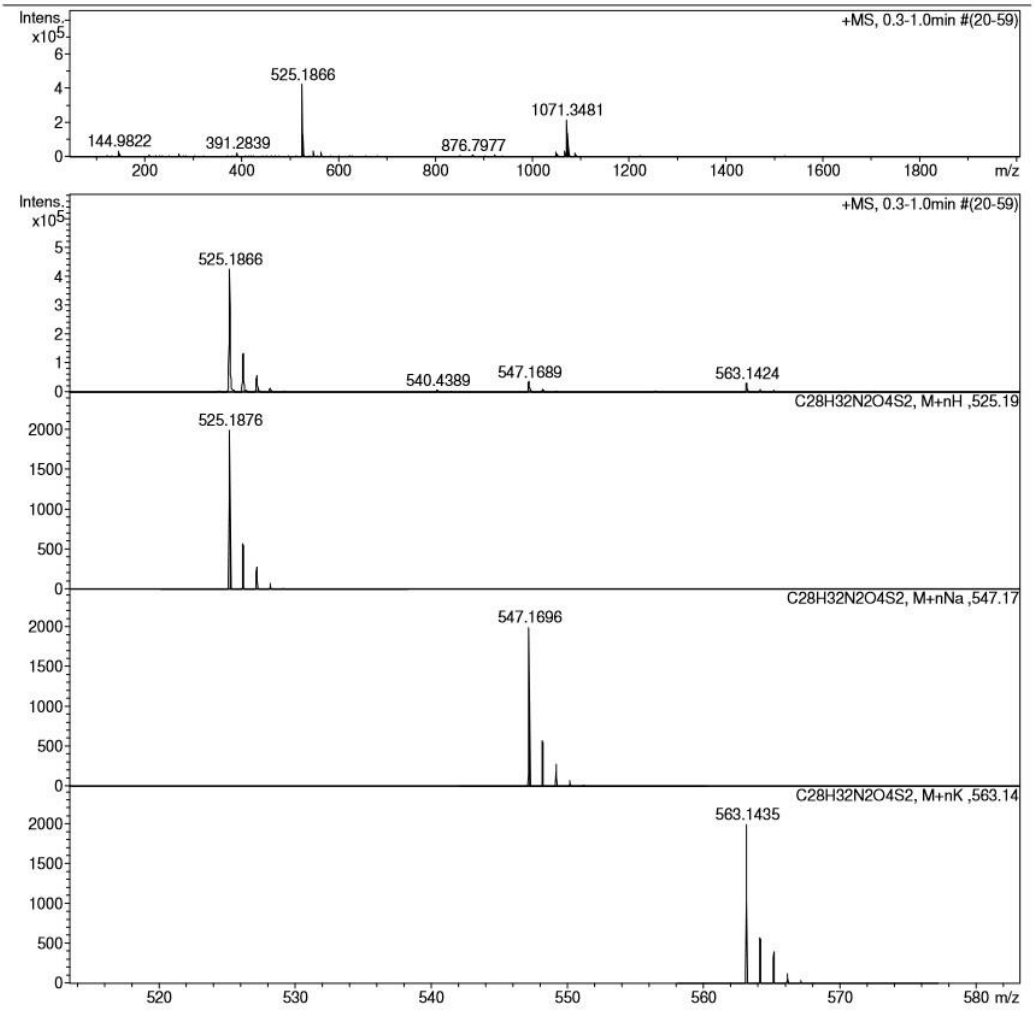
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2023\Doronin\0703036.d	Acquisition Date	03.07.2023 16:50:47
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN M-987	Instrument / Ser#	micrOTOF 10248
Comment	C28H32N2O4S2 mH525.1876 clb added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS of 2,6-di-tert-butyl-4-methyl-4-(phenylsulfonyl)cyclohexa-2,5-dien-1-one 6

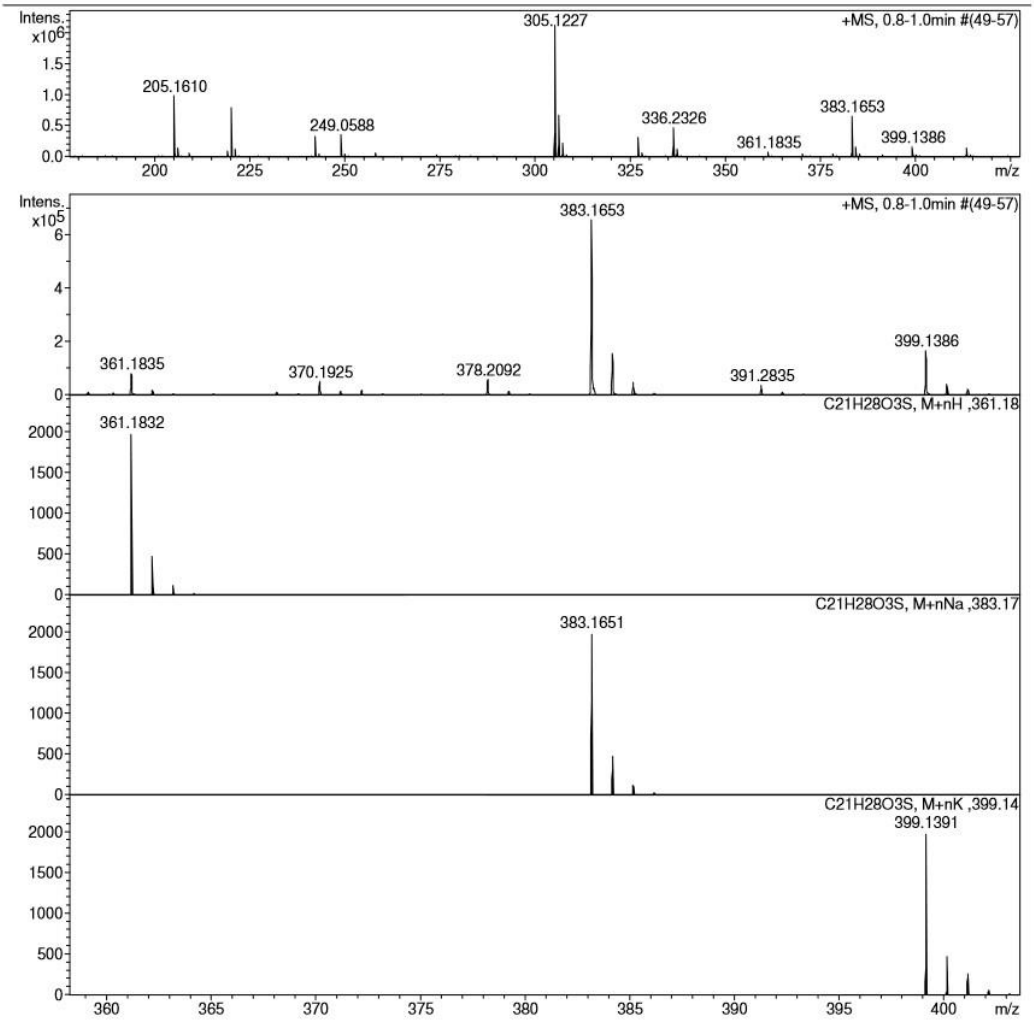
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2022\Doronin\0329042.d	Acquisition Date	29.03.2022 17:37:47
Method	tune_50-1600_pos_15_12.m	Operator	BDAL@DE
Sample Name	/TERN M-542	Instrument / Ser#	micrOTOF 10248
Comment	C21H28O3S mH 361.1831 calibrant added CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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