Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

The Azidosulfonylation of Terminal Alkynes Leading to β-azidovinyl Sulfones

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I. General information

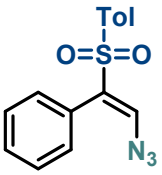
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Solvents were purified by standard procedure. Zhdankin reagents were synthesized according to the literature.[1] The products were purified by column chromatography over silica gel (300-400 size). NMR spectra were recorded on a Brüker Advance 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{19}F: 565 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on TSQ 8000 Evo by using EI method. Elemental Analysis were recorded on euro Vector EA 3000.

II. General procedures for the β-azidovinyl Sulfones

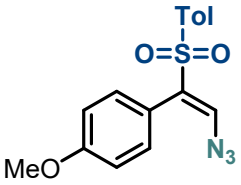
Under nitrogen, to a solution of alkynes (0.3 mmol, 1 equiv) in DMSO (2 ml) was added sodium sulfinate **2** (0.9 mmol, 3 equiv) and the hypervalent iodine reagent **I** (0.9 mmol, 3 equiv) subsequently. The mixture was stirred at 40 °C. After completion indicated by TLC, the resulting mixture was extracted by dichloromethane (3 x 20 mL). The combined organic layer was washed with brine (3 x 10 mL) and dried over $MgSO_4$, which is then concentrated under reduced pressure. The residue is purified by column chromatography on silica gel with petroleum ether as eluent to provide **3 & 4**.

Note: Product can't be analyzed by **HRMS**, probably due to the decomposition.

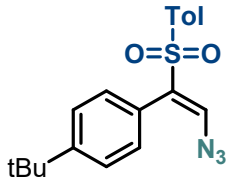
III. Analytical data for 3 & 4 and 5.



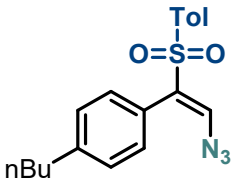
(3a). White soild (85% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.35-7.32 (m, 1H), 7.30-7.27 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.3, 137.9, 136.2, 131.5, 130.6 , 129.5, 129.4, 128.3, 128.2, 128.1,21.6. **IR** (KBr, cm^{-1}) 2179 (N_3).



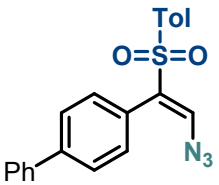
(3b). Colorless oil (78% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 9 Hz, 2H), 6.81 (d, *J* = 9 Hz, 2H), 3.79 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.3, 144.2, 137.6, 136.3, 132.0, 131.3, 129.5, 128.1, 120.2, 113.8, 55.2, 21.6 . **IR** (KBr, cm^{-1}) 2140 (N_3).



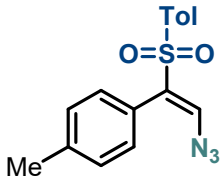
(3c). Colorless oil (82% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H), 1.29 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.5, 144.1, 137.8, 136.4, 131.5, 130.1, 129.5, 128.1, 125.3, 125.2, 34.7, 31.1, 21.6. **IR** (KBr, cm^{-1}) 2138 (N_3).



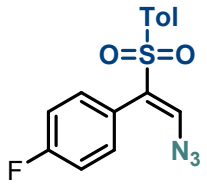
(3d). Colorless oil (75% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 1.59 – 1.54 (m, 2H), 1.35 – 1.29 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.3, 144.1, 137.6, 136.3, 131.5, 130.3, 129.4, 128.3, 128.1, 125.3, 35.4, 33.1, 22.2, 21.5, 13.9. **IR** (KBr, cm^{-1}) 2158 (N_3).



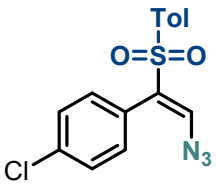
(3e). Colorless oil (80% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 4H), 7.43 (t, *J* = 7.8 Hz, *2*H), 7.37 –7.34 (m, 1H), 7.22 – 7.20 (m, 4H), 2.38 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.3, 142.0, 140.1, 138.1, 136.3, 131.1, 130.9, 129.6, 128.8, 128.2, 127.7, 127.2, 127.1, 127.0, 21.6. **IR** (KBr, cm^{-1}) 2136 (N_3).



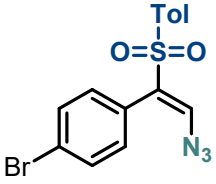
(3f). Colorless oil (80% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.2, 139.5, 137.8, 136.3, 131.6, 130.4, 129.5, 129.1, 128.2, 125.2, 21.6, 21.3. **IR** (KBr, cm^{-1}) 2133 (N_3). **Elemental Analysis**: N(%): 13.281, C(%): 60.895, H(%): 5.240, S(%): 10.532, O(%): 10.052.



(3g). White soild (86% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.12 (m, 2 H), 6.98 (m, 2H), 2.39 (s, 3H) **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.2 (d, $J_{C\text{-}F}$ = 250.3 Hz), 144.4, 138.3, 136.0, 132.5 (d, $J_{C\text{-}F}$ = 8.7 Hz), 130.4, 129.6, 128.1, 124.2 (d, $J_{C\text{-}F}$ = 3.7 Hz), 115.5(d, $J_{C\text{-}F}$ = 22.4 Hz), 21.6; ^{19}F NMR (564 MHz, $CDCl_3$): δ −111.8. **IR** (KBr, cm^{-1}) 2129 (N_3).

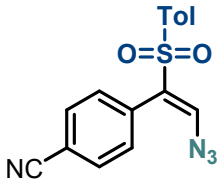


(3h). White soild (67% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 9 Hz, 2H), 2.39 (s, 3H) **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.5, 138.4, 136.0, 135.6, 131.8, 130.2, 129.6, 128.7 , 128.1, 126.8, 21.6 **IR** (KBr, cm^{-1}) 2152 (N_3).

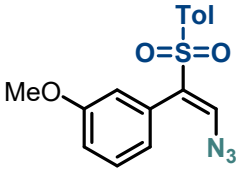


(3i). Colorless oil (75% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (s , 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). **^{13}C**

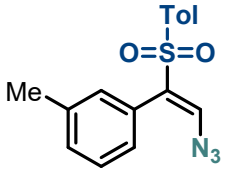
NMR (150 MHz, $CDCl_3$) δ 144.5, 138.5 , 136.0, 132.1, 131.7, 130.2, 129.7, 128.1, 127.3, 123.9, 21.6. **IR** (KBr, cm^{-1}) 2159 (N_3).



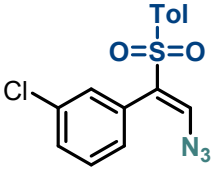
(3j). Colorless oil (70% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.8, 139.4, 135.8, 133.4, 132.0, 131.2, 129.8, 129.3, 128.0, 118.2, 113.0, 21.6. **IR** (KBr, cm^{-1}) 2161 (N_3).



(3k). Colorless oil (73% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.21-7.18 (m, 3H), 6.88-6.87 (m, 1H), 6.68-6.66 (m, 2H), 3.73 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.3, 138.0, 136.2, 131.3, 129.5, 129.3, 128.3, 122.9, 115.7, 115.4, 55.2, 21.6. **IR** (KBr, cm^{-1}) 2134 (N_3).

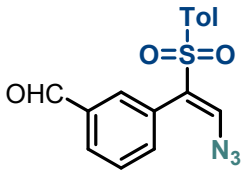


(3l). Colorless oil (yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.17-7.13 (m, 2H), 6.96 (s, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.3, 138.1, 137.8, 136.2, 131.7, 131.1, 130.2, 129.5, 128.3, 128.2, 127.6, 21.6, 21.4. **IR** (KBr, cm^{-1}) 2132 (N_3).

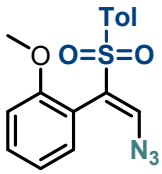


(3m). Colorless oil (76% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.32-7.30 (m, 1H), 7.24-7.21 (m, 3H), 7.13 (s, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 2.39 (s, 3H).

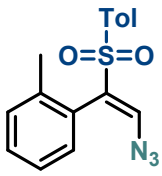
^{13}C NMR (150 MHz, $CDCl_3$) δ 144.5, 138.7, 136.0, 134.2, 130.5, 130.1, 129.9, 129.7, 129.6, 129.5, 128.7, 128.2, 21.6. **IR** (KBr, cm^{-1}) 2141 (N_3).



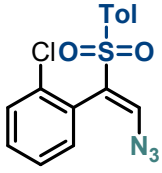
(3n). Colorless oil (65% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.92 (s, 1H), 7.86 (d, J = 6.6 Hz, 1H), 7.60 (s, 1H), 7.51 – 7.45 (m, 4H), 7.20 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 191.6, 144.7, 139.0, 136.4, 136.3, 135.9, 132.2, 130.0, 129.9, 129.7, 129.6, 129.1, 128.1, 21.6. **IR** (KBr, cm^{-1}) 2174 (N_3).



(3o). Colorless oil (65% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 3H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.71(d, *J* = 8.4 Hz, 1H), 3.35 (s, 3H), 2.38(s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.3, 143.8, 138.7, 136.6, 132.5, 131.4, 129.0, 128.5, 127.9, 120.4, 116.6, 110.5, 55.1, 21.5. **IR** (KBr, cm^{-1}) 2134 (N_3).

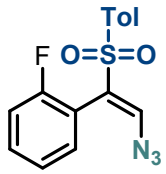


(3p). Colorless oil (60% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.26-7.24 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.13-7.10 (m, 2H), 6.93 (d, *J* = 7.2 Hz, 1H), 2.41(s, 3H), 1.85(s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.4, 138.6, 138.2, 136.0, 131.2, 130.7, 129.9, 129.7, 129.5, 128.5,127.3,125.5, 21.6, 19.1. **IR** (KBr, cm^{-1}) 2132 (N_3).

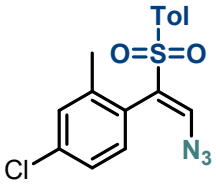


(3q). Colorless oil (75% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.34-7.26 (m, 4H), 7.20 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ

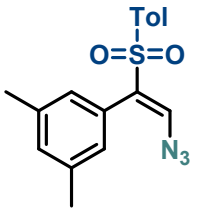
144.5, 139.7, 135.9, 135.2, 133.0, 131.0, 129.5, 129.4, 128.5, 128.1, 127.1, 126.6, 21.6. **IR** (KBr, cm^{-1}) 2174 (N_3).



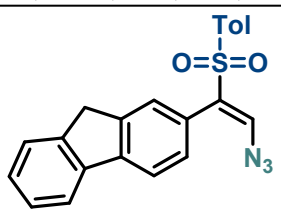
(3r). Colorless oil (70% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.28-7.24 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.08-7.06 (m, 1H), 6.86 (t, *J* = 9.0 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.9 (d, *J* = 249.5 Hz), 144.4, 140.1, 136.1, 132.5 (d, *J* = 1.8 Hz), 131.7 (d, *J* = 8.3 Hz), 129.5, 128.1, 124.8, 124.1(d, *J* = 3.6 Hz), 116.0(d, *J* = 15.8 Hz), 115.4(d, *J* = 21.5 Hz), 21.6. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -112.9. **IR** (KBr, cm^{-1}) 2164 (N_3).



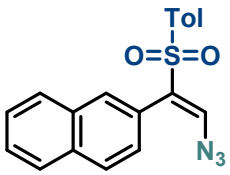
(3s). Colorless oil (62% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.13-7.10 (m, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 2.41 (s, 3H), 1.82 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.7, 140.5, 138.8, 135.8, 135.6, 132.4, 130.0, 129.6, 129.4, 128.4, 125.9, 125.8, 21.7, 19.0. **IR** (KBr, cm^{-1}) 2147 (N_3).



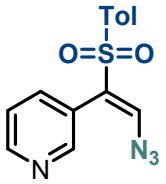
(3t). Colorless oil (70% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.95 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1 H), 6.80 (d, *J* = 7.8 Hz, 1H), 2.41 (s, 3H), 2.30 (m, 3H), 1.81 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.3, 139.8, 138.3, 138.2, 136.1, 131.0, 130.8, 129.5, 128.5, 126.4, 124.3, 21.6, 21.3, 19.0. **IR** (KBr, cm^{-1}) 2181 (N_3).



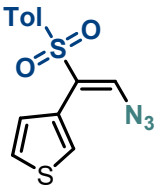
(3u). Colorless oil (92% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.40 (s, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.34-7.31(m, 1H), 7.17(d, *J* = 7.8 Hz, 1H), 7.06(d, *J* = 7.8 Hz, 1H), 3.86(s, 2H), 2.36(s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.2, 143.6, 143.2, 142.9, 140.8, 137.8, 136.2, 131.9, 129.5, 129.3, 128.2, 127.4, 127.1, 126.9, 126.3, 125.1, 120.2, 119.6, 36.9, 21.6. **IR** (KBr, cm^{-1}) 2179 (N_3).



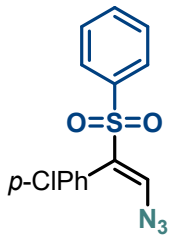
(3v). Colorless oil (75% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.77-7.74 (m, 2H), 7.69 (s, 1H), 7.52-7.47 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.35(s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.3, 138.3, 136.3, 133.3, 132.8, 131.4, 130.5, 129.6, 128.5, 128.2, 128.0, 127.7, 127.4, 127.0, 126.4, 125.7, 21.6. **IR** (KBr, cm^{-1}) 2157 (N_3).



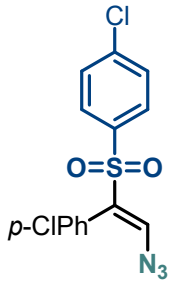
(3w). Colorless oil (65% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.2 Hz, 1H), 8.19 (s, 1H), 7.95 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.30-7.27 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.7, 150.1, 144.7, 139.5, 138.0, 135.7, 129.8, 128.0, 127.9, 125.0, 123.2, 21.6. **IR** (KBr, cm^{-1}) 2171 (N_3).



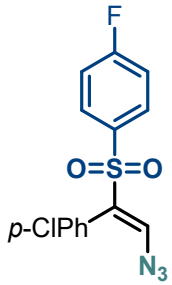
(3x). Colorless oil (62% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 3 Hz, 1H), 7.26-7.24 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 4.8 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.2, 137.4, 136.5, 129.6, 128.6, 127.8, 127.6, 127.4, 126.4, 125.3, 21.6. **IR** (KBr, cm^{-1}) 2137 (N_3).



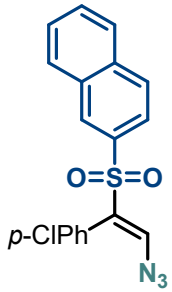
(4a). Colorless oil (65% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.61(d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.9, 138.9, 135.7, 133.4, 131.8, 129.9, 129.0, 128.7, 128.1, 126.6. **IR** (KBr, cm^{-1}) 2180 (N_3).



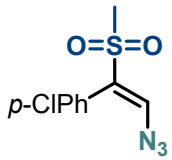
(4b). Colorless oil (68% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.2, 139.4, 137.5, 135.8, 131.8, 129.5, 129.4, 129.3, 128.8, 126.3. **IR** (KBr, cm^{-1}) 2158 (N_3).



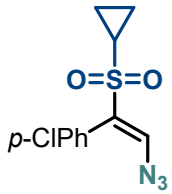
(4c). Colorless oil (72% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.63–7.61 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.6 (d, *J* = 255 Hz), 139.0, 135.8, 134.9 (d, *J* = 3.6 Hz), 131.8, 131.0 (d, *J* = 9.6 Hz), 129.7, 128.8, 126.5, 116.4(d, *J* = 22.7 Hz). **IR** (KBr, cm^{-1}) 2163 (N_3).



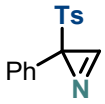
(4d). Colorless oil (72% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 6.6 Hz, 2H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.61(t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.11(d, *J* = 8.4 Hz, 2H), 6.85(t, *J* = 8.4 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.8, 135.6, 135.3, 133.9, 132.8, 131.7, 131.5, 131.2, 130.5, 129.2, 128.5, 128.3, 126.9, 126.6, 124.2, 123.8. **IR** (KBr, cm^{-1}) 2144 (N_3).



(4e). Colorless oil (83% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75, 7.46-7.42 (dd, *J* = 8.5, 16.2, 4H), 2.80 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.3, 136.1, 131.5, 129.2, 128.6, 126.7, 41.3. **IR** (KBr, cm^{-1}) 2131 (N_3).

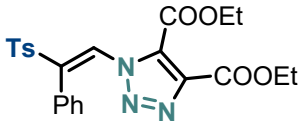


(4f). Colorless oil (77% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86(s, 1H), 7.63-7.61 (dd, *J* = 5.0, 9.5, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.09 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.6, 135.8, 131.8, 128.9, 128.8 , 127.2, 30.4, 5.5. **IR** (KBr, cm^{-1}) 2159 (N_3).

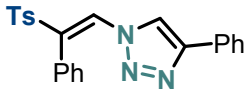


(5a). General procedures for Synthesis of 5a: **3a** (0.3 mmol) was dissolved in toluene (2.0 mL) in a Schlenk tube, and the solution was irradiated with a high-pressure mercury lamp (100 W). After 3 hours, the mixture was concentrated under vacuum and purified by column chromatography on silica gel with petroleum ether and ethyl acetate to afford **5a** (74%) as a colorless crystal; **^{1}H NMR** (600 MHz, $CDCl_3$) δ. 7.60 (d, *J* = 7.9 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1 H),

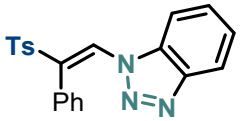
7.38 (t, *J* = 7.8 Hz, 2H), 7.32-7.29 (m, 4H), 5.10 (s, 1H), 2.46 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ. 146.7, 130.5, 130.1, 129.8, 129.8, 129.0, 125.6, 113.5, 63.1, 21.8. **HRMS** (ESI) m/z calcd. for $C_{15}H_{13}NO_2SNa$ $[M+Na]^+$ 294.3238, found 294.3230.



(5b). General procedures for Synthesis of 5b: **3a** (0.3 mmol), Dimethyl acetylenedicarboxylate (0.36 mmol) in water (5 mL) at 70 °C. After work-up, the crude residue was purified by flash column chromatography on silica gel (PE : EA = 5 : 1) to give **5b** (85%) as a colorless crystal; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.24-7.20 (m, 4H), 7.0 (d, *J* = 7.5 Hz, 2 H), 4.48 (q, *J* = 6.9, 13.8, 2H), 4.39 (q, *J* = 6.9 Hz, 13.8 Hz, 2H), 2.40 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 157.3, 145.3, 142.9, 139.7, 134.2, 131.0, 130.0, 129.8, 129.7, 128.9, 128.3, 128.1, 127.7, 63.5, 62.0, 21.7, 14.0, 13.9. **HRMS** (ESI) m/z calcd. for $C_{19}H_{18}F_2N_4ONa$ $[M+Na]^+$ $C_{23}H_{23}N_3O_6SNa$, 469.5120, found 469.5124.



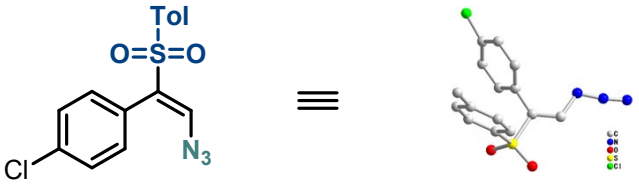
(5c). General procedures for Synthesis of 5c: **3a** (0.3 mmol), CuTc (30% mmol), phenylacetylene (0.6 mmol) in toluene (3 ml) at 25 °C. After work-up, the crude residue was purified by flash column chromatography on silica gel (PE : EA = 9 : 1) to give **5c** (70%) as a colorless crystal; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.56-7.51 (m, 5H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35-7.30 (m, 3H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.86 (s, 1H), 2.42 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.2, 145.1, 134.8, 133.0, 131.2, 130.5, 130.3, 129.7, 129.6, 129.5, 129.1, 128.9, 128.9, 128.5, 125.9, 117.4, 21.7. **HRMS** (ESI) m/z calcd. for : $C_{23}H_{19}N_3O_2SNa$ $[M+Na]^+$ 424.4738, found 424.4732.



(5d). General procedures for synthesis of 5d: **3a** (0.3 mmol), (trimethylsilyl)phenyl triflate (1.2 equiv), CsF (0.6 mmol) in MeCN (2 ml) at r.t for 24 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (PE : EA = 9 : 1) to give **5d** (63%) as a

colorless crystal; **^{1}H NMR** (600 MHz, $CDCl_3$) δ. 8.80 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.14 (m, 3H), 2.39 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ. 145.7, 144.8, 135.2, 133.9, 132.6, 130.8, 129.7, 129.6, 129.5, 128.9, 128.7, 128.5, 125.2, 120.4, 110.3, 21.6. **HRMS** (ESI) m/z calcd. for $C_{21}H_{17}N_3O_2SNa$ $[M+Na]^+$ 389.4358, found 389.4353.

IV. X-ray crystallography of 3h



The structure of **3h**

Empirical formula	$C_{15}H_{12}ClN_3O_2S$
Temperature	298.15 K
Wavelength	0.71073Å
Unit cell dimension	a = 16.0974(10) Å alpha = 90°. b = 11.1555(8) Å beta = 90°. c = 17.8712(11) Å gamma = 90°.
Volume	3209.2(4) $Å^3$
Z	8
Calculated density	1.382 g/cm^3
Absorption coefficient	0.377 mm^{-1}
F(000)	1376.0
Crystal size	0.31 × 0.21 × 0.15 mm^3
Theta range for data collection	7.306 to 58.538°
Reflection collected/unique	12699
Data / restraints / parameters	3856/0/200
Goodness-of-fit on F^2	1.048
Final R indices [I>=2sigma(I)]	R_1 = 0.0592, wR_2 = 0.1310
Final R indices (all data)	R_1 = 0.1260, wR_2 = 0.1603

V. Reference

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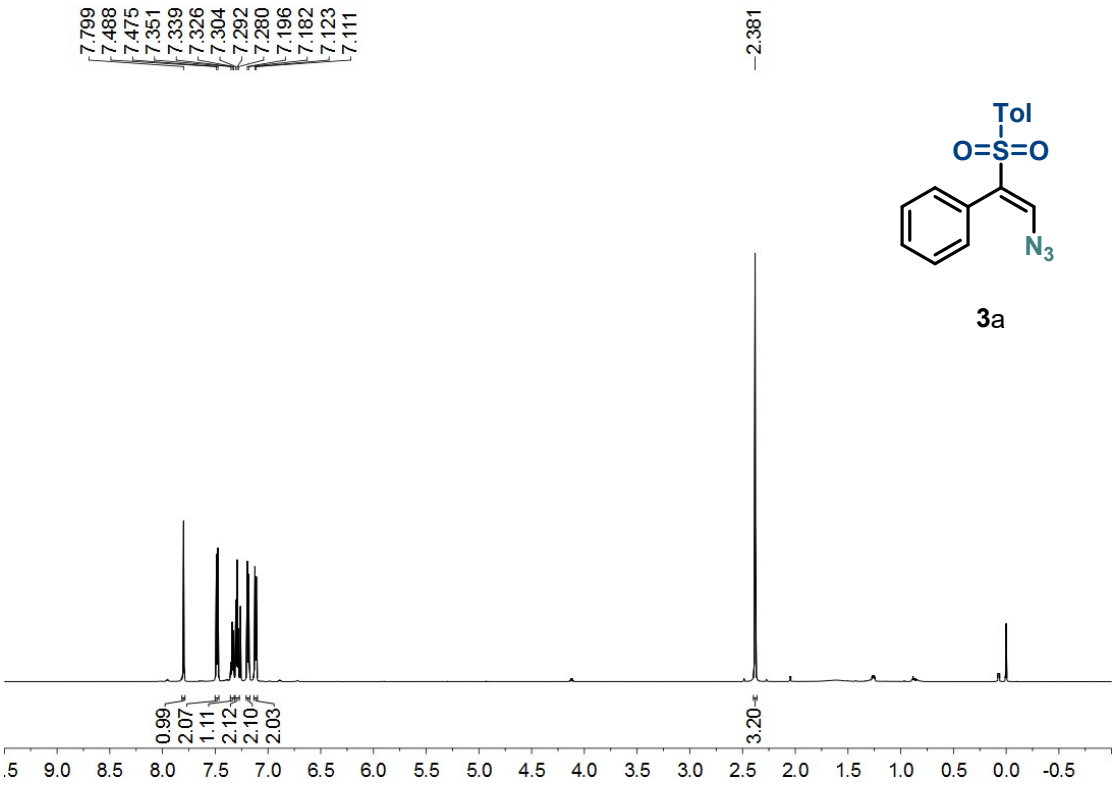
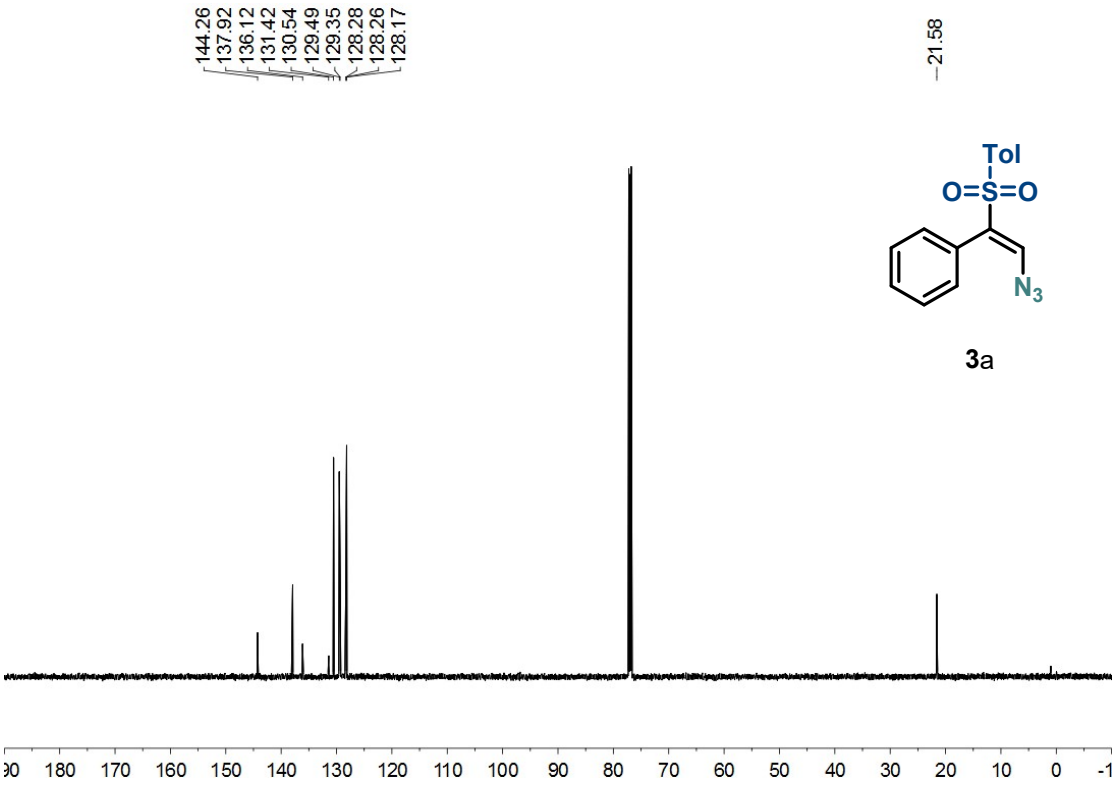
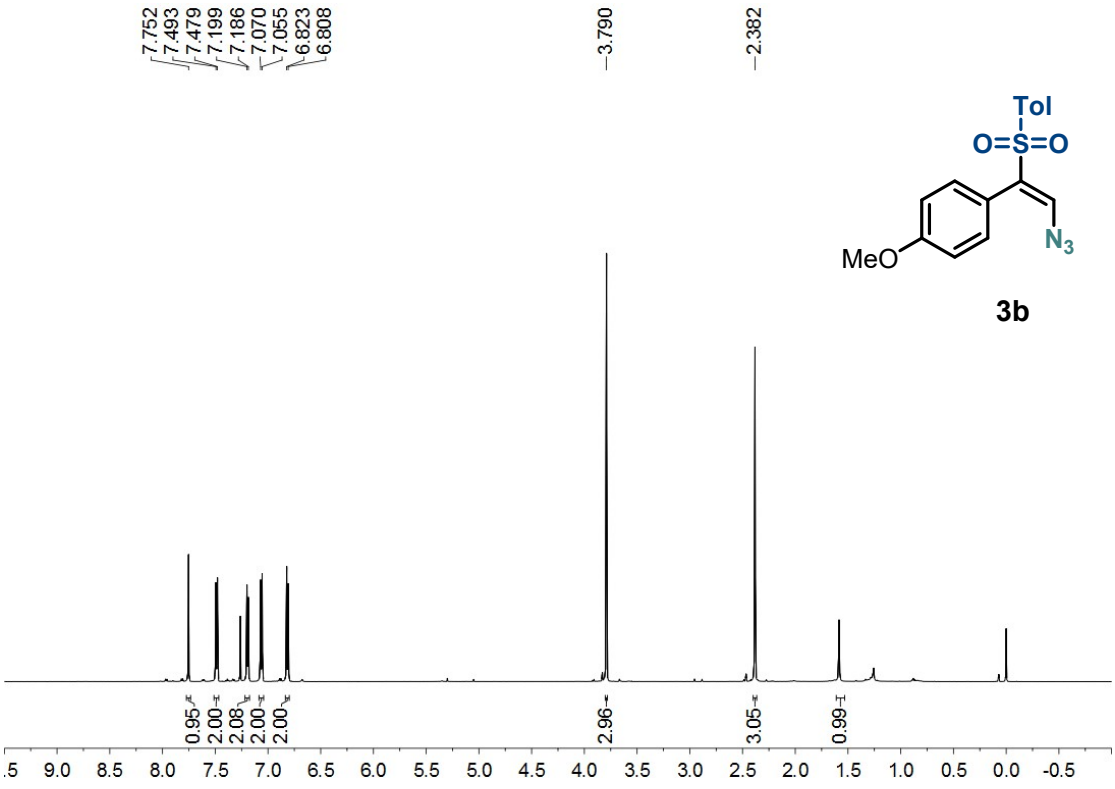
VI. NMR spectra for 3, 4 & 5.



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7.479
7.199
7.186
7.070
7.055
6.823
6.808
3.790
2.382
Tol
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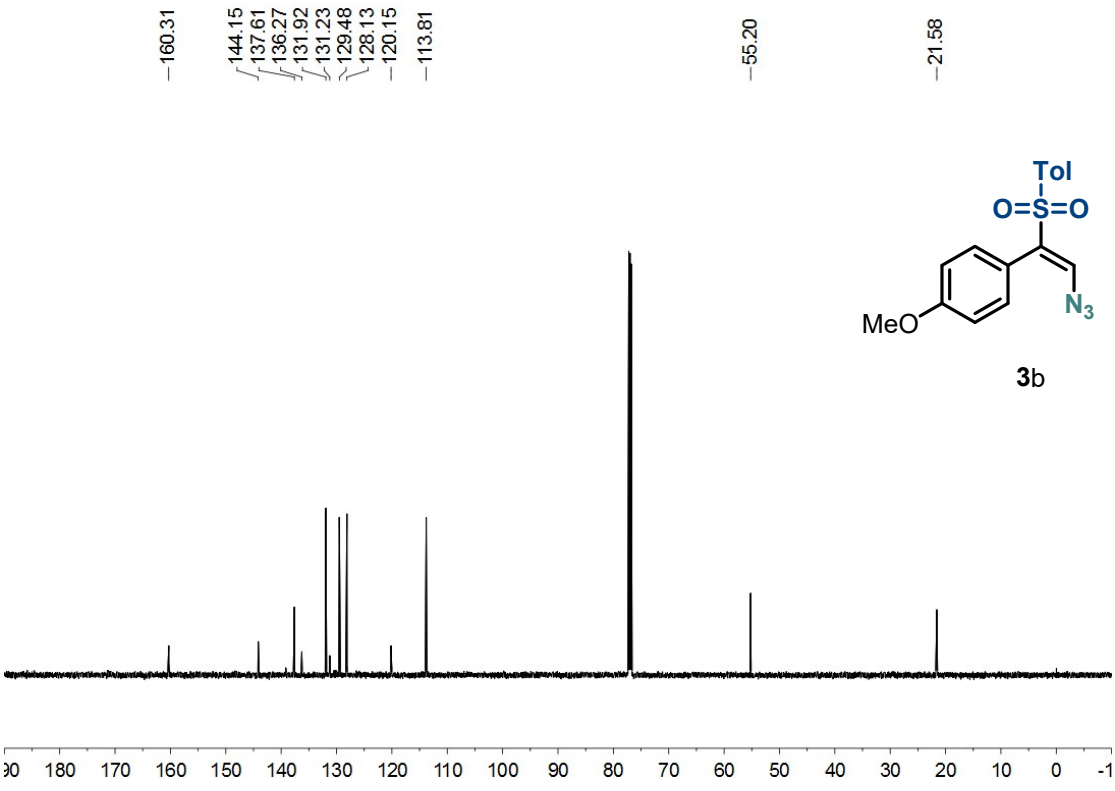
MeO
N3
3b
0.95
2.00
2.08
2.00
2.00
2.96
3.05
0.99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144.15
137.61
136.27
131.92
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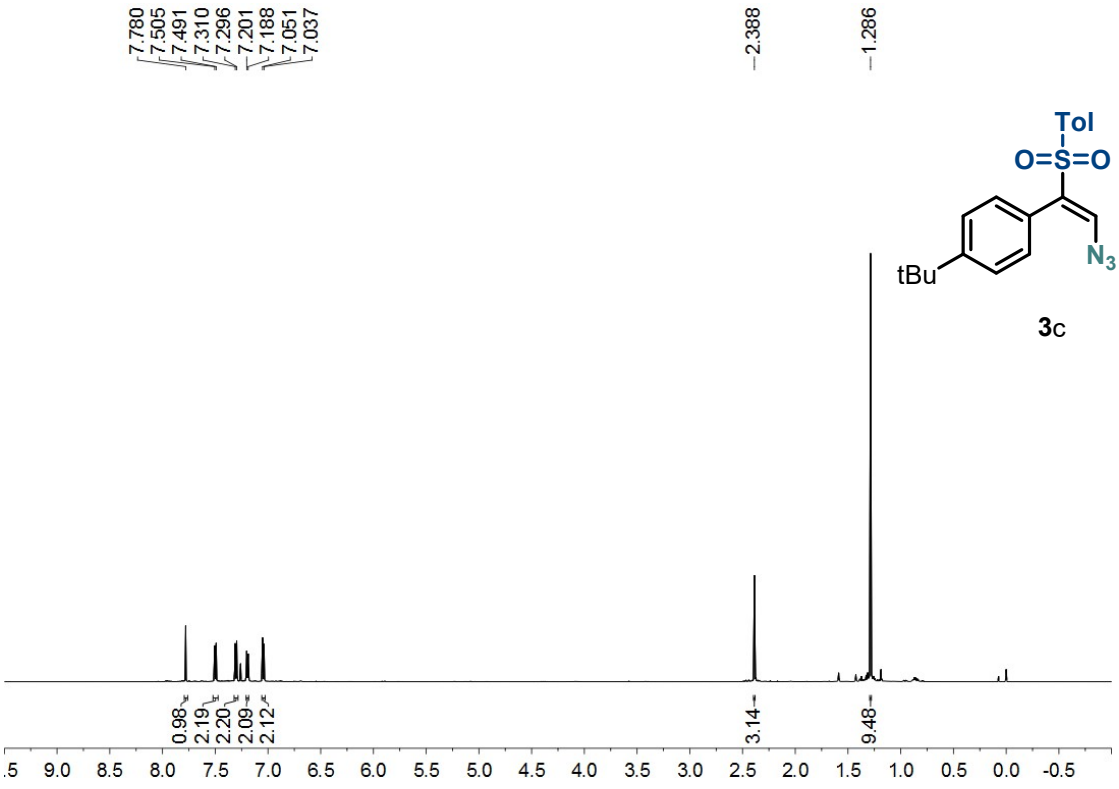
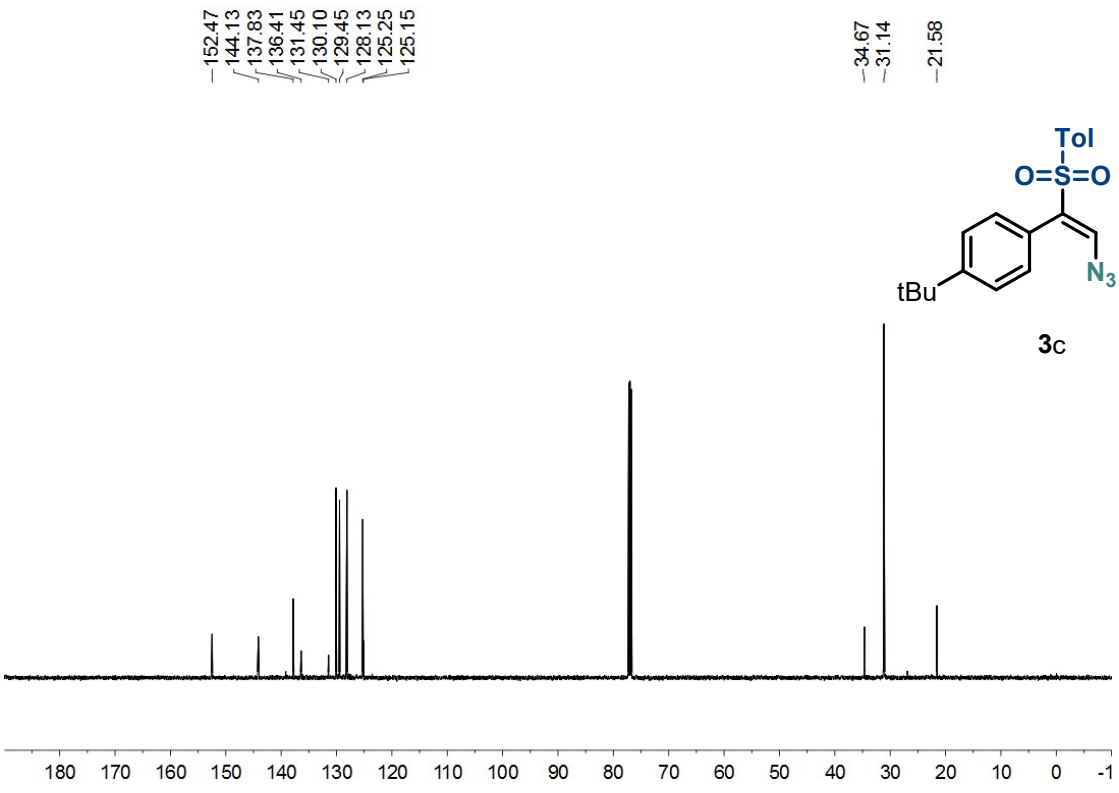
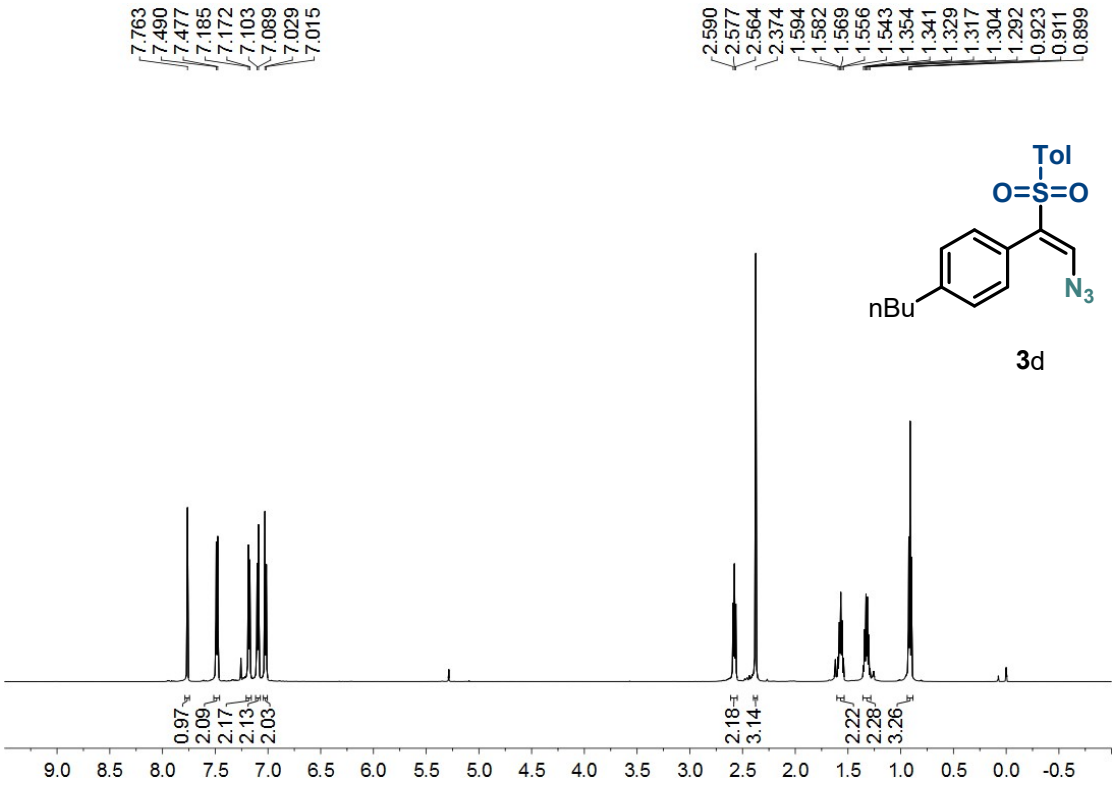
120.15
113.81
55.20
21.58
Tol
O=S=O
MeO
N3
3b

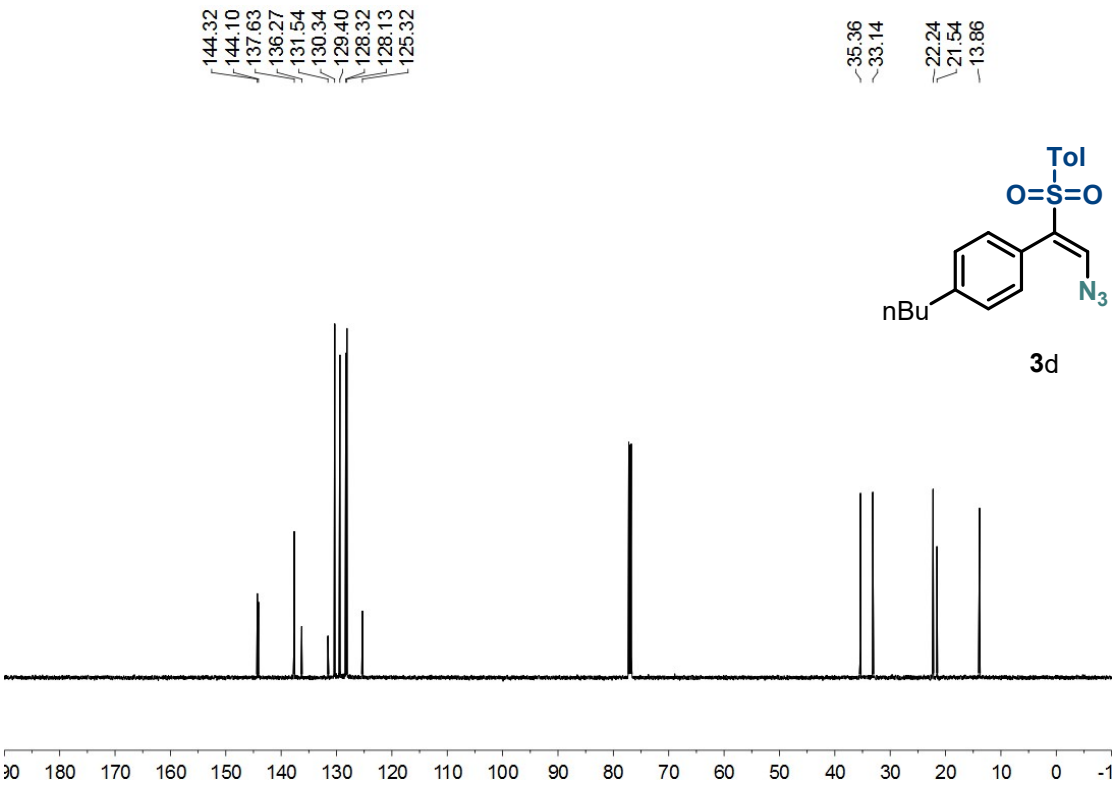

7.780
7.505
7.491
7.310
7.296
7.201
7.188
7.051
7.037
2.388
1.286
Tol
O=S=O
N3
tBu
0.98
2.19
2.20
2.09
2.12
3.14
9.48

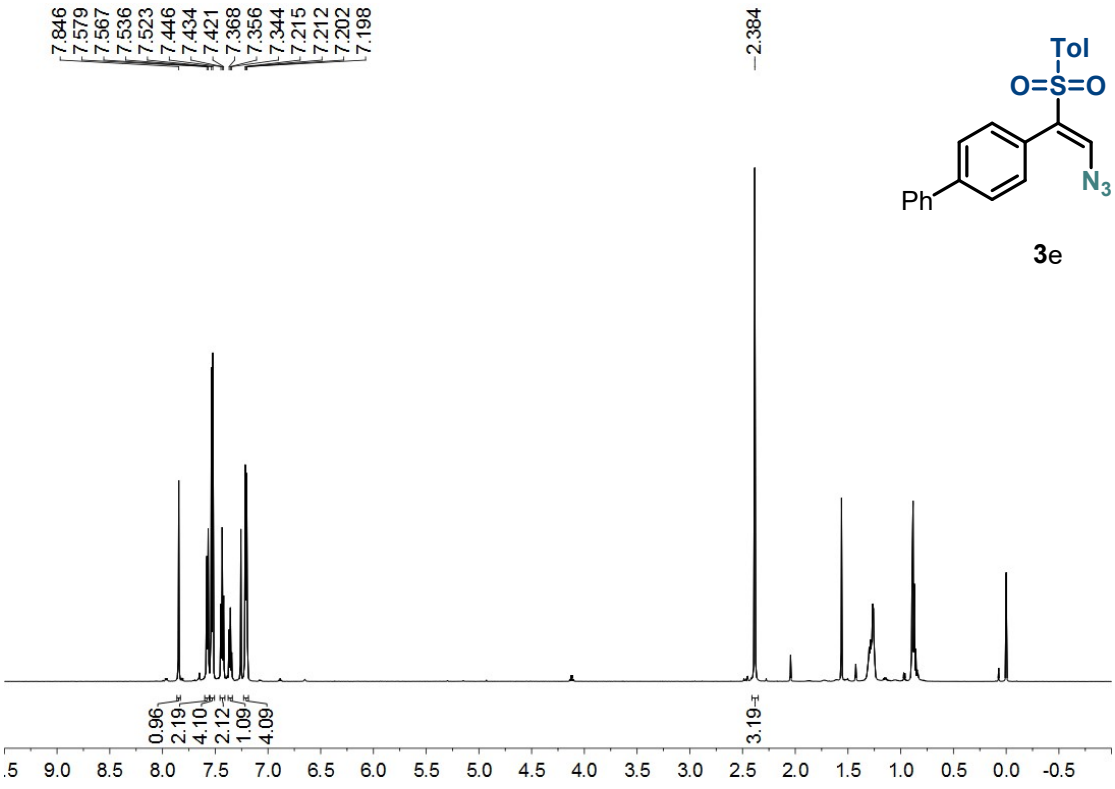
3c

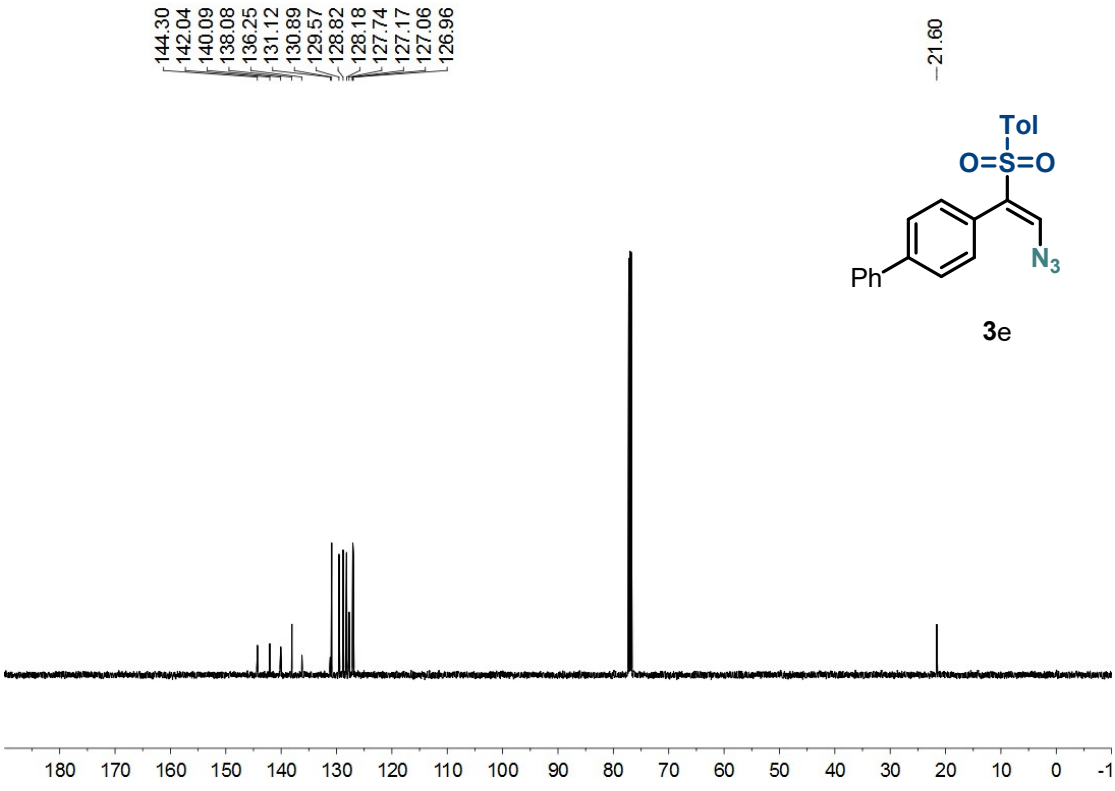

152.47
144.13
137.83
136.41
131.45
130.10
129.45
128.13
125.25
125.15
34.67
31.14
21.58
Tol
O=S=O
N3
tBu

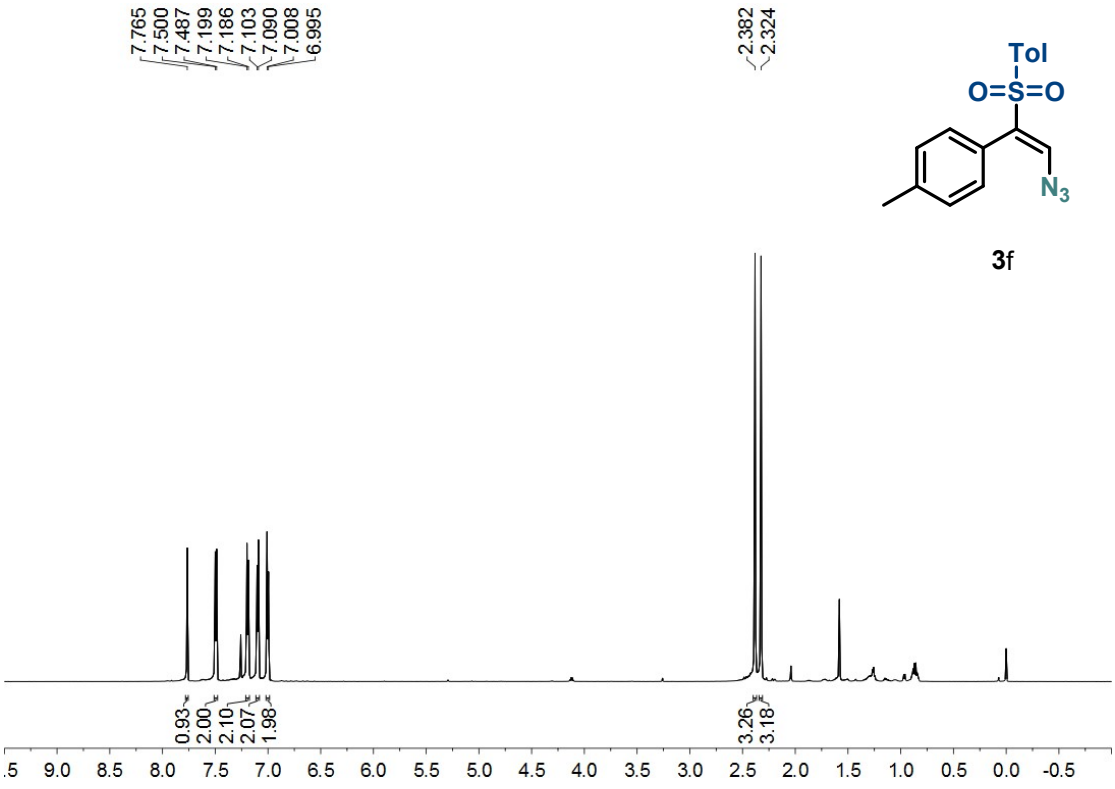
3c

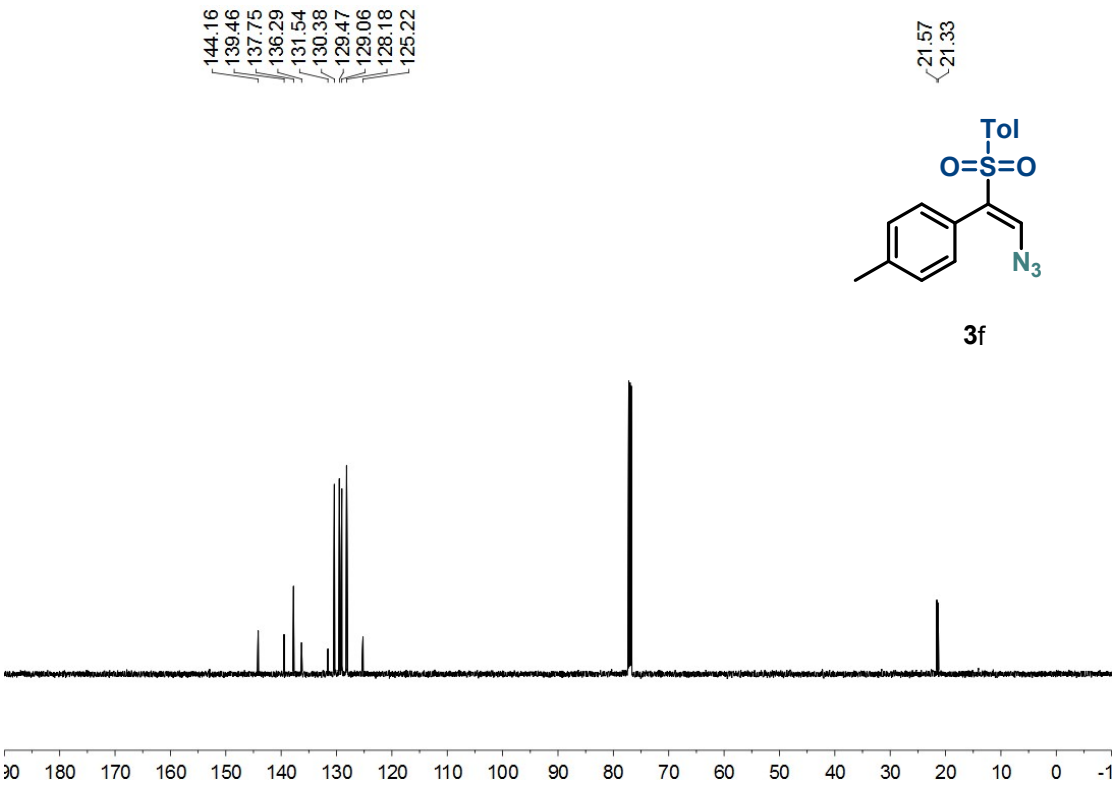

7.763
7.490
7.477
7.185
7.172
7.103
7.089
7.029
7.015
2.590
2.577
2.564
2.374
1.594
1.582
1.569
1.556
1.543
1.354
1.341
1.329
1.317
1.304
1.292
0.923
0.911
0.899
Tol
O=S=O
N3
nBu
3d
0.97
2.09
2.17
2.13
2.03
2.18
3.14
2.22
2.28
3.26
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

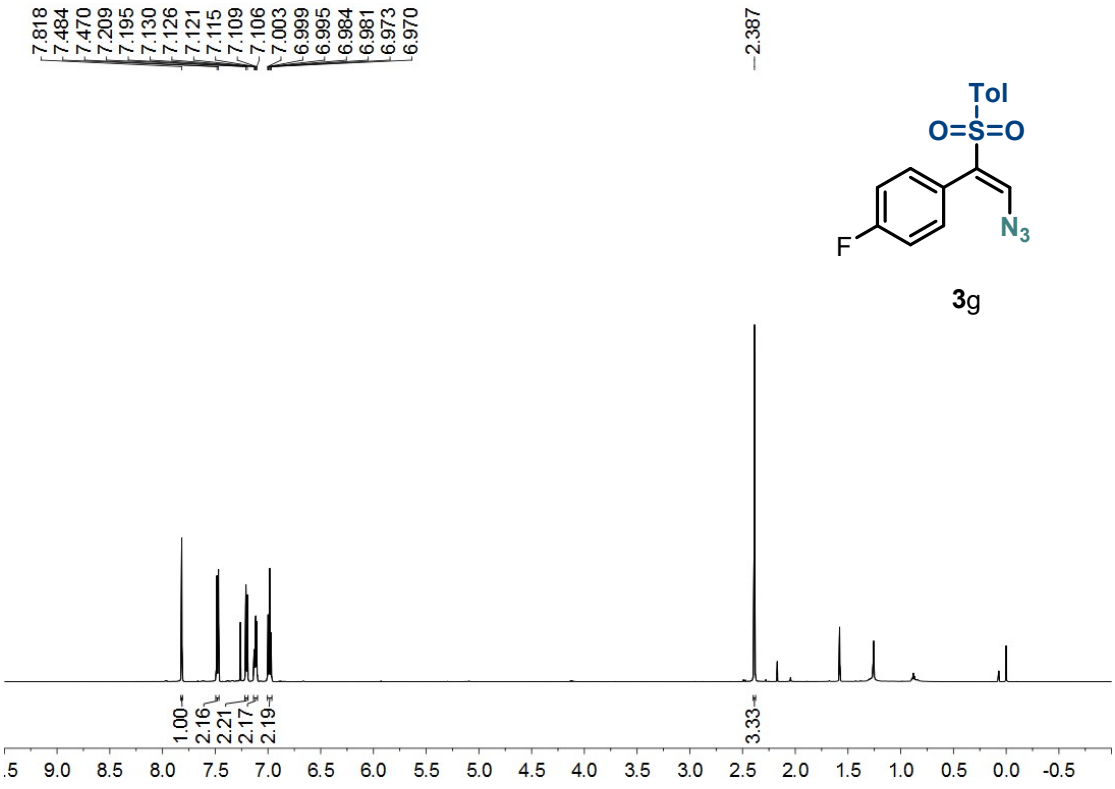

144.32
144.10
137.63
136.27
131.54
130.34
129.40
128.32
128.13
125.32
35.36
33.14
22.24
21.54
13.86
Tol
O=S=O
N3
nBu
3d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1


7.846
7.579
7.567
7.536
7.523
7.446
7.434
7.421
7.368
7.356
7.344
7.215
7.212
7.202
7.198
2.384
Tol
O=S=O
N3
Ph
3e
0.96
2.19
4.10
2.12
1.09
4.09
3.19

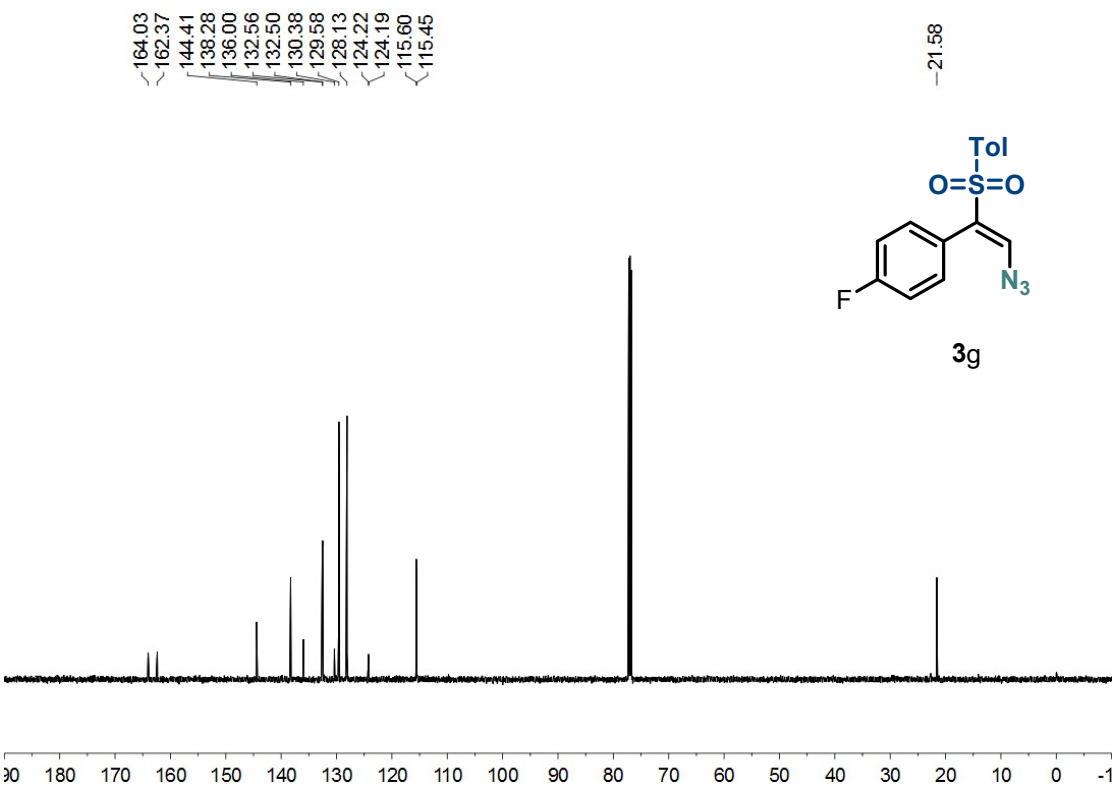

144.30
142.04
140.09
138.08
136.25
131.12
130.89
129.57
128.82
128.18
127.74
127.17
127.06
126.96
21.60
Tol
O=S=O
N3
Ph
3e


7.765
7.500
7.487
7.199
7.186
7.103
7.090
7.008
6.995
2.382
2.324
Tol
O=S=O
N3
3f
0.93
2.00
2.10
2.07
1.98
3.26
3.18

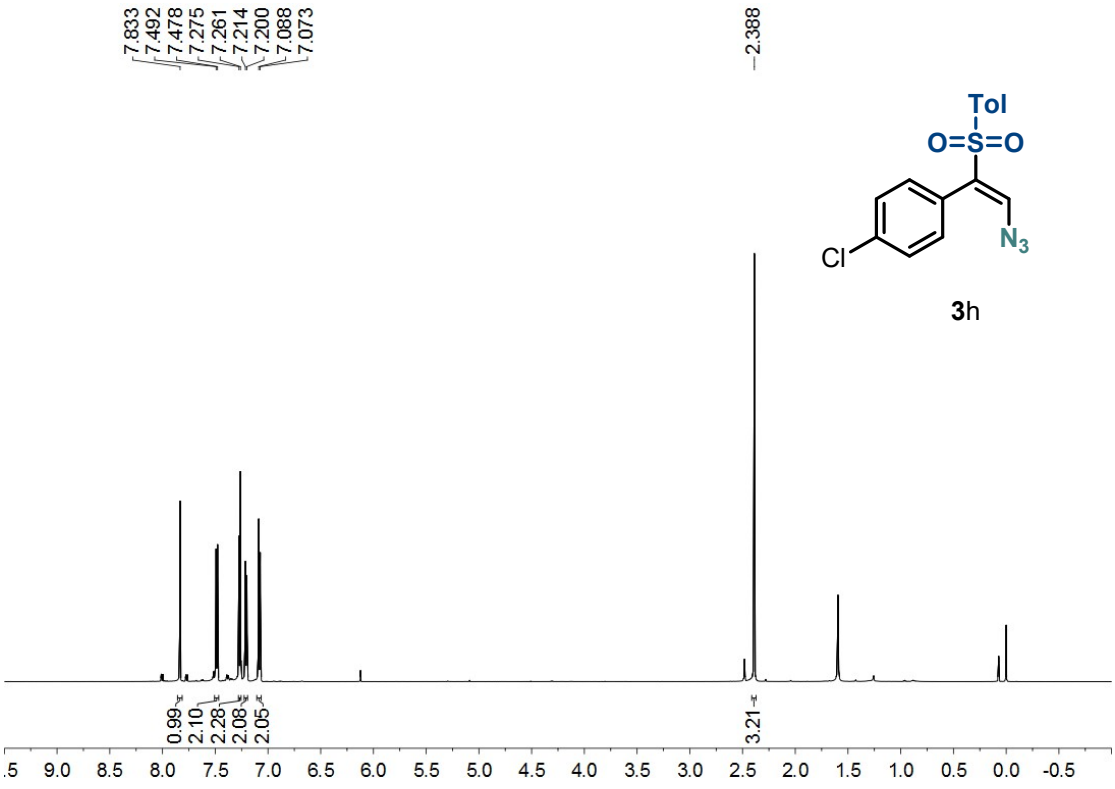

144.16
139.46
137.75
136.29
131.54
130.38
129.47
129.06
128.18
125.22
21.57
21.33
Tol
O=S=O
N3
3f

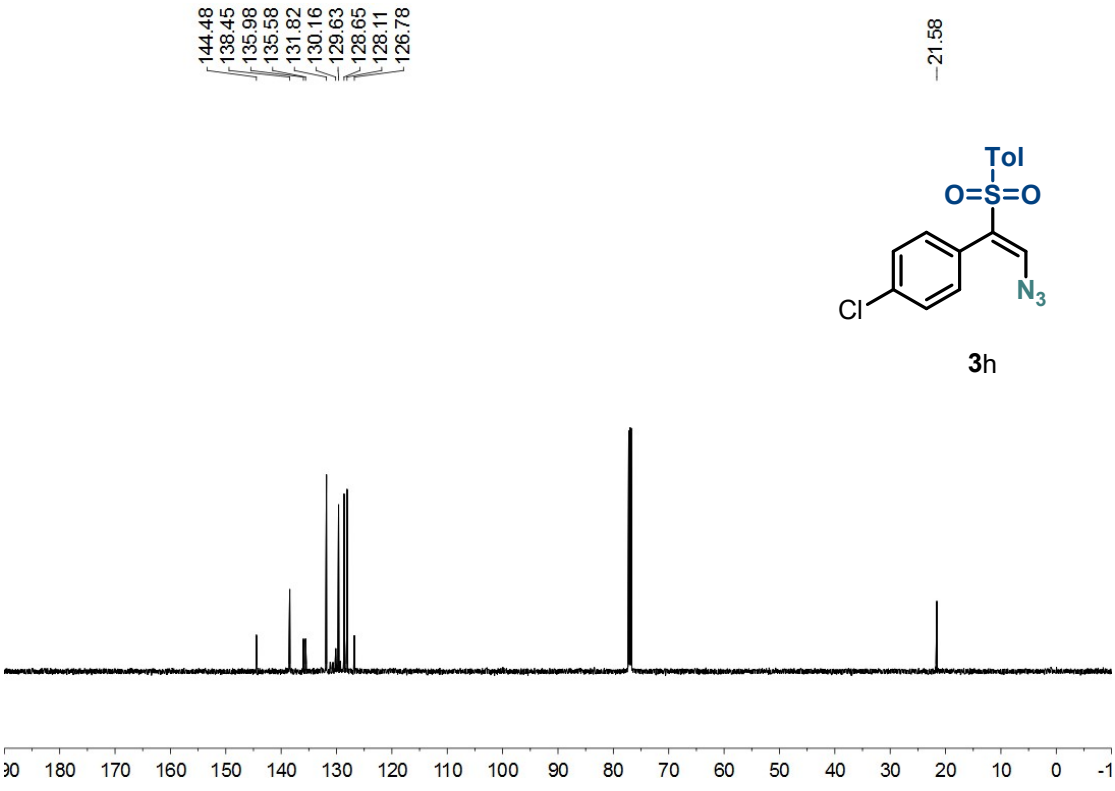

7.818
7.484
7.470
7.209
7.195
7.130
7.126
7.121
7.115
7.109
7.106
7.003
6.999
6.995
6.984
6.981
6.973
6.970
2.387
Tol
O=S=O
N3
F
1.00
2.16
2.21
2.17
2.19
3.33

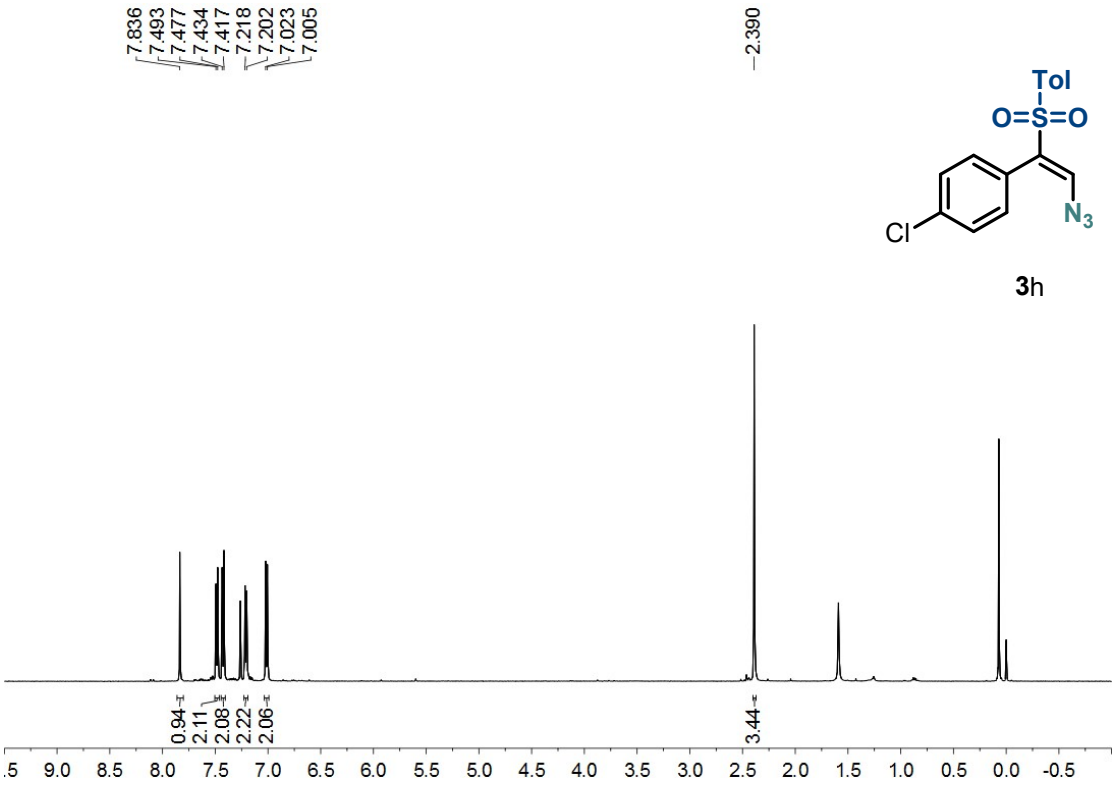
3g


164.03
162.37
144.41
138.28
136.00
132.56
132.50
130.38
129.58
128.13
124.22
124.19
115.60
115.45
21.58
Tol
O=S=O
N3
F

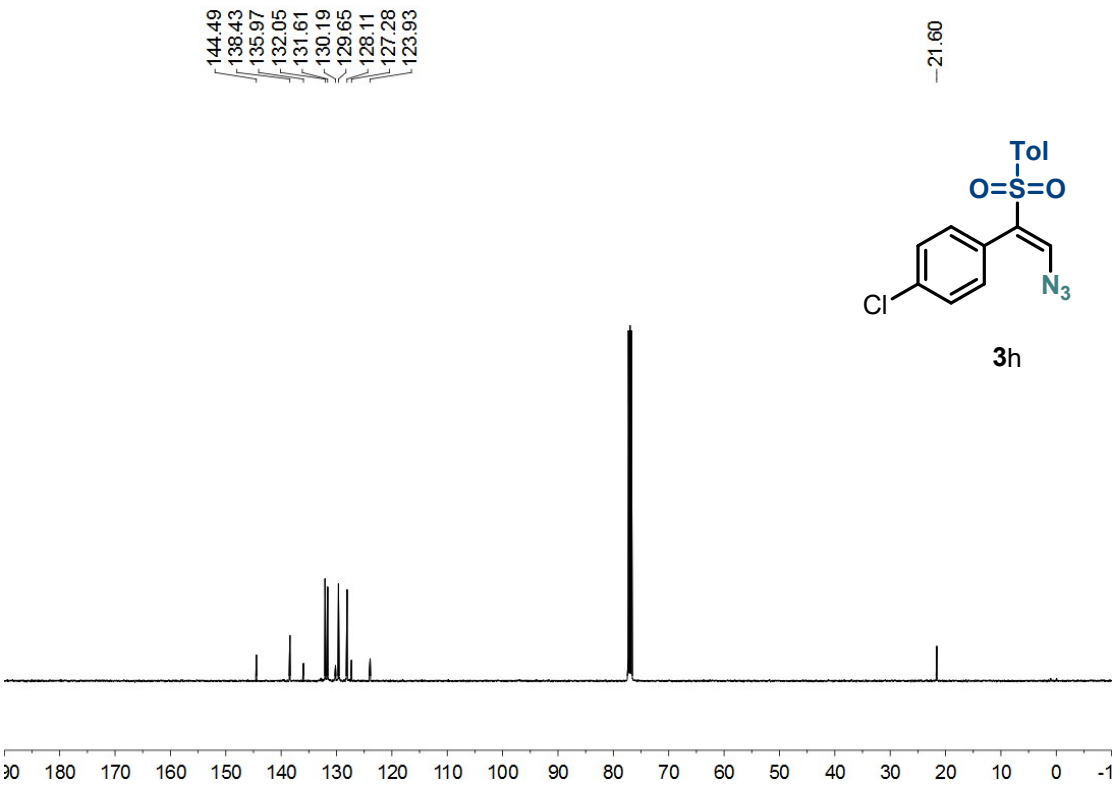
3g


7.833
7.492
7.478
7.275
7.261
7.214
7.200
7.088
7.073
2.388
Tol
O=S=O
Cl
N3
3h
0.99
2.10
2.28
2.08
2.05
3.21
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 -0.5

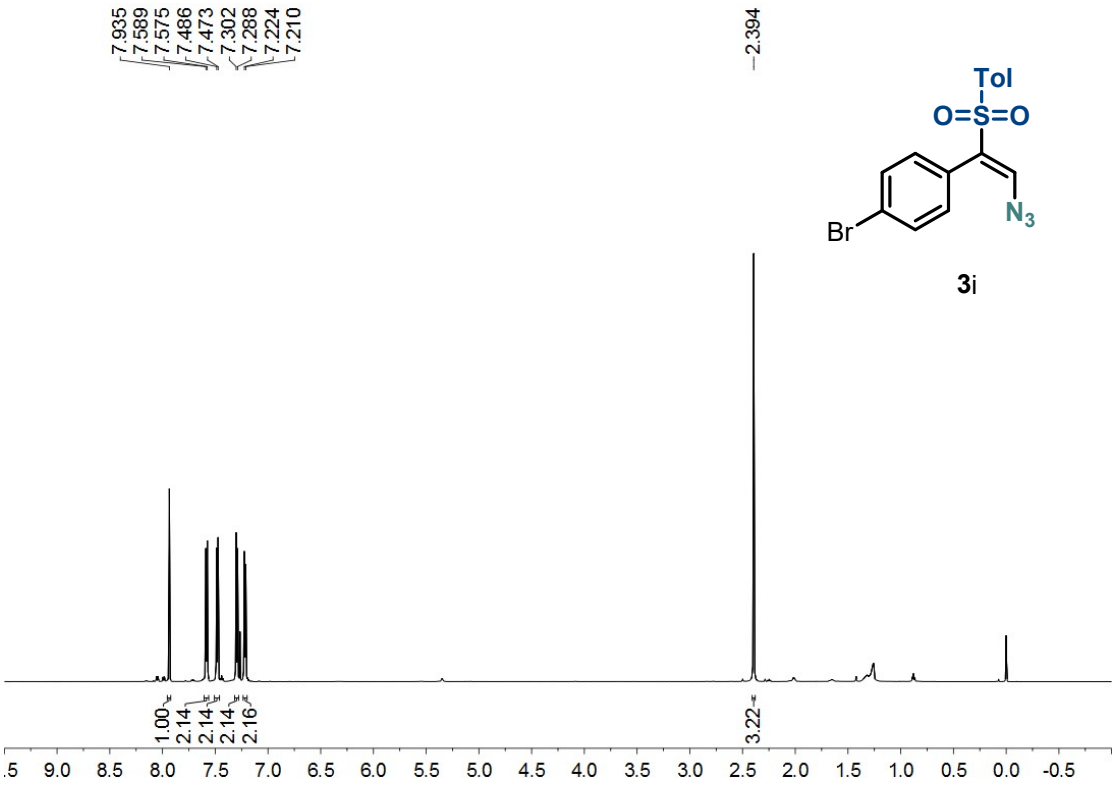

144.48
138.45
135.98
135.58
131.82
130.16
129.63
128.65
128.11
126.78
21.58
Tol
O=S=O
Cl
N3
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

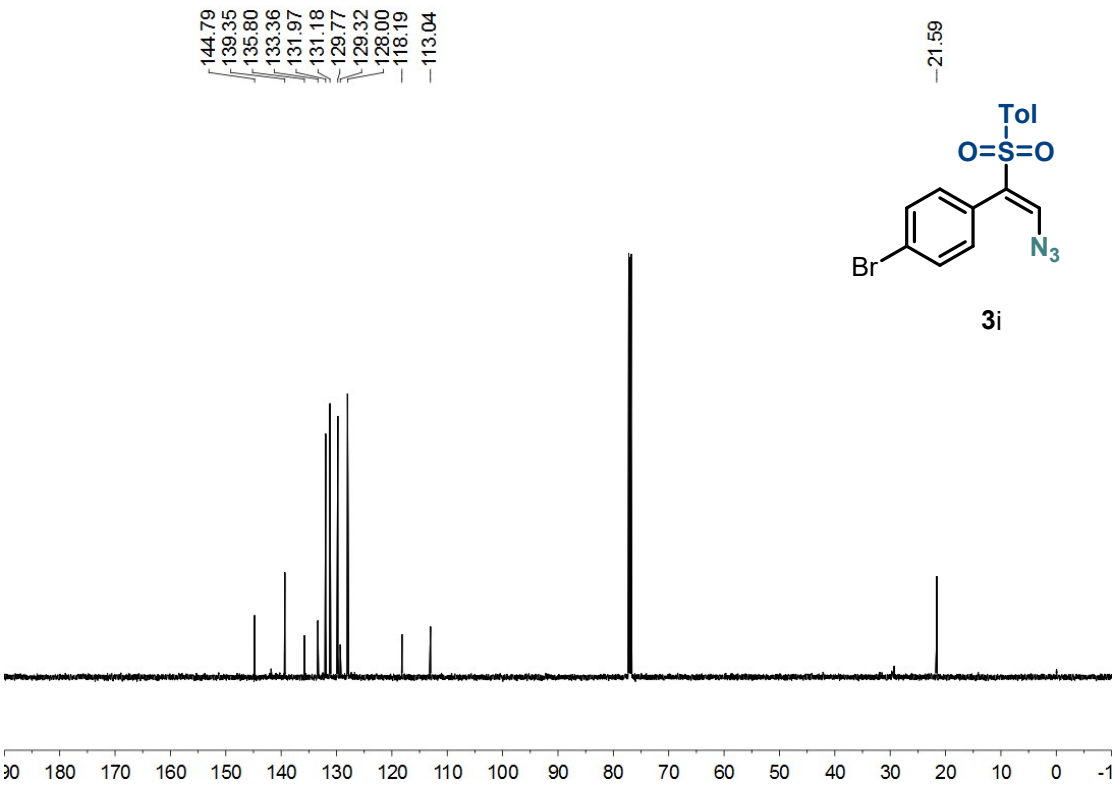

7.836
7.493
7.477
7.434
7.417
7.218
7.202
7.023
7.005
2.390
Tol
O=S=O
N3
Cl
0.94
2.11
2.08
2.22
2.06
3.44

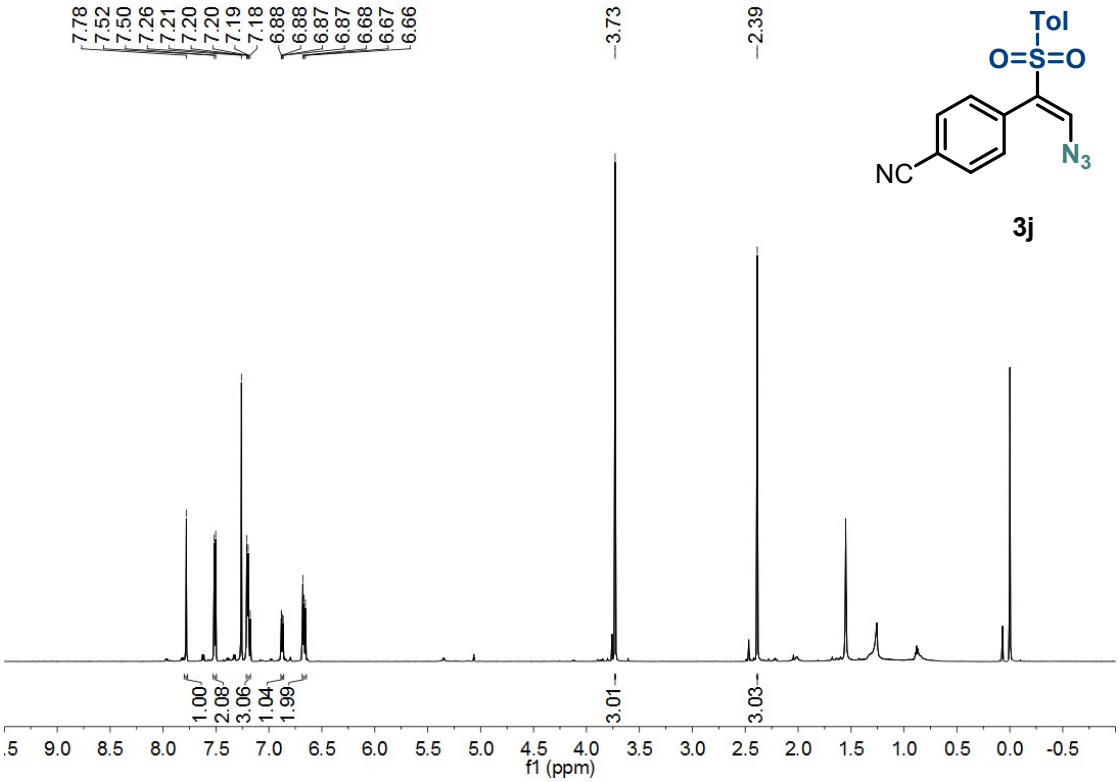
3h

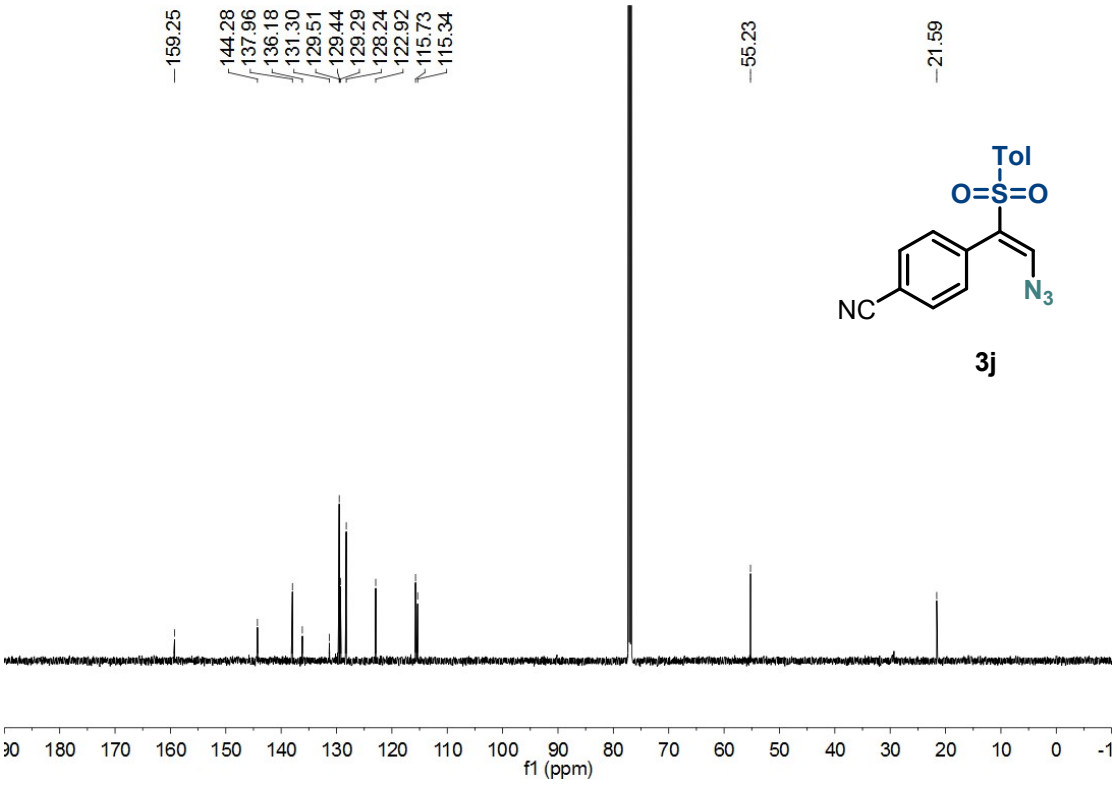

144.49
138.43
135.97
132.05
131.61
130.19
129.65
128.11
127.28
123.93
21.60
Tol
O=S=O
N3
Cl

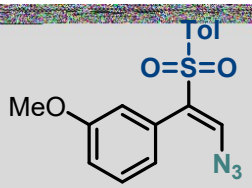
3h


7.935
7.589
7.575
7.486
7.473
7.302
7.288
7.224
7.210
2.394
Tol
O=S=O
Br
N3
3i
1.00
2.14
2.14
2.14
2.16
3.22

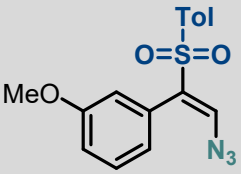

144.79
139.35
135.80
133.36
131.97
131.18
129.77
129.32
128.00
118.19
113.04
21.59
Tol
O=S=O
Br
N3
3i


7.78
7.52
7.50
7.26
7.21
7.20
7.20
7.19
7.18
6.88
6.88
6.87
6.87
6.68
6.67
6.66
3.73
2.39
Tol
O=S=O
N3
NC
3j
1.00
2.08
3.06
1.04
1.99
3.01
3.03
f1 (ppm)

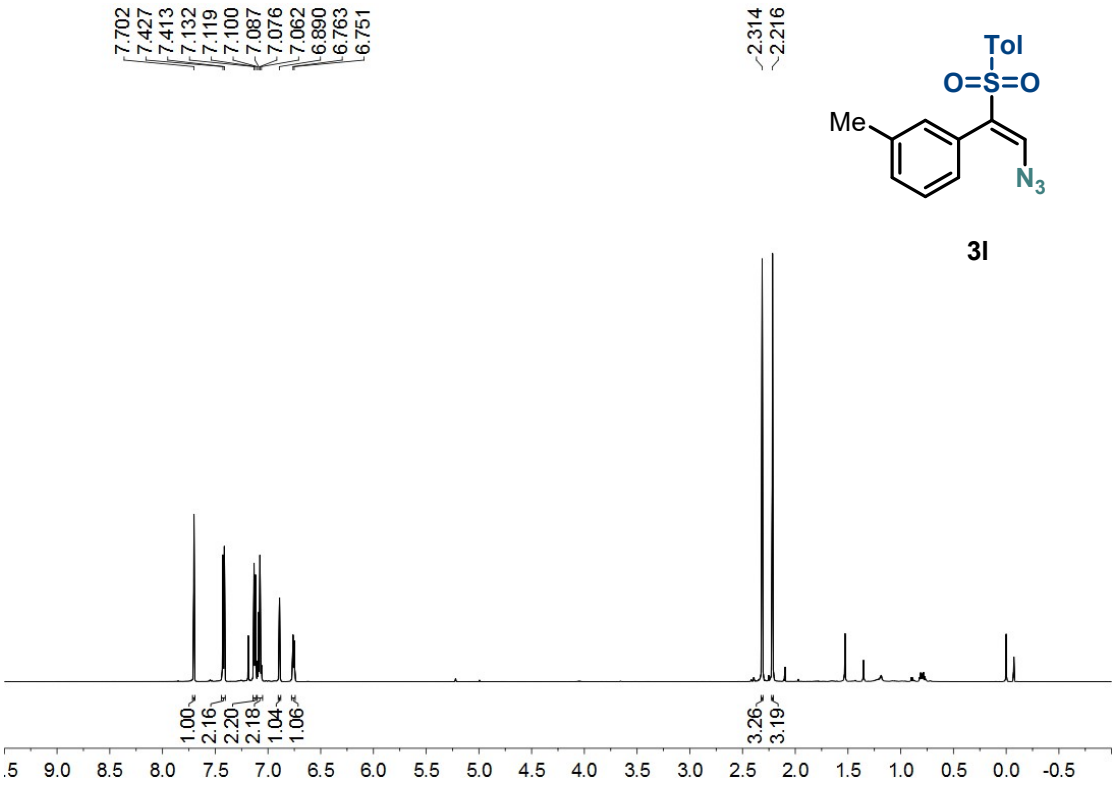

159.25
144.28
137.96
136.18
131.30
129.51
129.44
129.29
128.24
122.92
115.73
115.34
55.23
21.59
Tol
O=S=O
N3
NC
3j
f1 (ppm)



3k



3k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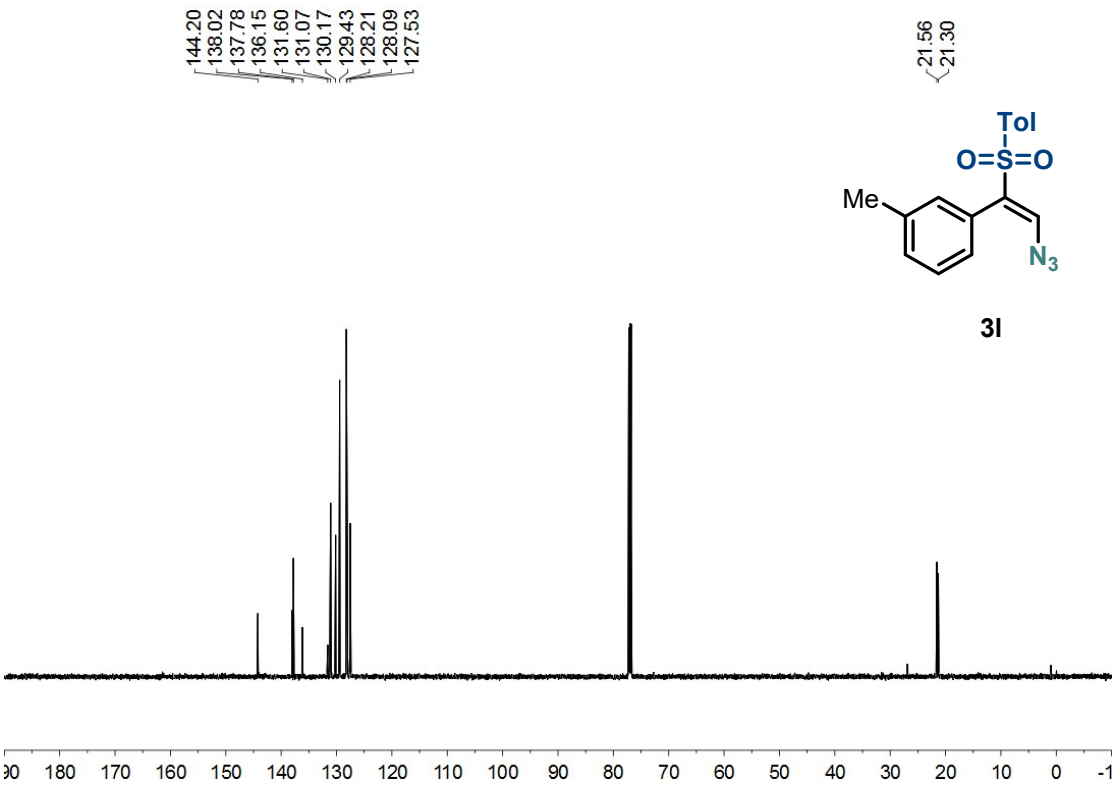
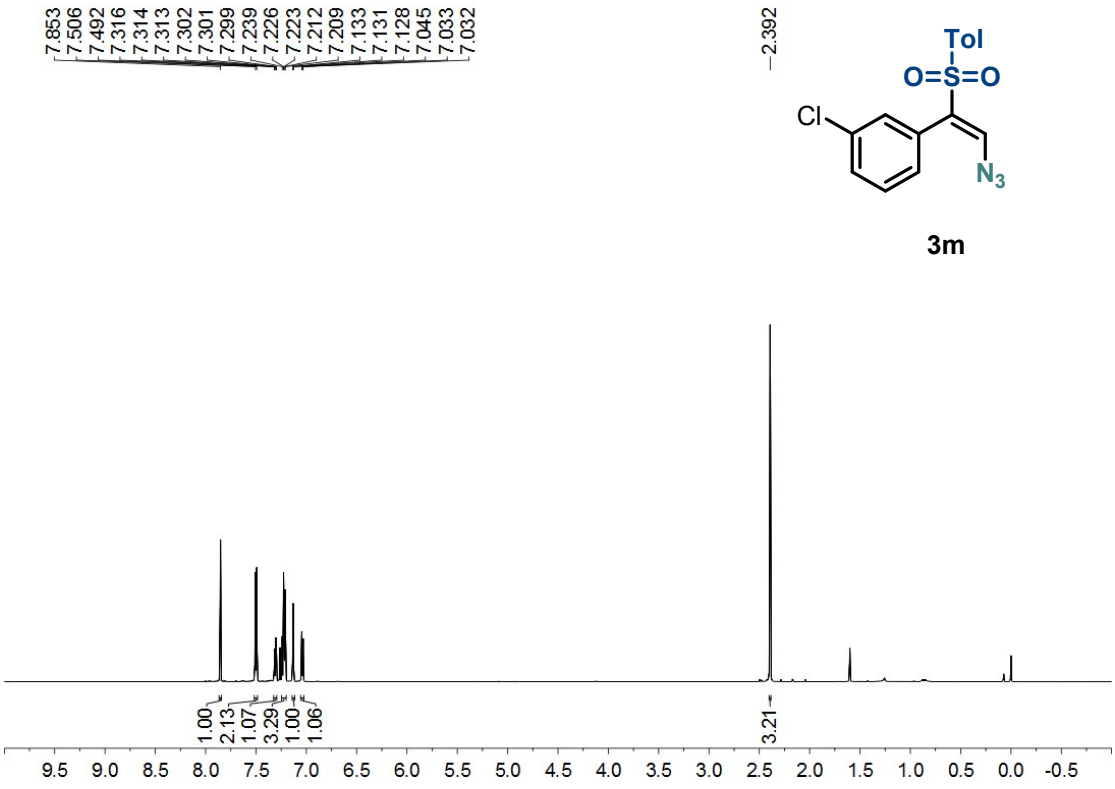
7.427
7.413
7.132
7.119
7.100
7.087
7.076
7.062
6.890
6.763
6.751
2.314
2.216
Tol
O=S=O
Me
N3
3l
1.00
2.16
2.20
2.18
1.04
1.06
3.26
3.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


144.20
138.02
137.78
136.15
131.60
131.07
130.17
129.43
128.21
128.09
127.53
21.56
21.30
Tol
O=S=O
Me
N3
3l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1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7.506
7.492
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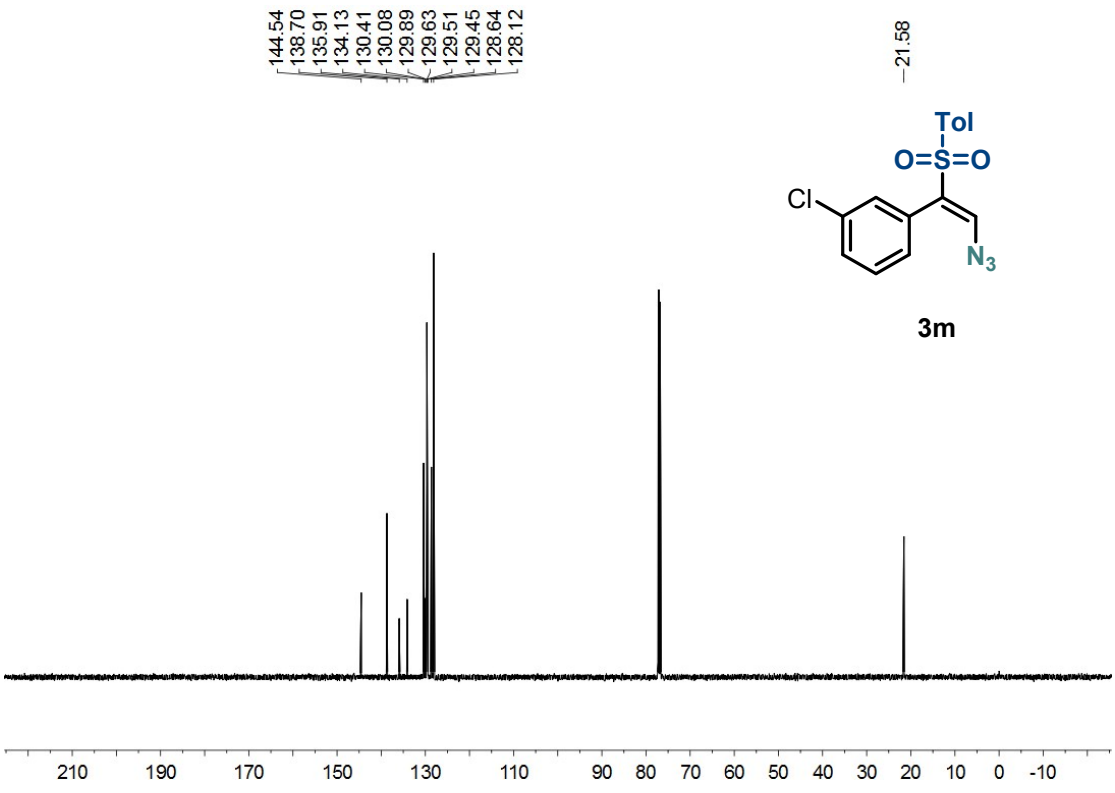
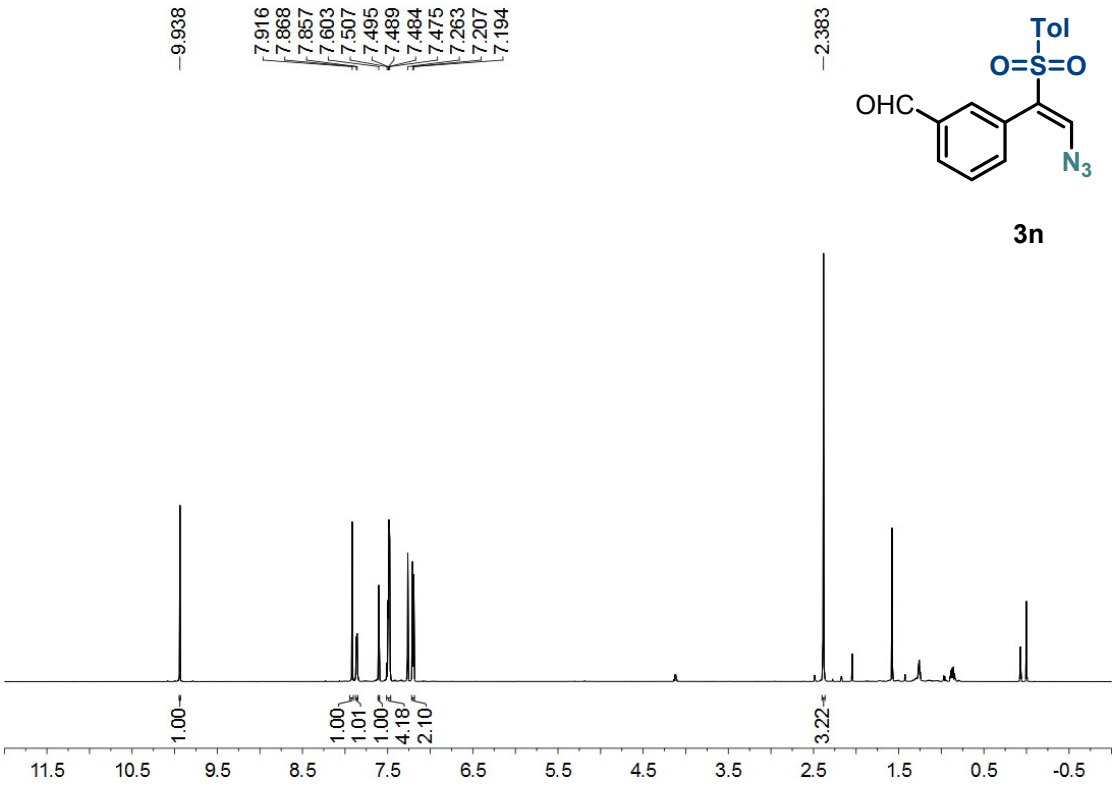
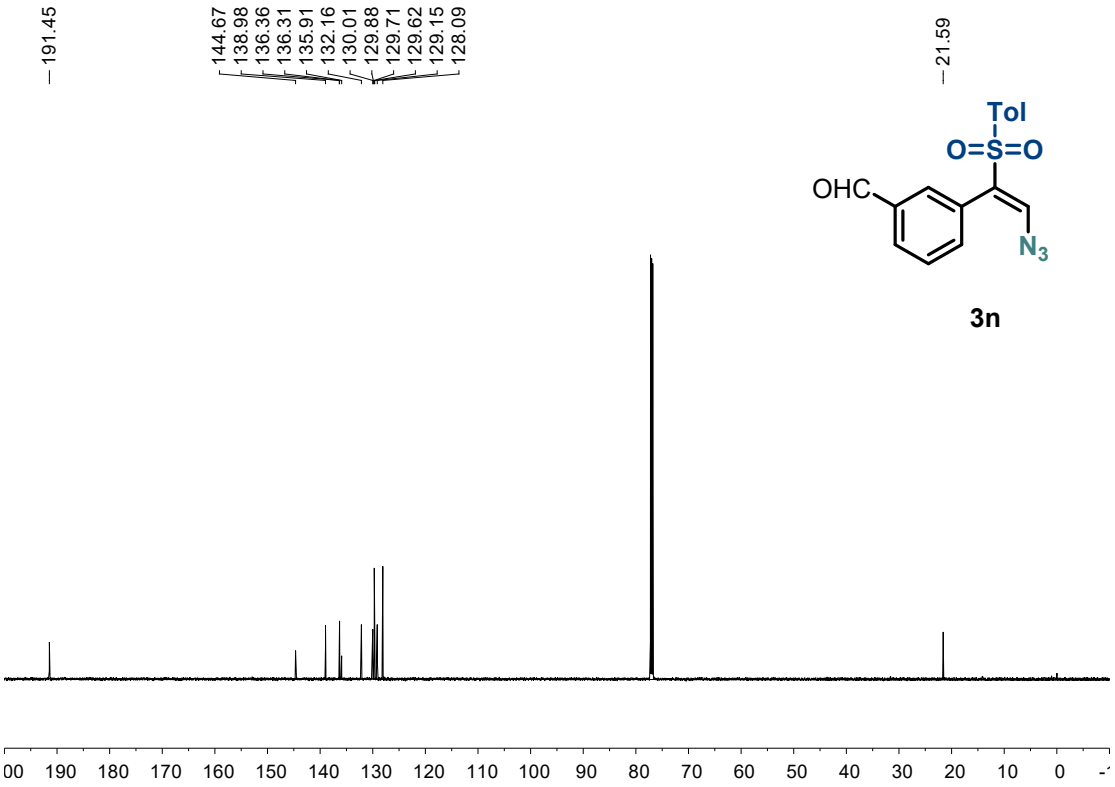
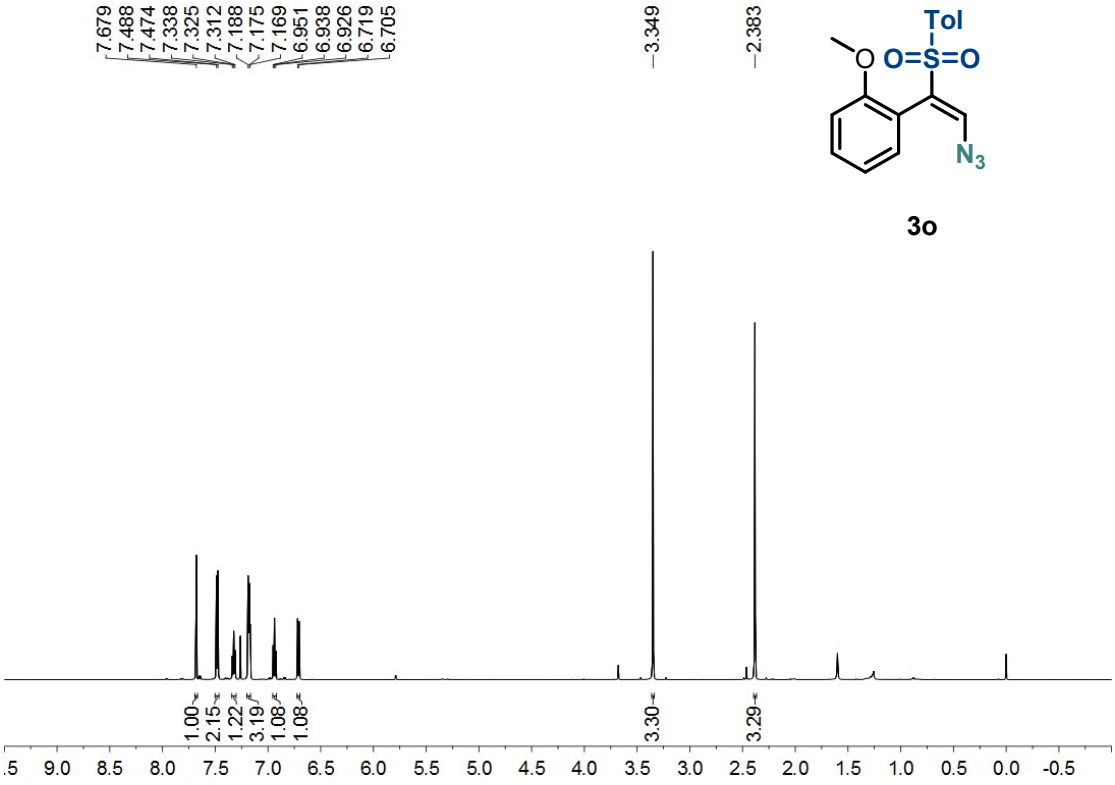
7.314
7.313
7.302
7.301
7.299
7.239
7.226
7.223
7.212
7.209
7.133
7.131
7.128
7.045
7.033
7.032
2.392
Tol
O=S=O
Cl
N3
3m
1.00
2.13
1.07
3.29
1.00
1.06
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

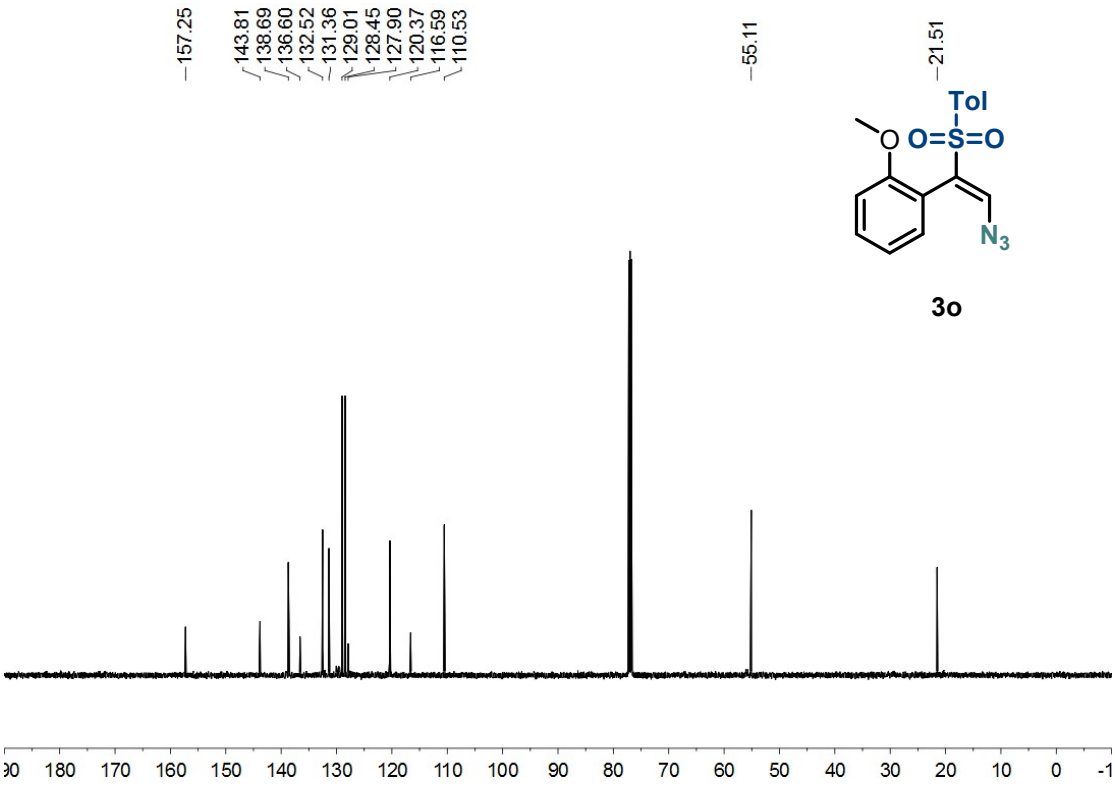

144.54
138.70
135.91
134.13
130.41
130.08
129.89
129.63
129.51
129.45
128.64
128.12
21.58
Tol
O=S=O
Cl
N3
3m
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10


9.938
7.916
7.868
7.857
7.603
7.507
7.495
7.489
7.484
7.475
7.263
7.207
7.194
2.383
Tol
O=S=O
OHC
N3
3n
1.00
1.00
1.01
1.00
4.18
2.10
3.22
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

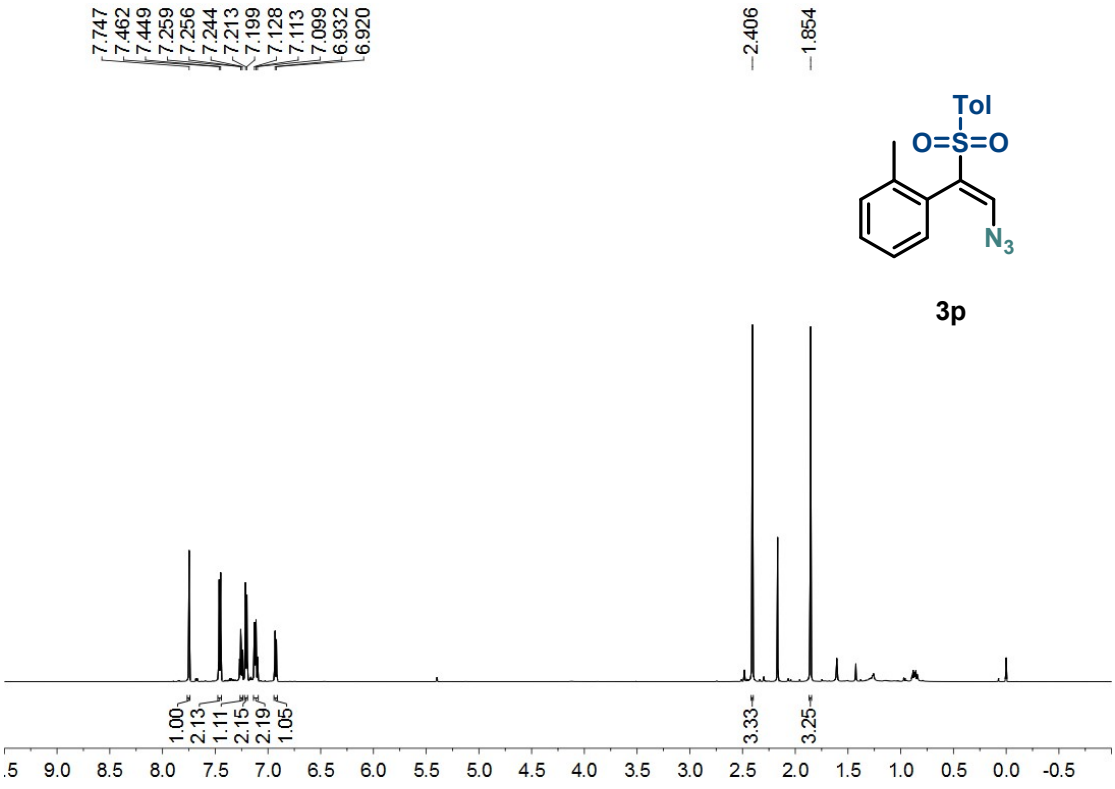

191.45
144.67
138.98
136.36
136.31
135.91
132.16
130.01
129.88
129.71
129.62
129.15
128.09
21.59
Tol
O=S=O
OHC
N3
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

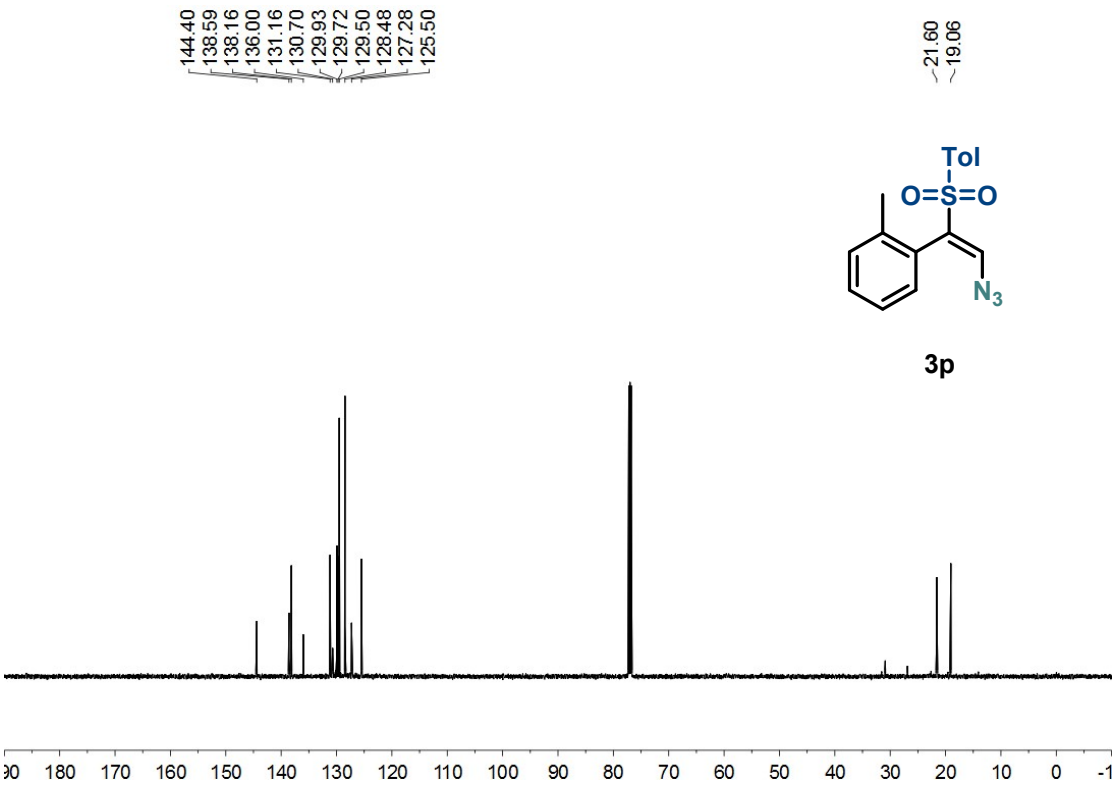

7.679
7.488
7.474
7.338
7.325
7.312
7.188
7.175
7.169
6.951
6.938
6.926
6.719
6.705
3.349
2.383
Tol
O=S=O
O
N3
1.00
2.15
1.22
3.19
1.08
1.08
3.30
3.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

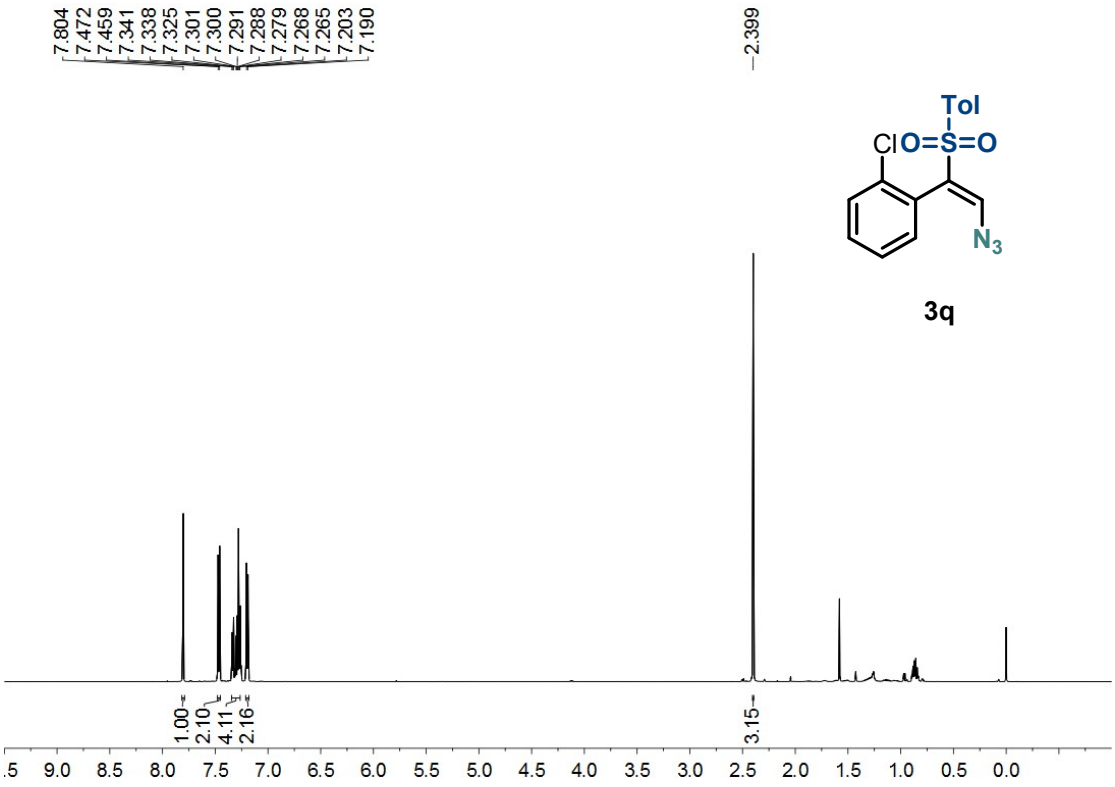
3o

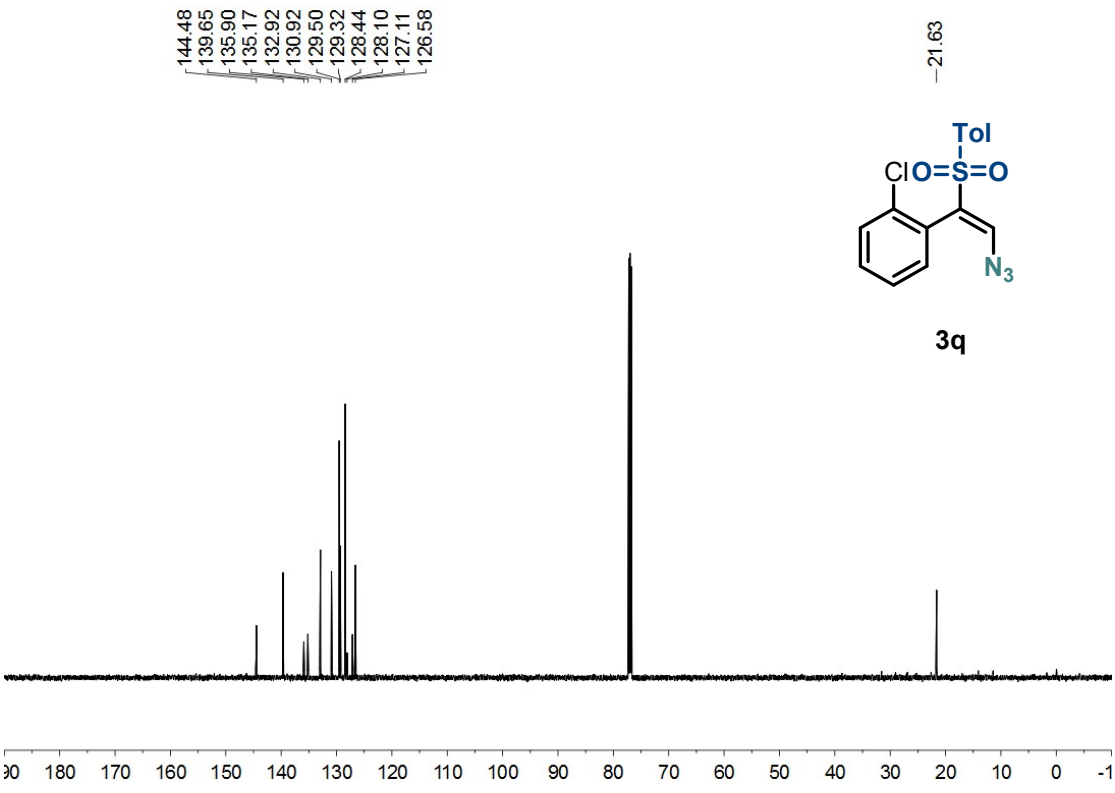

157.25
143.81
138.69
136.60
132.52
131.36
129.01
128.45
127.90
120.37
116.59
110.53
55.11
21.51
Tol
O=S=O
O
N3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

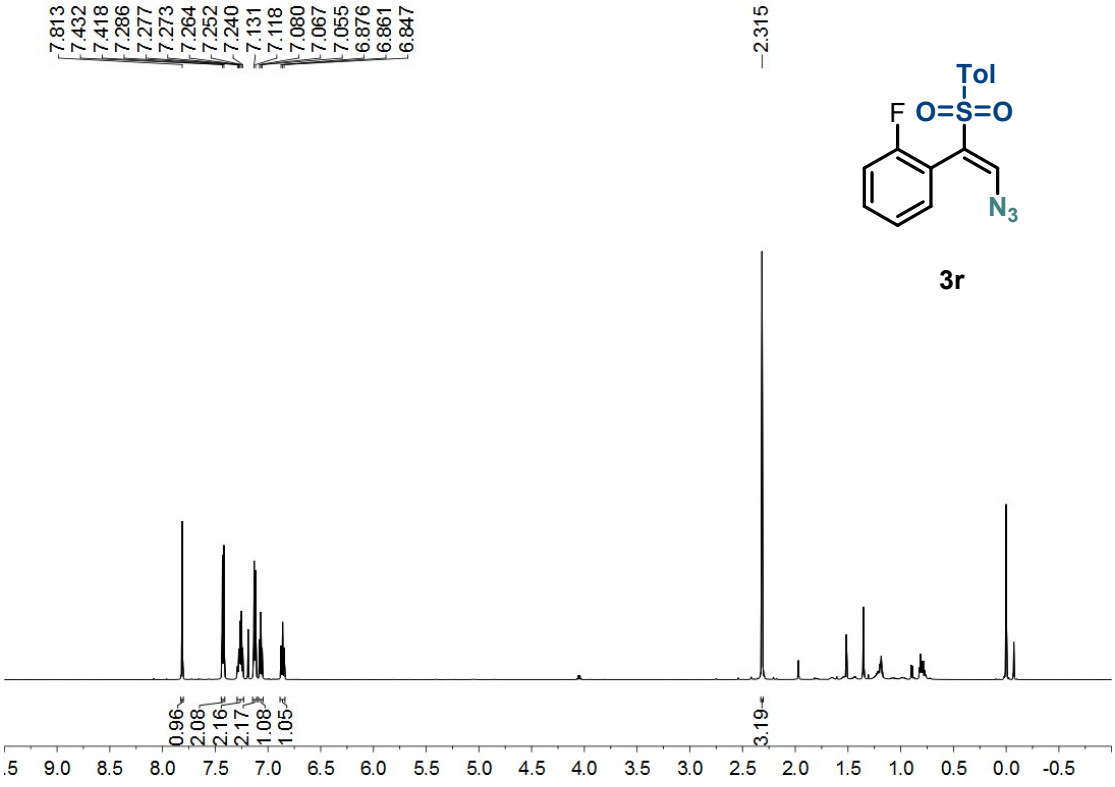
3o


7.747
7.462
7.449
7.259
7.256
7.244
7.213
7.199
7.128
7.113
7.099
6.932
6.920
2.406
1.854
Tol
O=S=O
N3
3p
1.00
2.13
1.11
2.15
2.19
1.05
3.33
3.25


144.40
138.59
138.16
136.00
131.16
130.70
129.93
129.72
129.50
128.48
127.28
125.50
21.60
19.06
Tol
O=S=O
N3
3p


7.804
7.472
7.459
7.341
7.338
7.325
7.301
7.300
7.291
7.288
7.279
7.268
7.265
7.203
7.190
2.399
Tol
ClO=S=O
N3
3q
1.00
2.10
4.11
2.16
3.15
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


144.48
139.65
135.90
135.17
132.92
130.92
129.50
129.32
128.44
128.10
127.11
126.58
21.63
Tol
ClO=S=O
N3
3q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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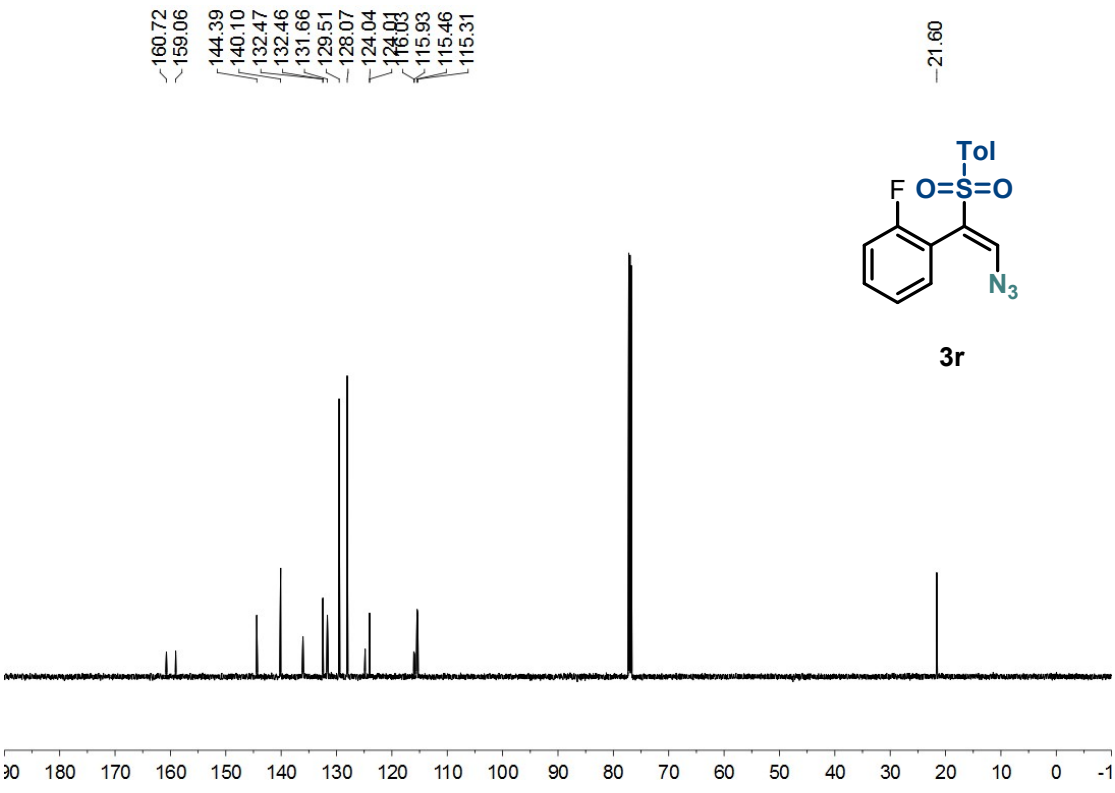
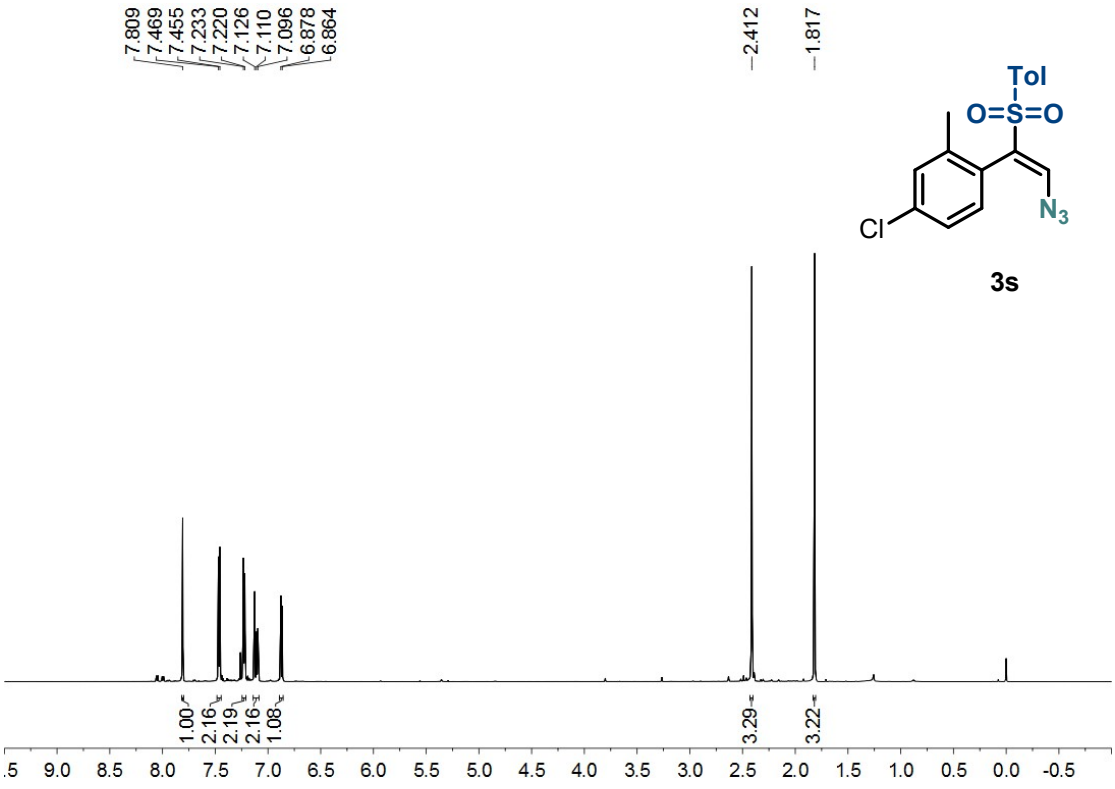
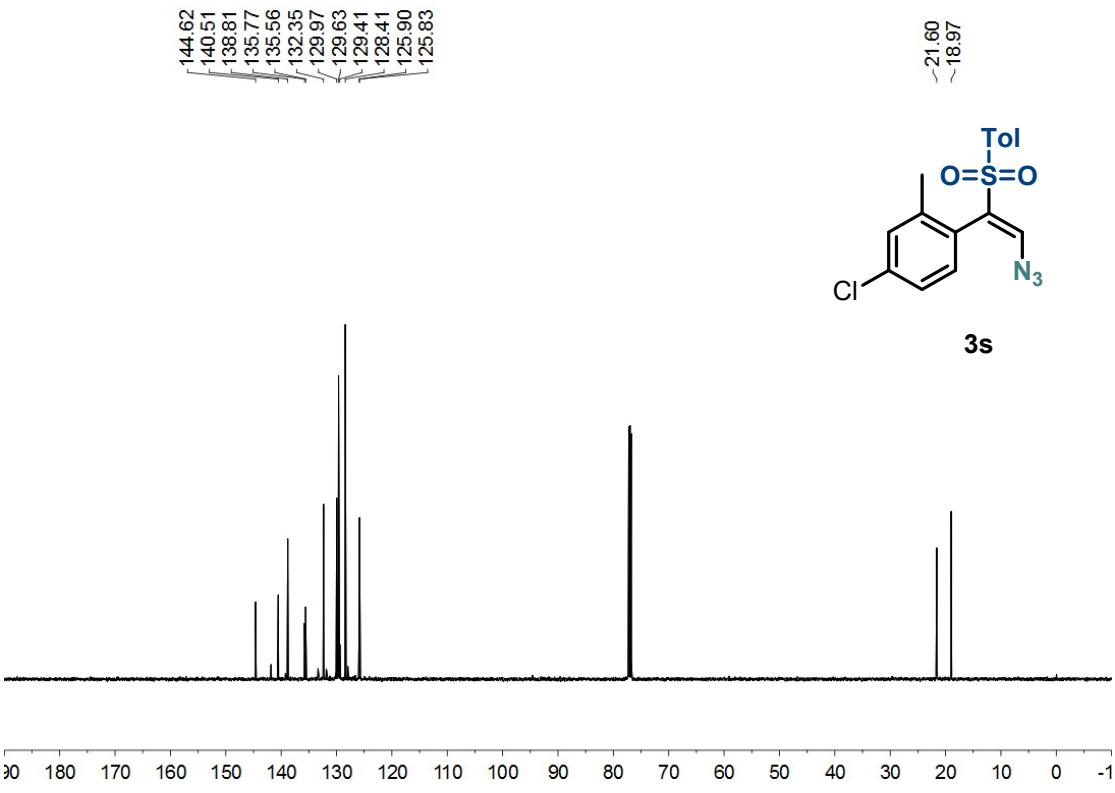
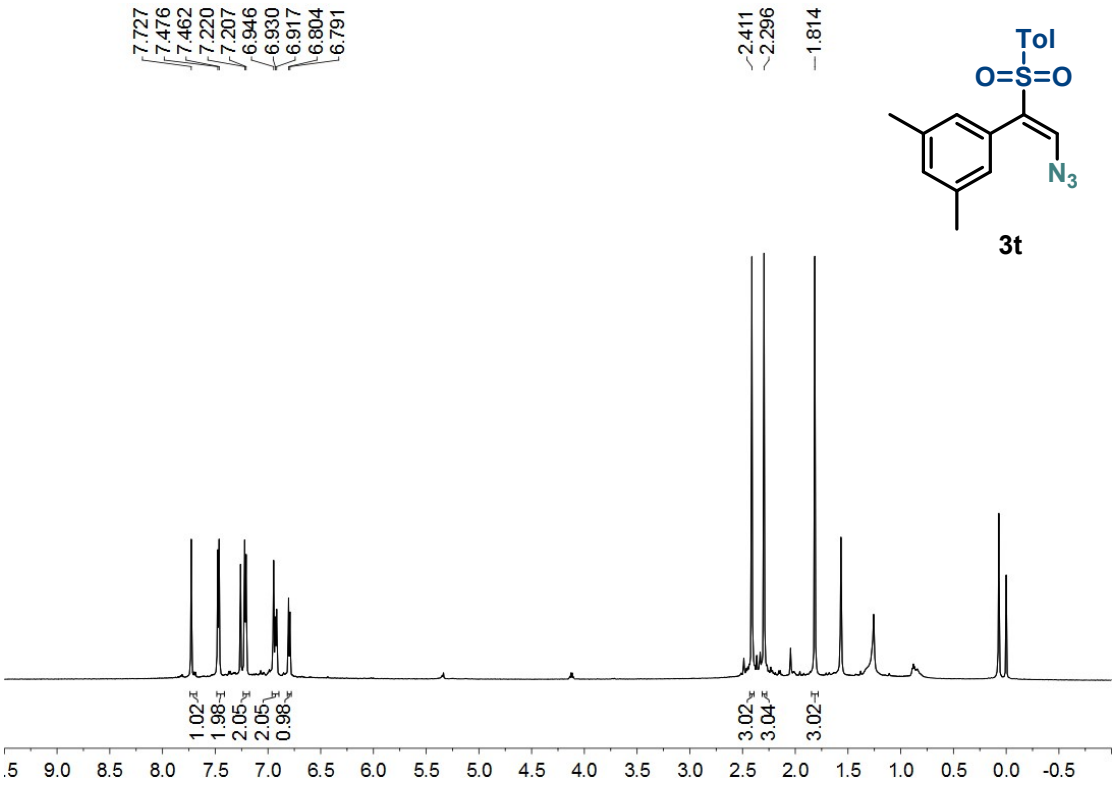
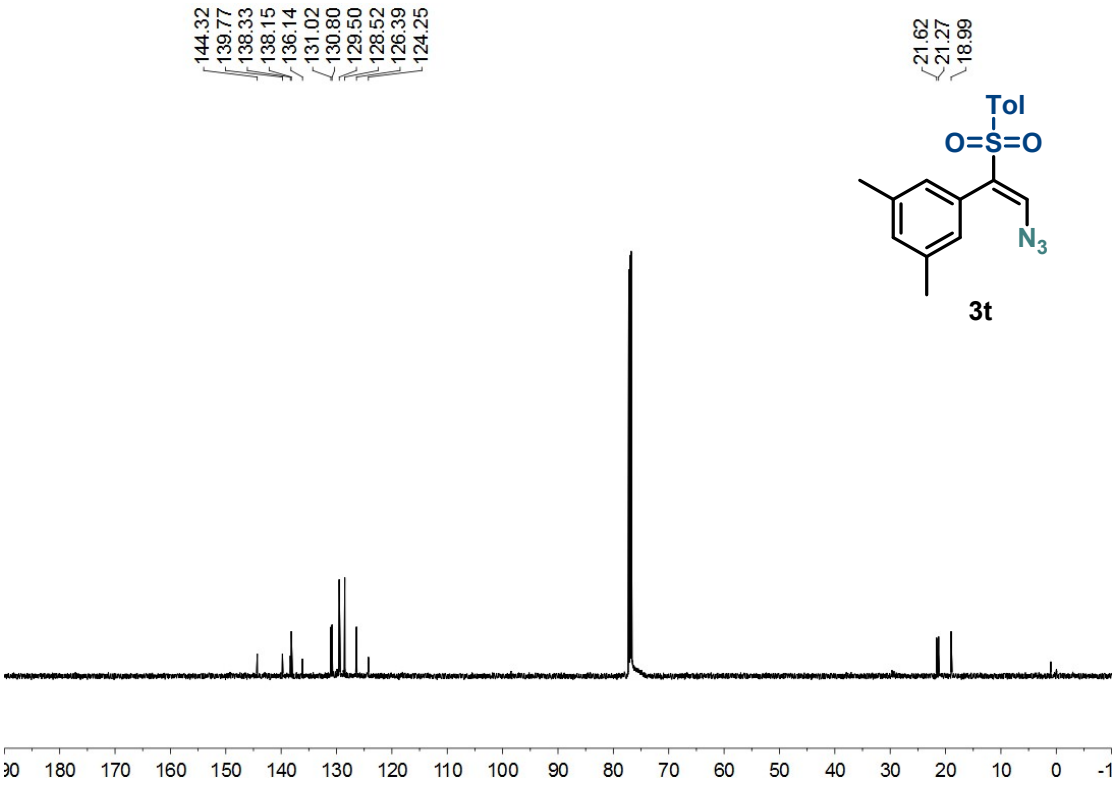
7.432
7.418
7.286
7.277
7.273
7.264
7.252
7.240
7.131
7.118
7.080
7.067
7.055
6.876
6.861
6.847
2.315
Tol
F O=S=O
N3
3r
0.96
2.08
2.16
2.17
1.08
1.05
3.19

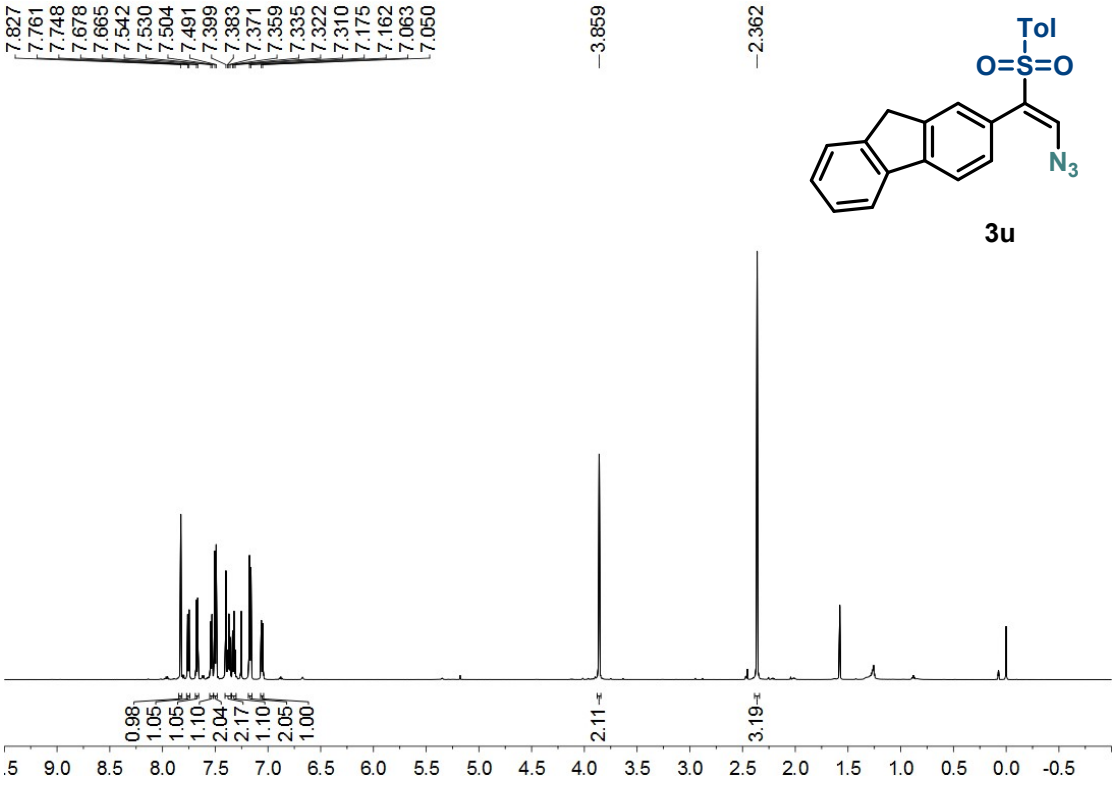

160.72
159.06
144.39
140.10
132.47
132.46
131.66
129.51
128.07
124.04
115.93
115.46
115.31
21.60
Tol
F O=S=O
N3
3r

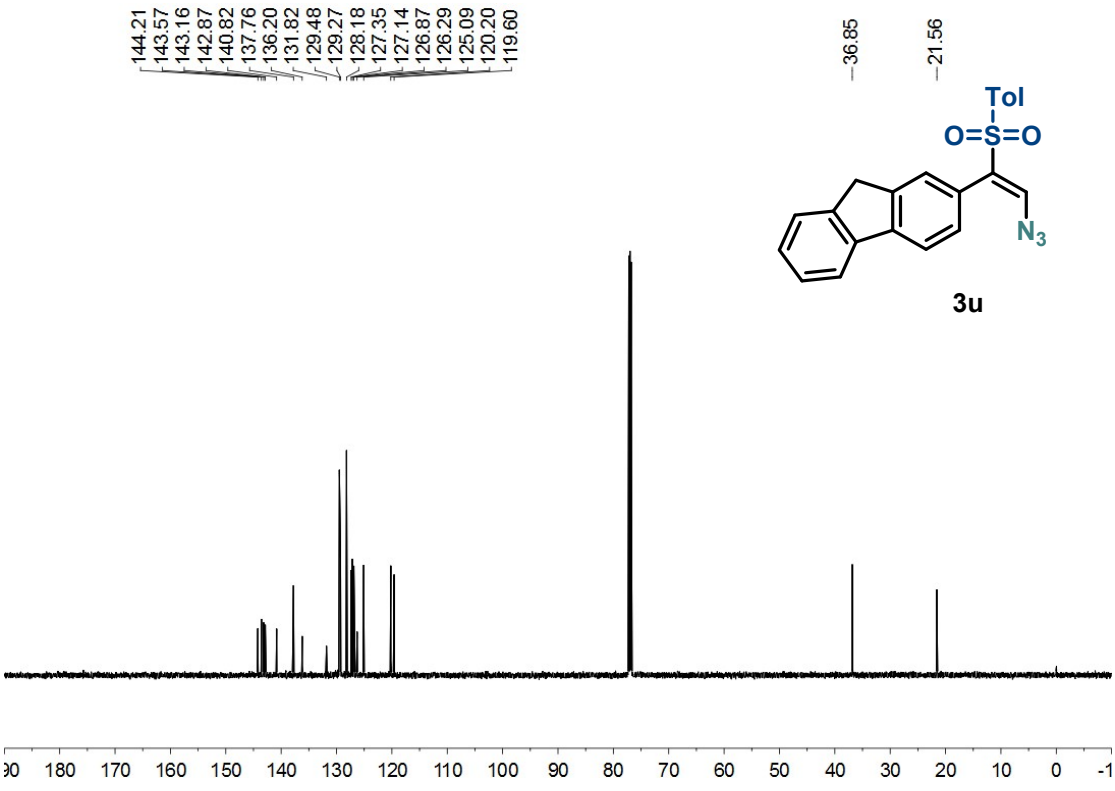

7.809
7.469
7.455
7.233
7.220
7.126
7.110
7.096
6.878
6.864
2.412
1.817
Tol
O=S=O
N3
Cl
3s
1.00
2.16
2.19
2.16
1.08
3.29
3.22

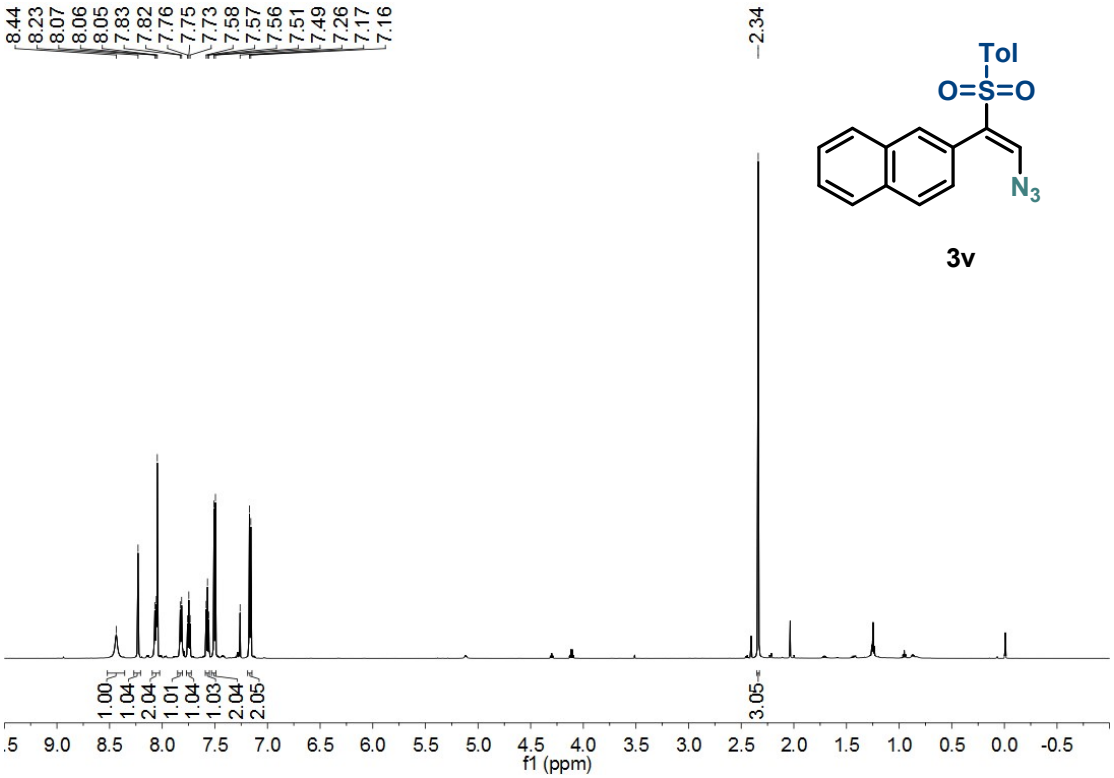

144.62
140.51
138.81
135.77
135.56
132.35
129.97
129.63
129.41
128.41
125.90
125.83
21.60
18.97
Tol
O=S=O
N3
Cl
3s

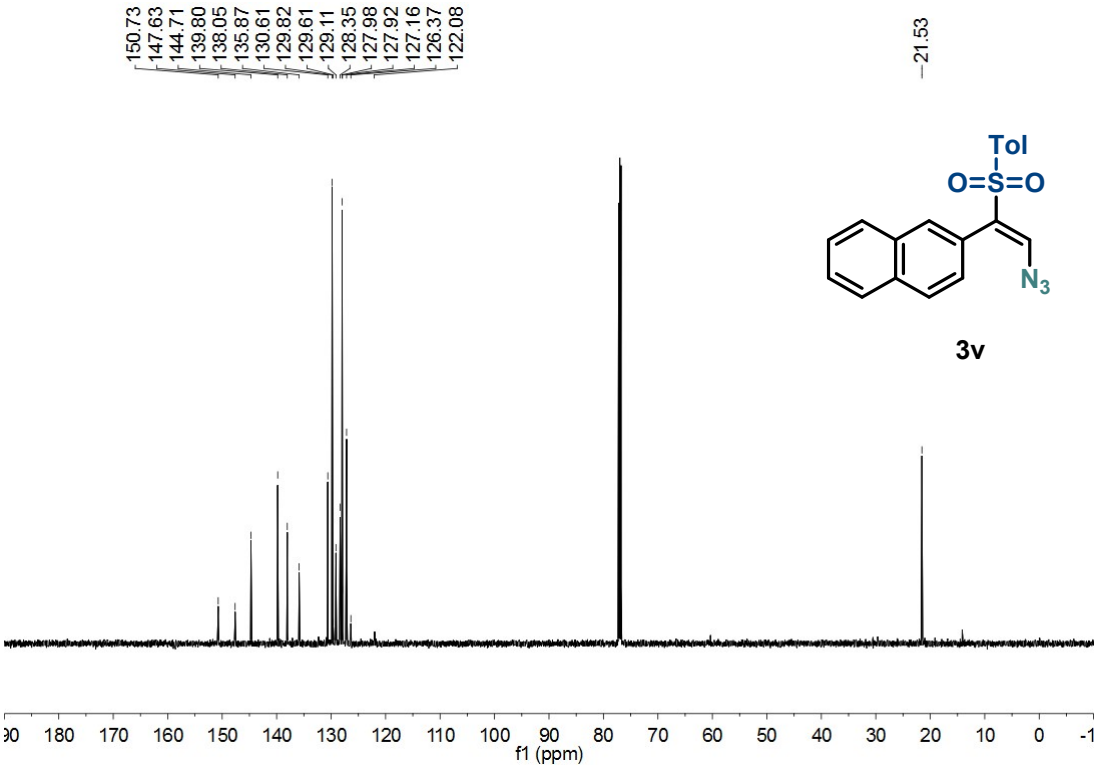

7.727
7.476
7.462
7.220
7.207
6.946
6.930
6.917
6.804
6.791
2.411
2.296
1.814
Tol
O=S=O
N3
3t
1.02
1.98
2.05
2.05
0.98
3.02
3.04
3.02

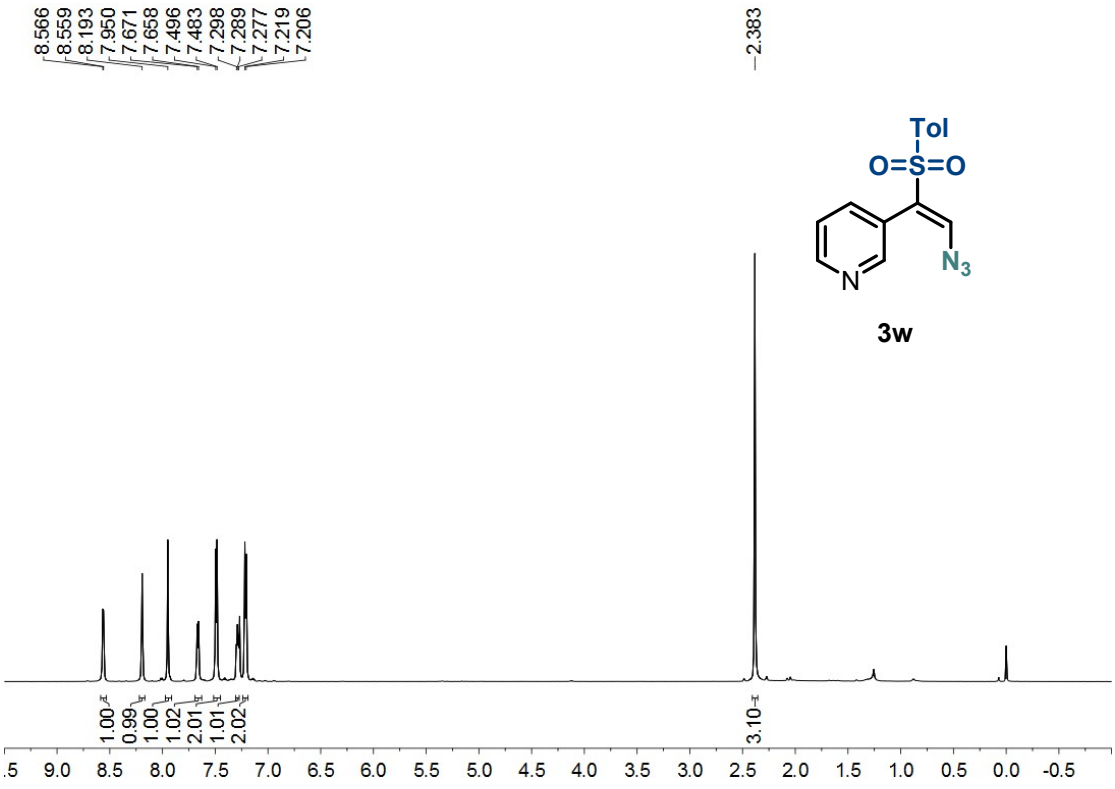

144.32
139.77
138.33
138.15
136.14
131.02
130.80
129.50
128.52
126.39
124.25
21.62
21.27
18.99
Tol
O=S=O
N3
3t

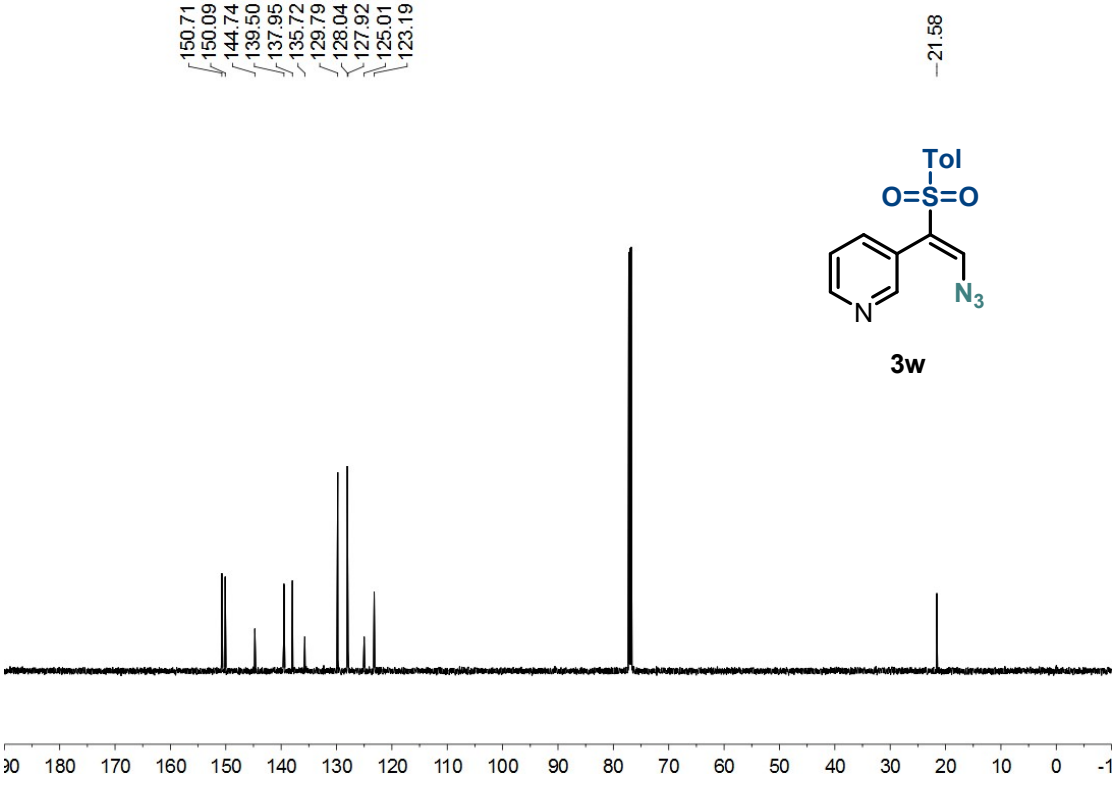

7.827
7.761
7.748
7.678
7.665
7.542
7.530
7.504
7.491
7.399
7.383
7.371
7.359
7.335
7.322
7.310
7.175
7.162
7.063
7.050
3.859
2.362
Tol
O=S=O
N3
3u
0.98
1.05
1.05
1.10
2.04
2.17
1.10
2.05
1.00
2.11
3.19

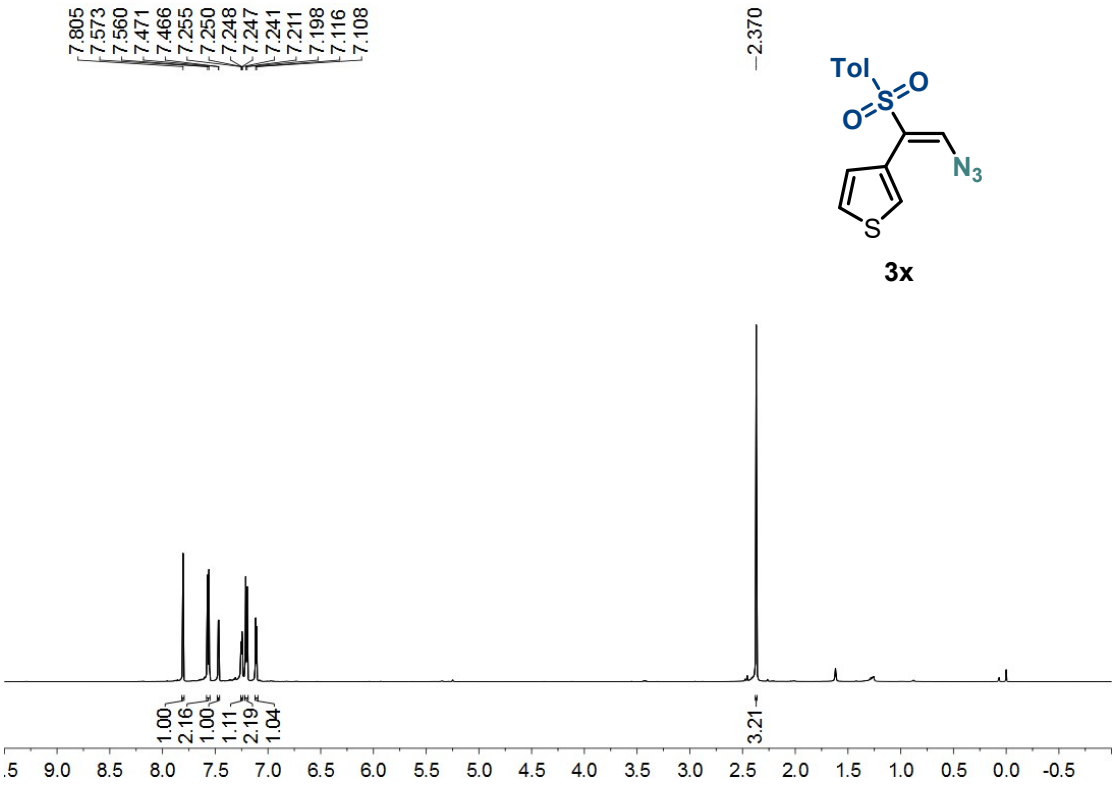

144.21
143.57
143.16
142.87
140.82
137.76
136.20
131.82
129.48
129.27
128.18
127.35
127.14
126.87
126.29
125.09
120.20
119.60
36.85
21.56
Tol
O=S=O
N3
3u


8.44
8.23
8.07
8.06
8.05
7.83
7.82
7.76
7.75
7.73
7.58
7.57
7.56
7.51
7.49
7.26
7.17
7.16
2.34
Tol
O=S=O
N3
3v
1.00
1.04
2.04
1.01
1.04
1.03
2.04
2.05
3.05
f1 (ppm)

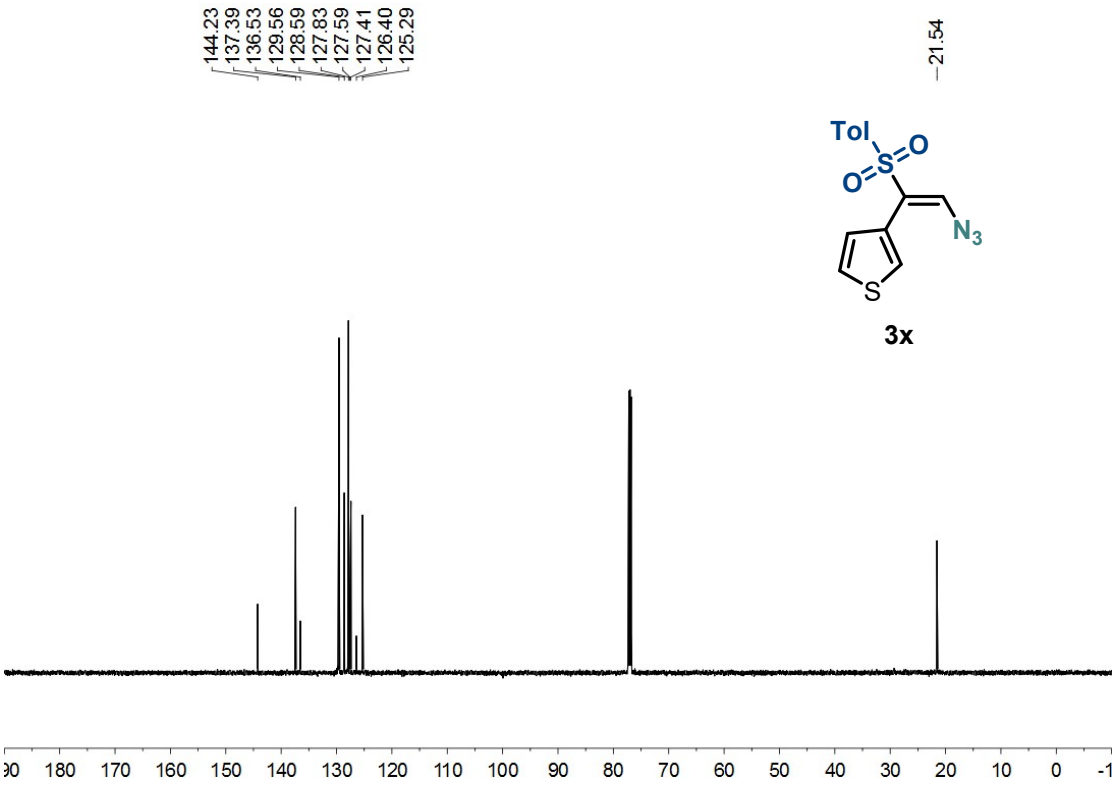

150.73
147.63
144.71
139.80
138.05
135.87
130.61
129.82
129.61
129.11
128.35
127.98
127.92
127.16
126.37
122.08
21.53
Tol
O=S=O
N3
3v
f1 (ppm)


8.566
8.559
8.193
7.950
7.671
7.658
7.496
7.483
7.298
7.289
7.277
7.219
7.206
2.383
Tol
O=S=O
N
N3
3w
1.00
0.99
1.00
1.02
2.01
1.01
2.02
3.10

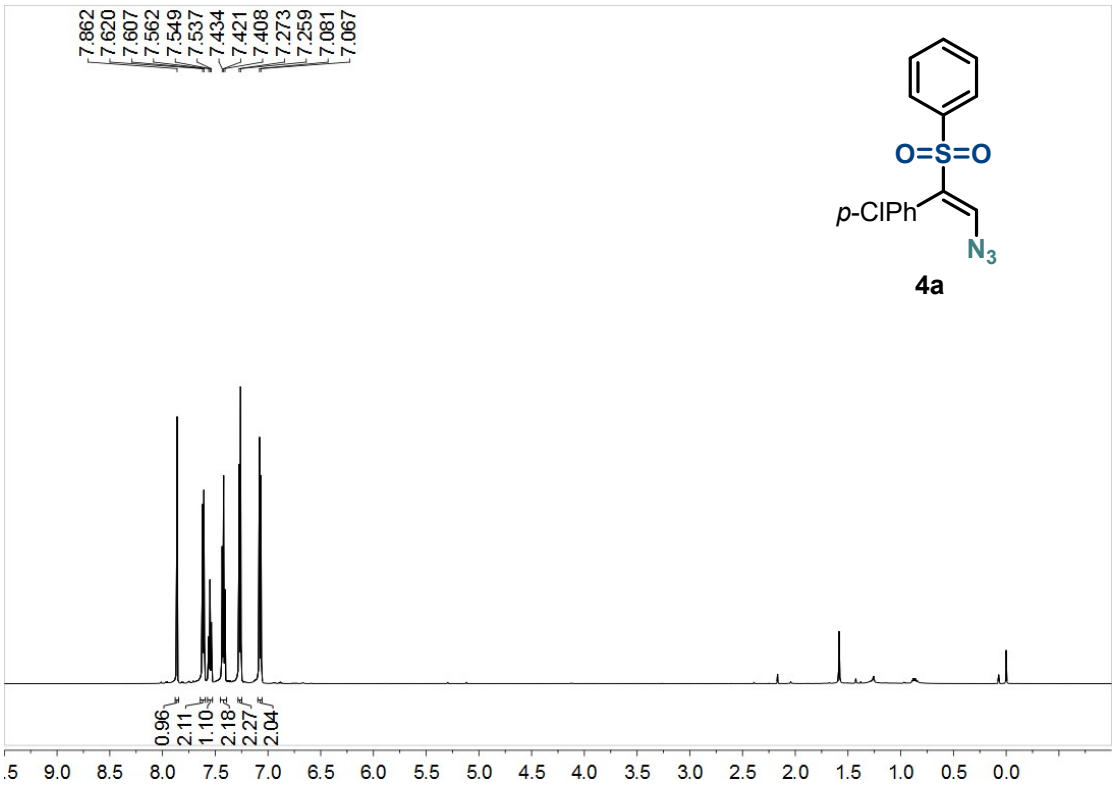

150.71
150.09
144.74
139.50
137.95
135.72
129.79
128.04
127.92
125.01
123.19
21.58
Tol
O=S=O
N
N3
3w

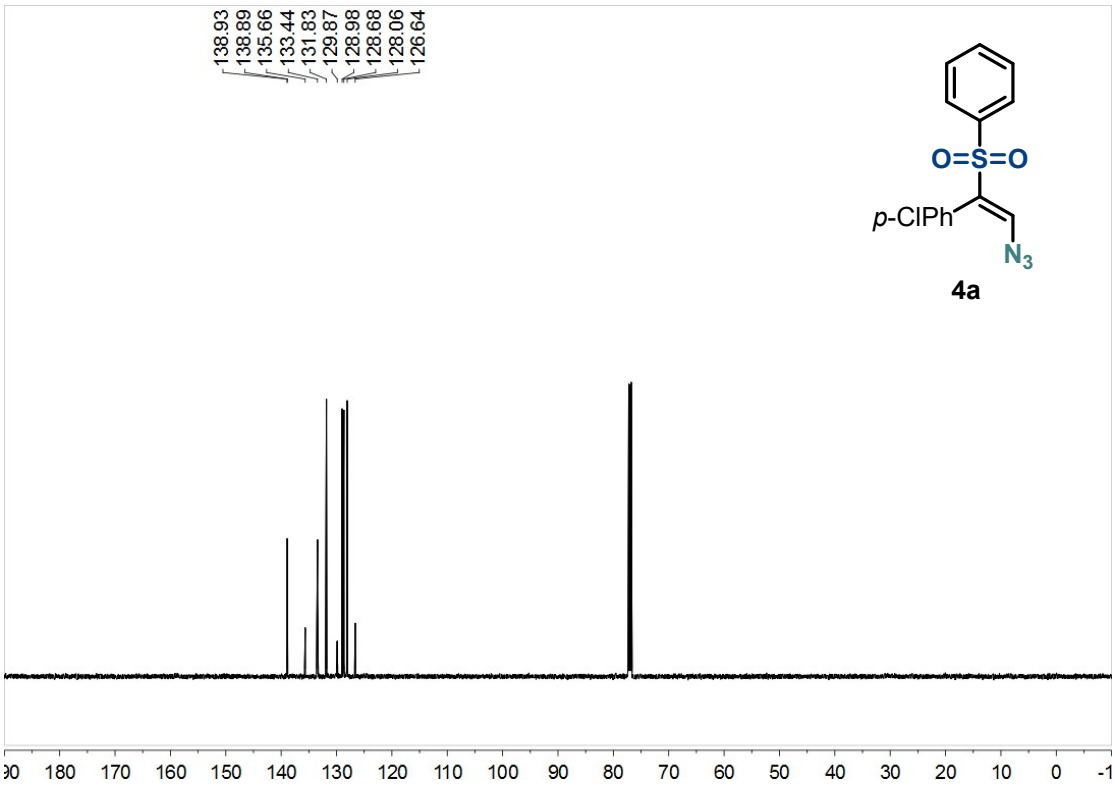

7.805
7.573
7.560
7.471
7.466
7.255
7.250
7.248
7.247
7.241
7.211
7.198
7.116
7.108
2.370
Tol
O=S=O
N3
S
1.00
2.16
1.00
1.11
2.19
1.04
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

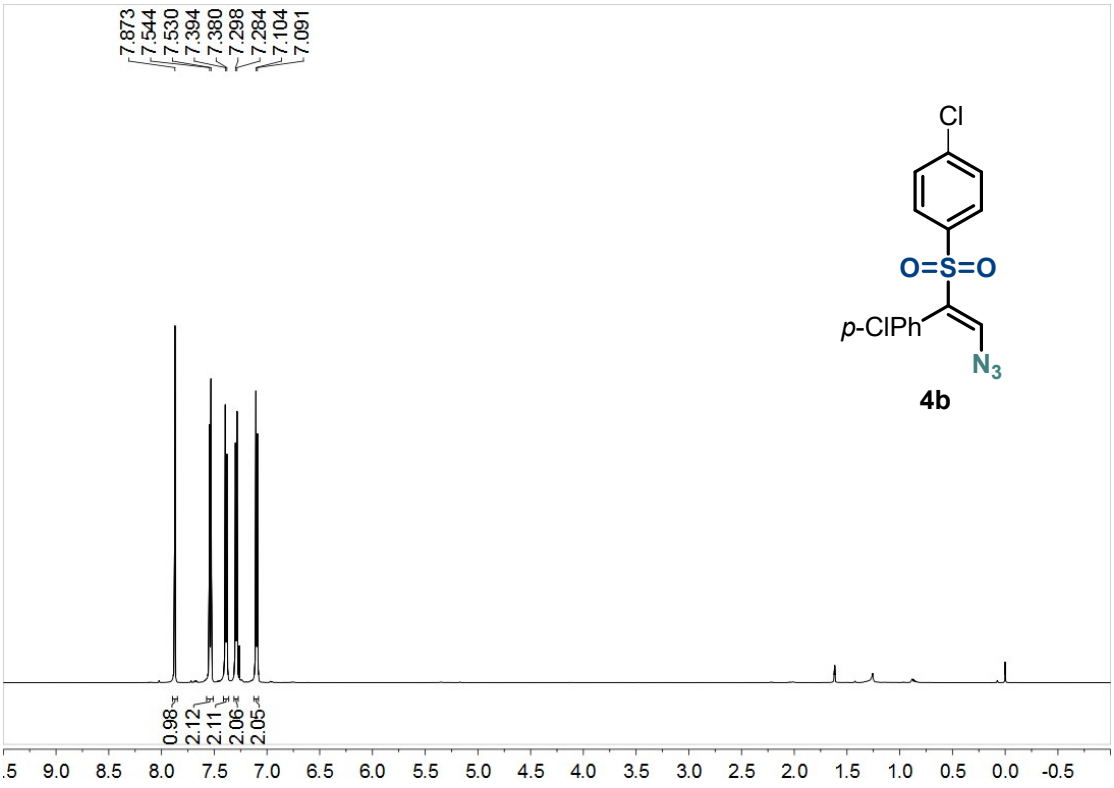
3x

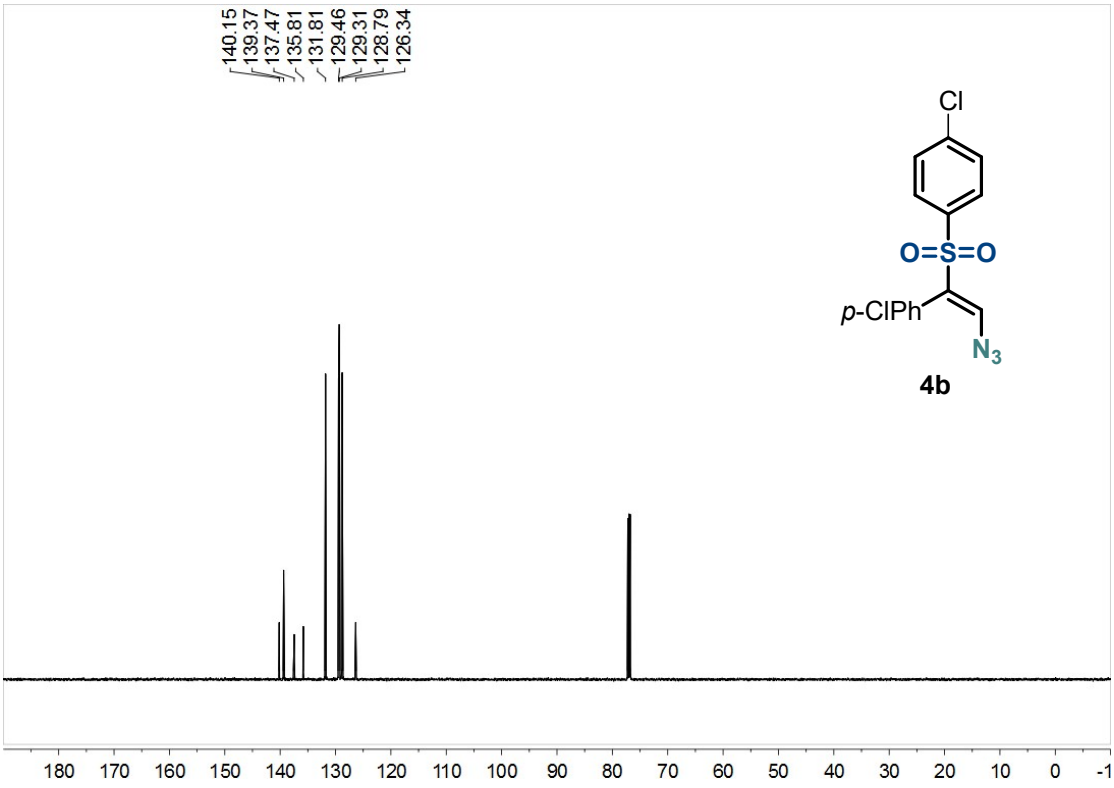

144.23
137.39
136.53
129.56
128.59
127.83
127.59
127.41
126.40
125.29
21.54
Tol
O=S=O
N3
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

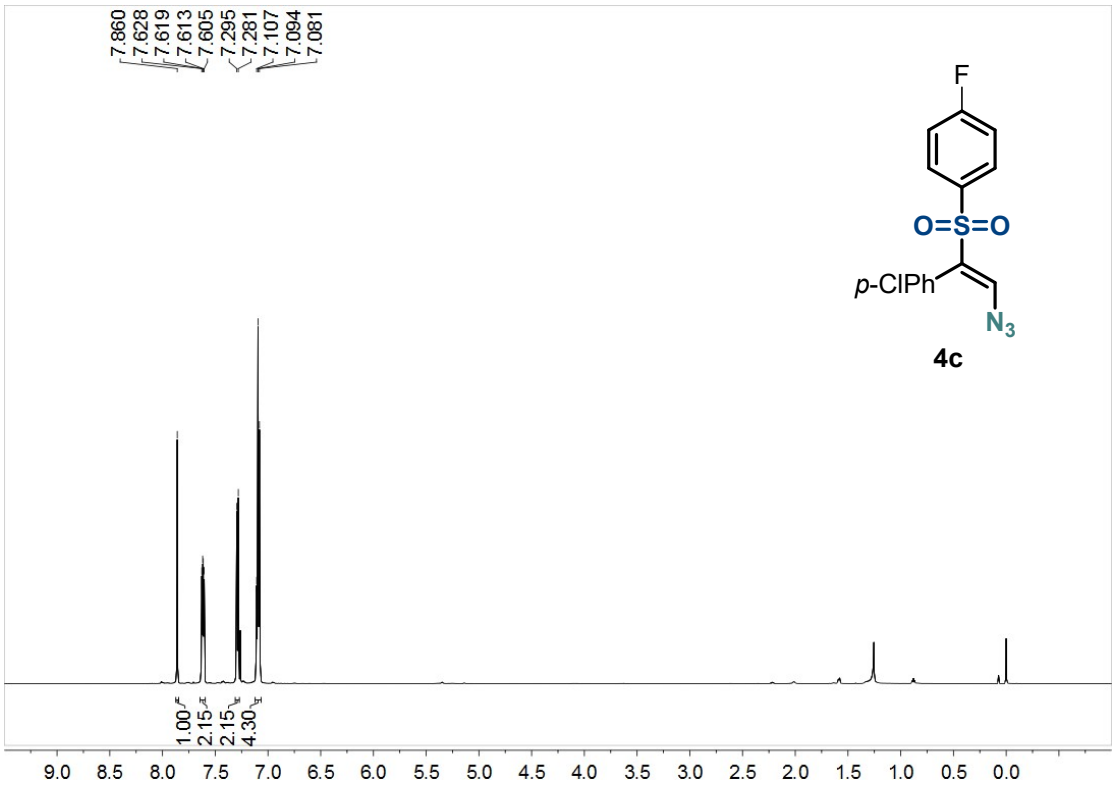
3x

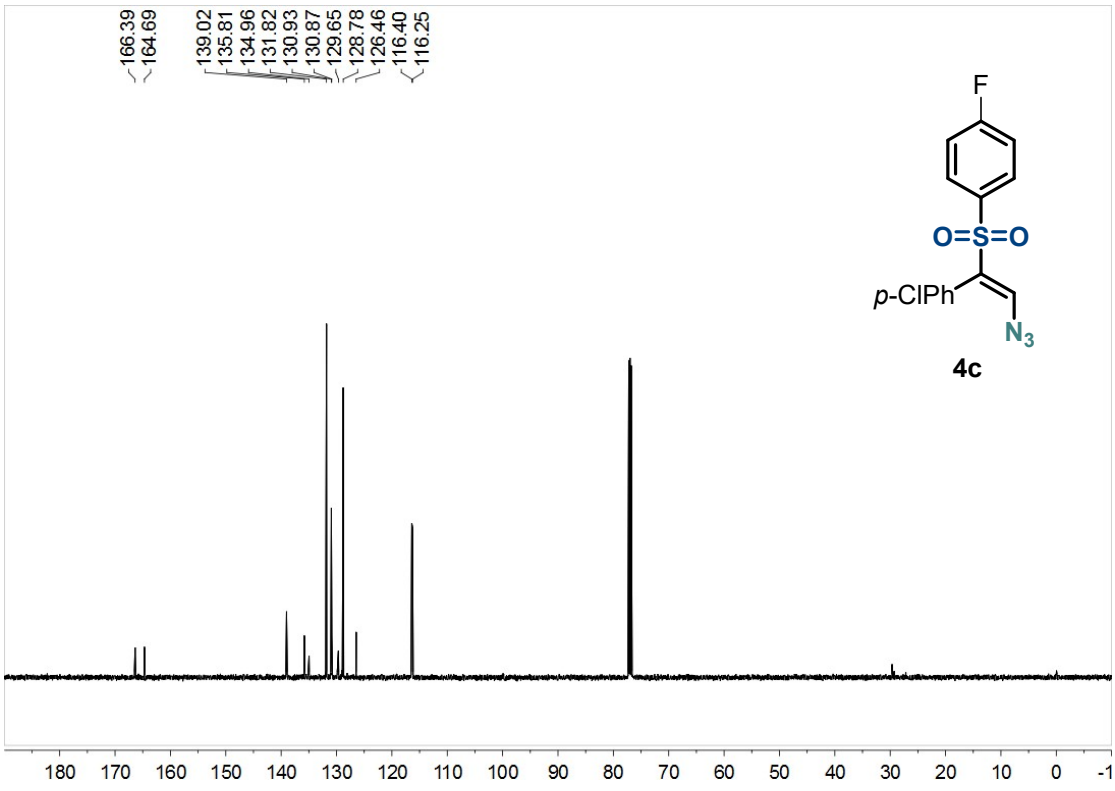

7.862
7.620
7.607
7.562
7.549
7.537
7.434
7.421
7.408
7.273
7.259
7.081
7.067
O=S=O
p-ClPh
N3
4a
0.96
2.11
1.10
2.18
2.27
2.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

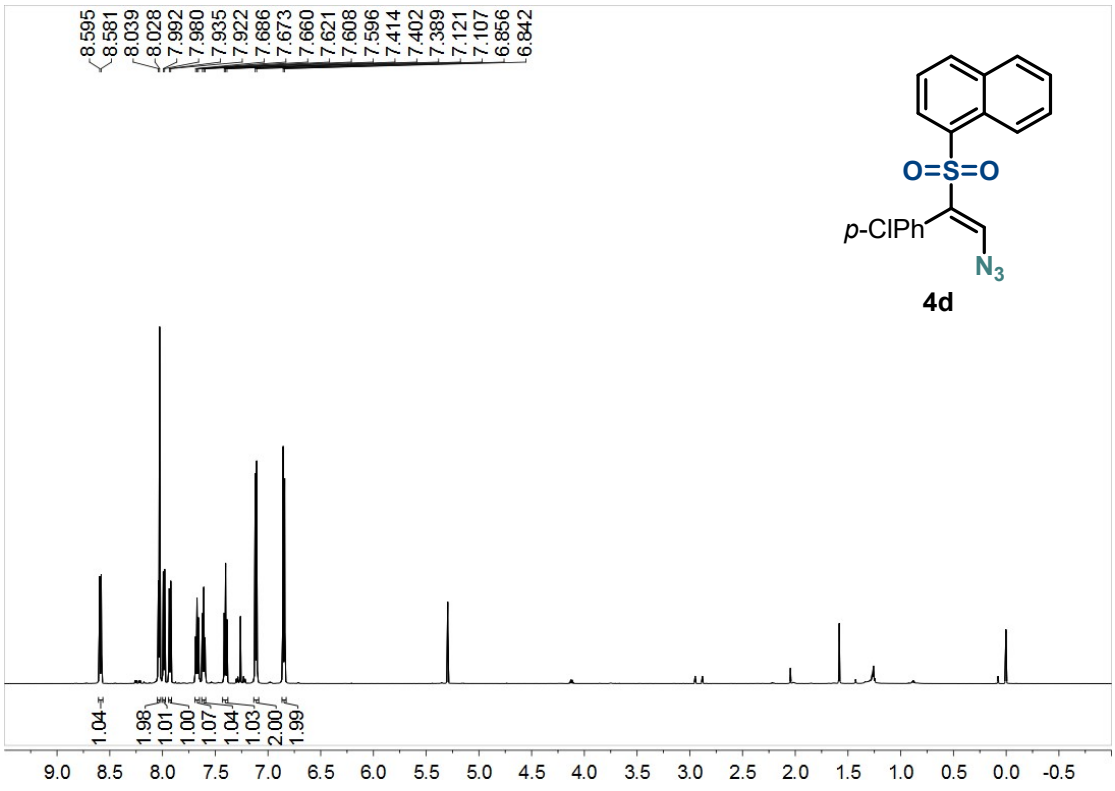

138.93
138.89
135.66
133.44
131.83
129.87
128.98
128.68
128.06
126.64
O=S=O
p-ClPh
N3
4a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

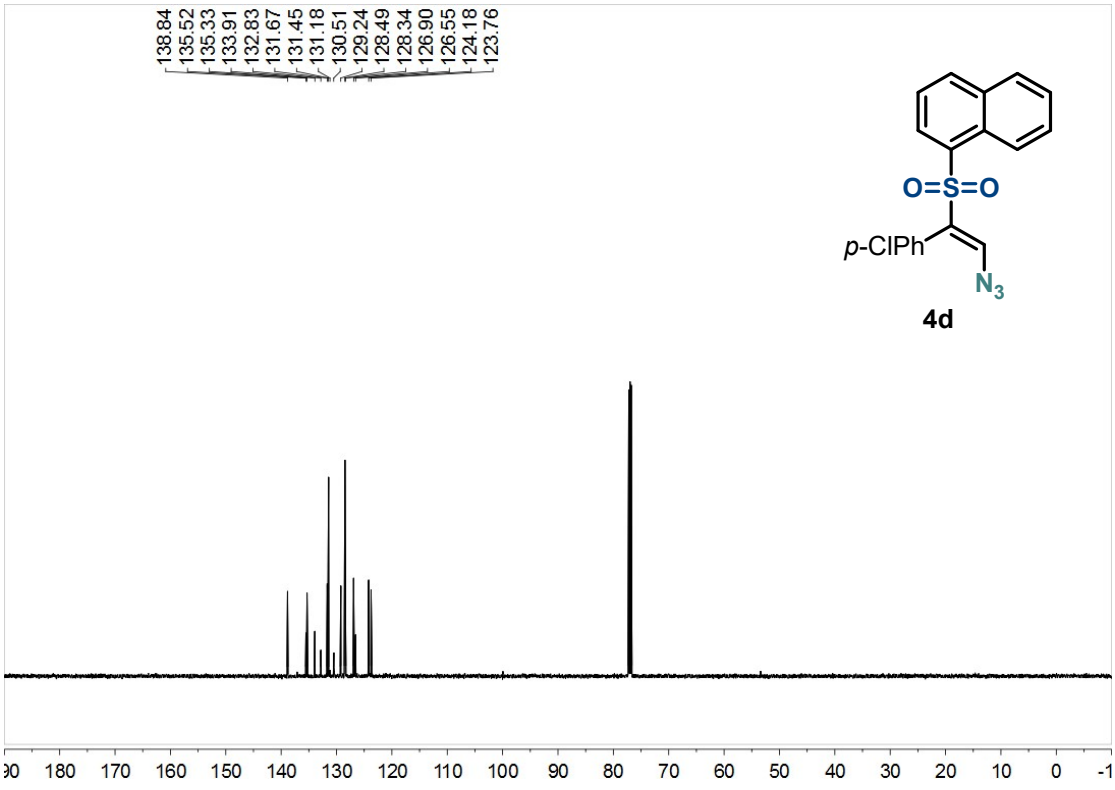

7.873
7.544
7.530
7.394
7.380
7.298
7.284
7.104
7.091
Cl
O=S=O
p-ClPh
N3
4b
0.98
2.12
2.11
2.06
2.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

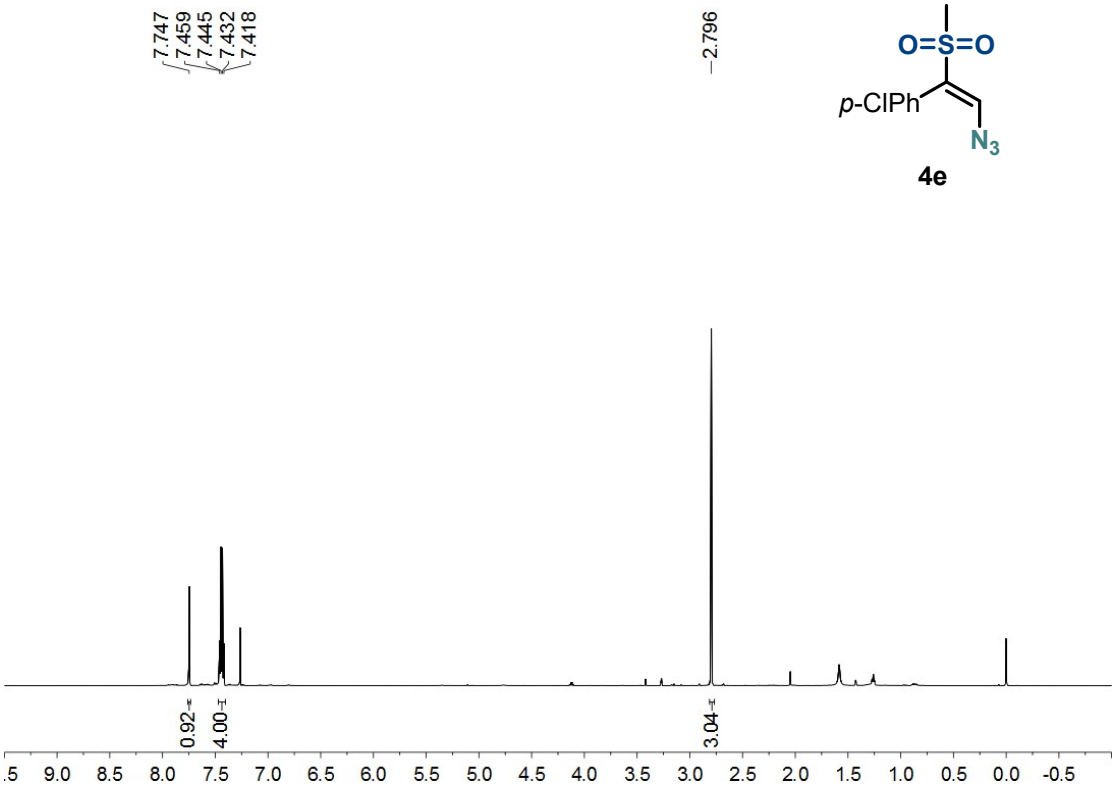

140.15
139.37
137.47
135.81
131.81
129.46
129.31
128.79
126.34
Cl
O=S=O
p-ClPh
N3
4b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

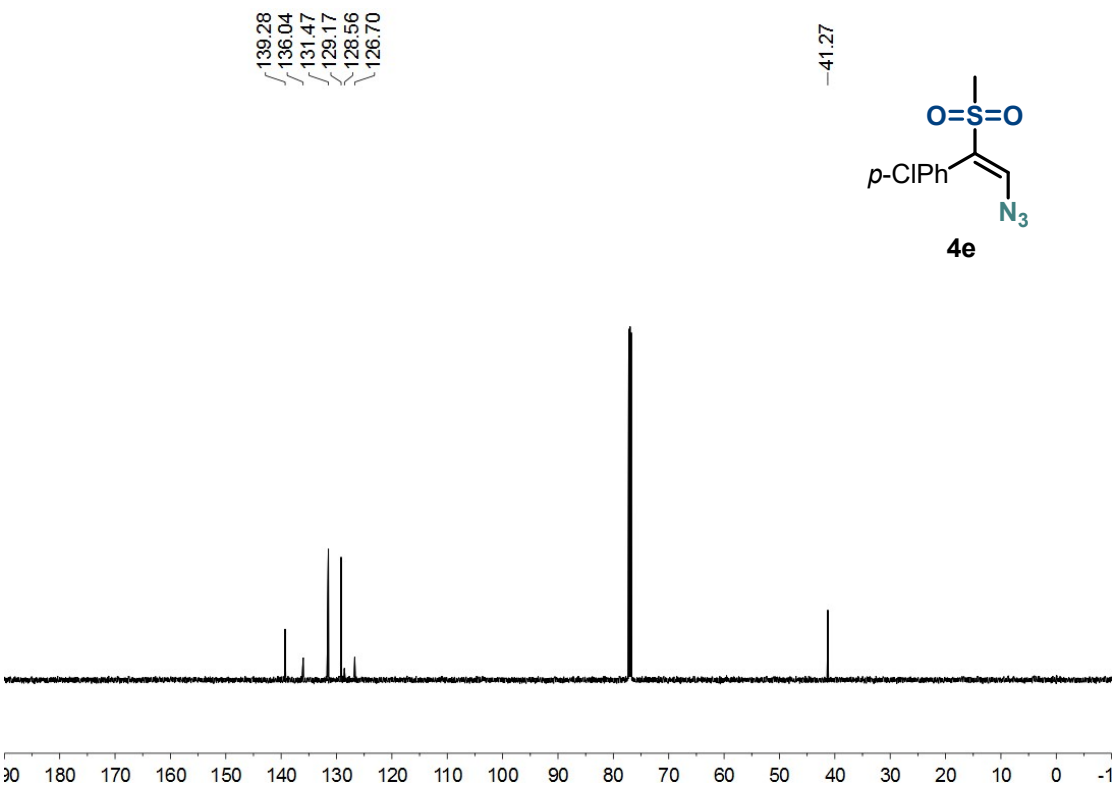

7.860
7.628
7.619
7.613
7.605
7.295
7.281
7.107
7.094
7.081
F
O=S=O
p-ClPh
N3
4c
1.00
2.15
2.15
4.30
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

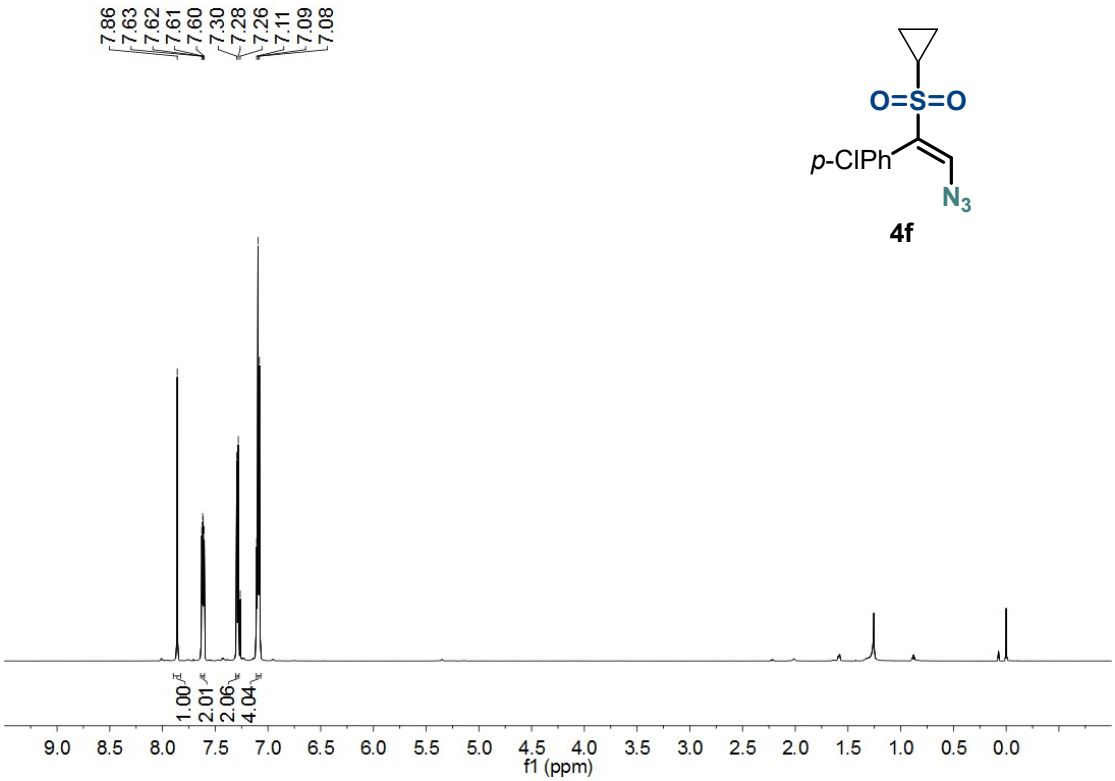

166.39
164.69
139.02
135.81
134.96
131.82
130.93
130.87
129.65
128.78
126.46
116.40
116.25
F
O=S=O
p-ClPh
N3
4c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

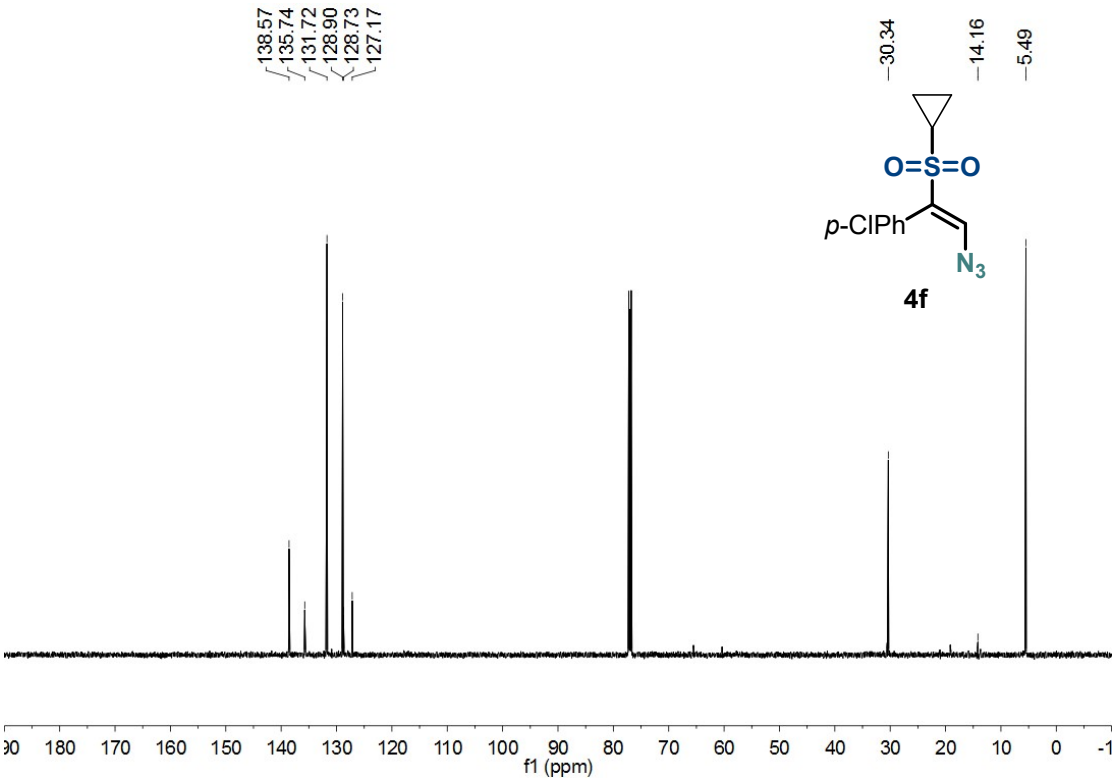

8.595
8.581
8.039
8.028
7.992
7.980
7.935
7.922
7.686
7.673
7.660
7.621
7.608
7.596
7.414
7.402
7.389
7.121
7.107
6.856
6.842
O=S=O
p-ClPh
N3
4d
1.04
1.98
1.01
1.00
1.07
1.04
1.03
2.00
1.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

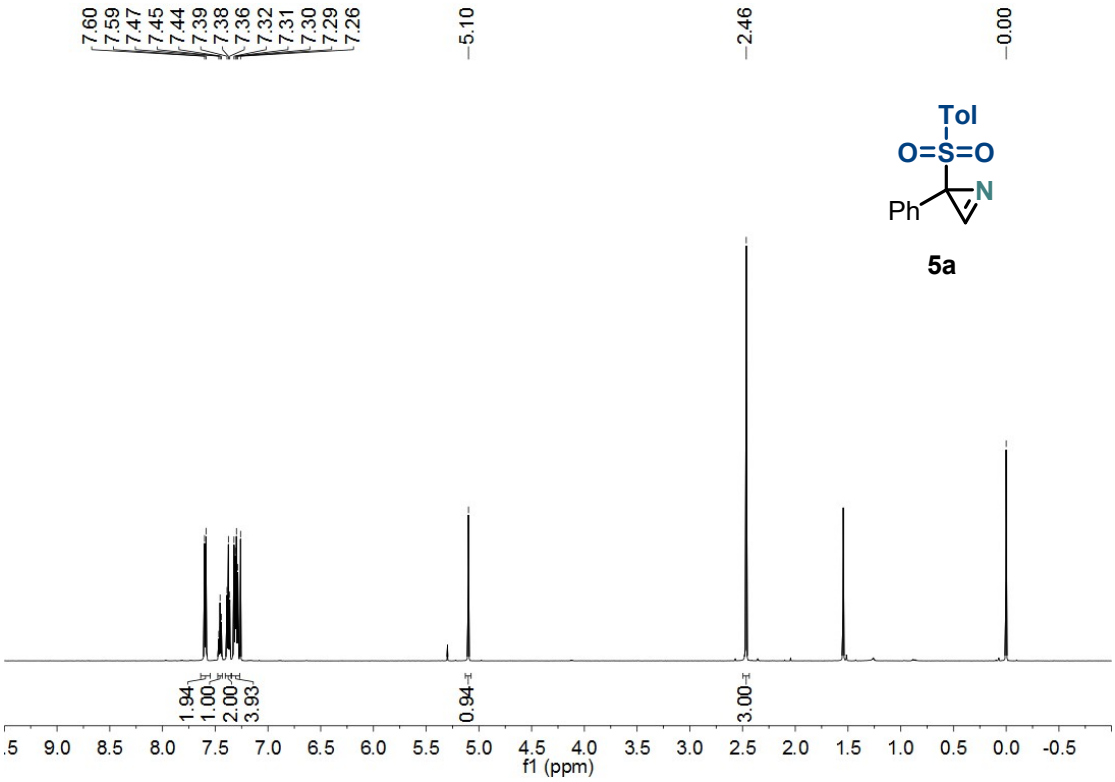

138.84
135.52
135.33
133.91
132.83
131.67
131.45
131.18
130.51
129.24
128.49
128.34
126.90
126.55
124.18
123.76
O=S=O
p-ClPh
N3
4d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

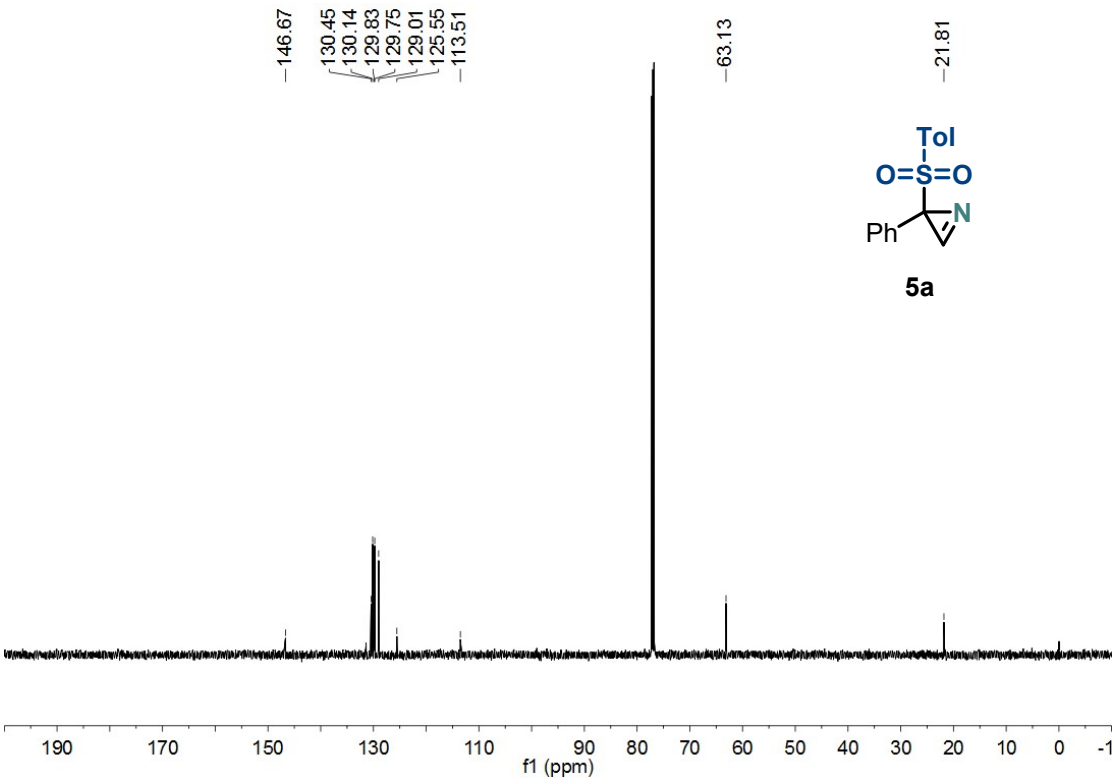

7.747
7.459
7.445
7.432
7.418
2.796
O=S=O
p-ClPh
N3
4e
0.92
4.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

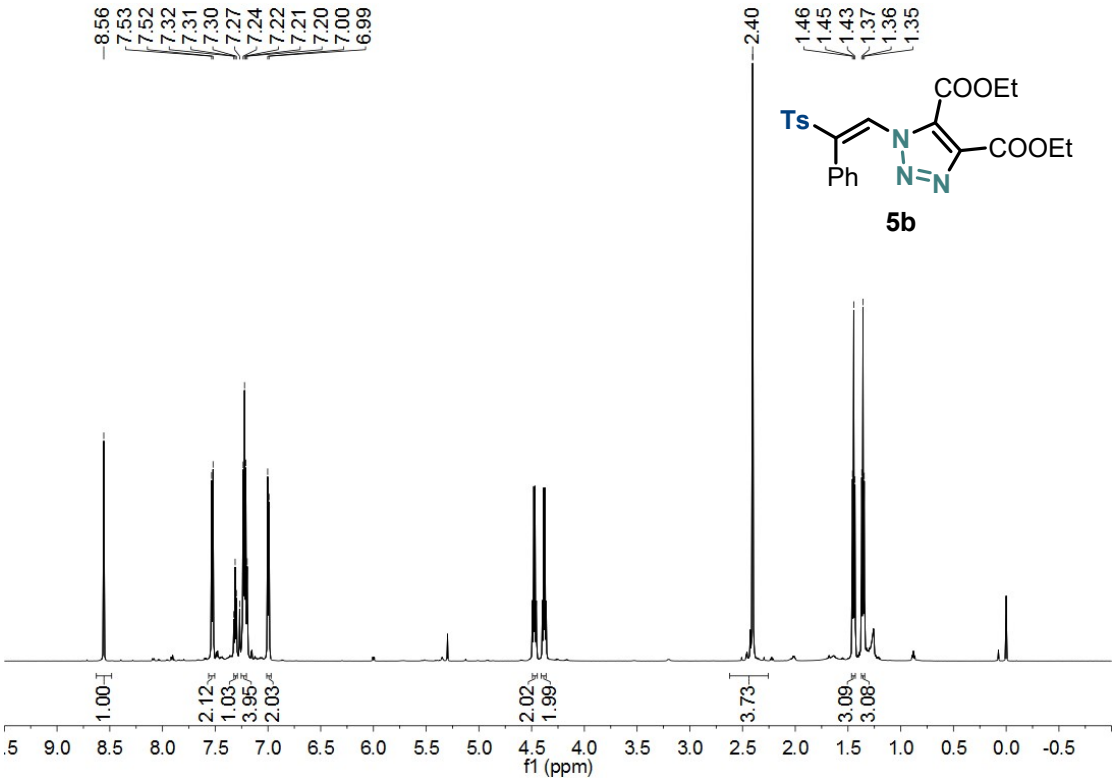

139.28
136.04
131.47
129.17
128.56
126.70
41.27
O=S=O
p-ClPh
N3
4e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

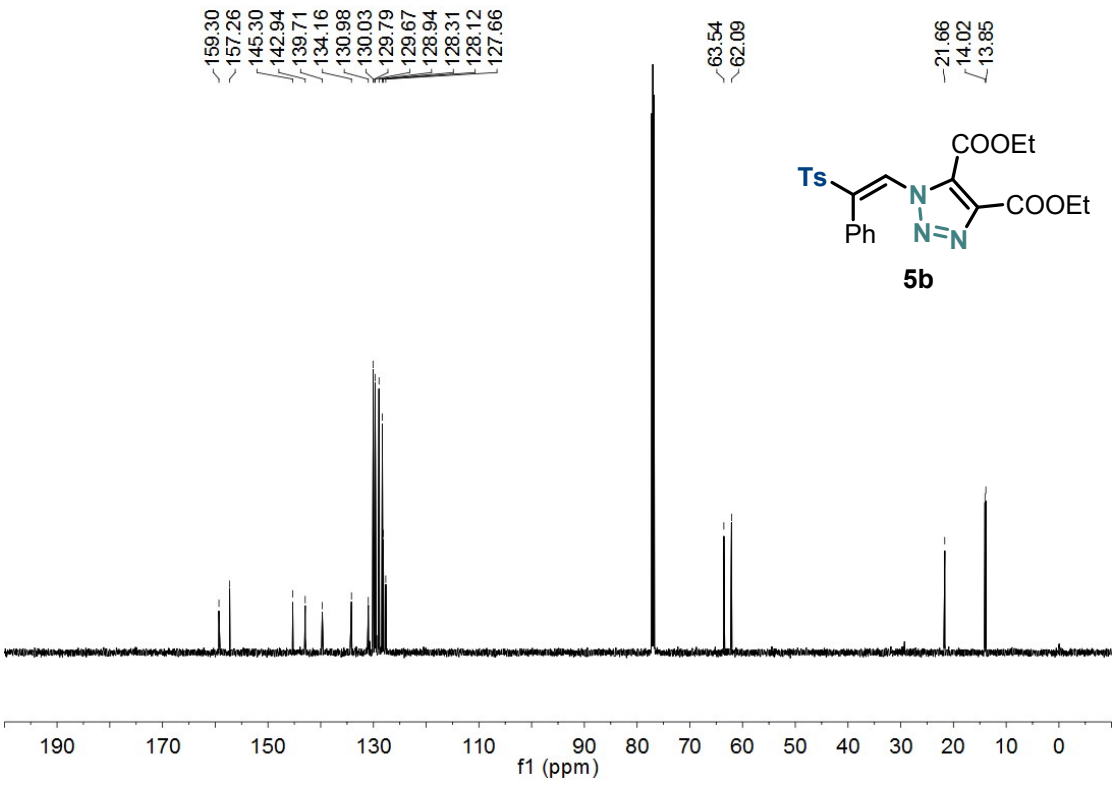

7.86
7.63
7.62
7.61
7.60
7.30
7.28
7.26
7.11
7.09
7.08
O=S=O
p-ClPh
N3
4f
1.00
2.01
2.06
4.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

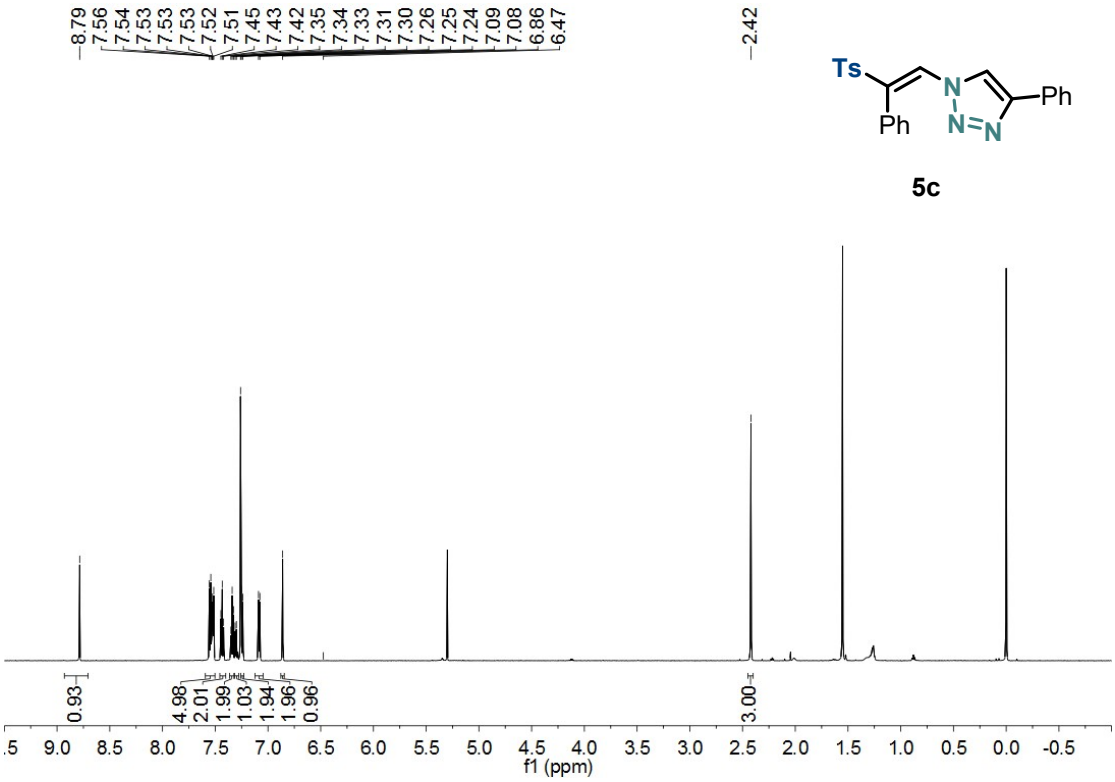

138.57
135.74
131.72
128.90
128.73
127.17
30.34
14.16
5.49
O=S=O
p-ClPh
N3
4f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.60
7.59
7.47
7.45
7.44
7.39
7.38
7.36
7.32
7.31
7.30
7.29
7.26
5.10
2.46
0.00
Tol
O=S=O
N
Ph
5a
1.94
1.00
2.00
3.93
0.94
3.00
f1 (ppm)

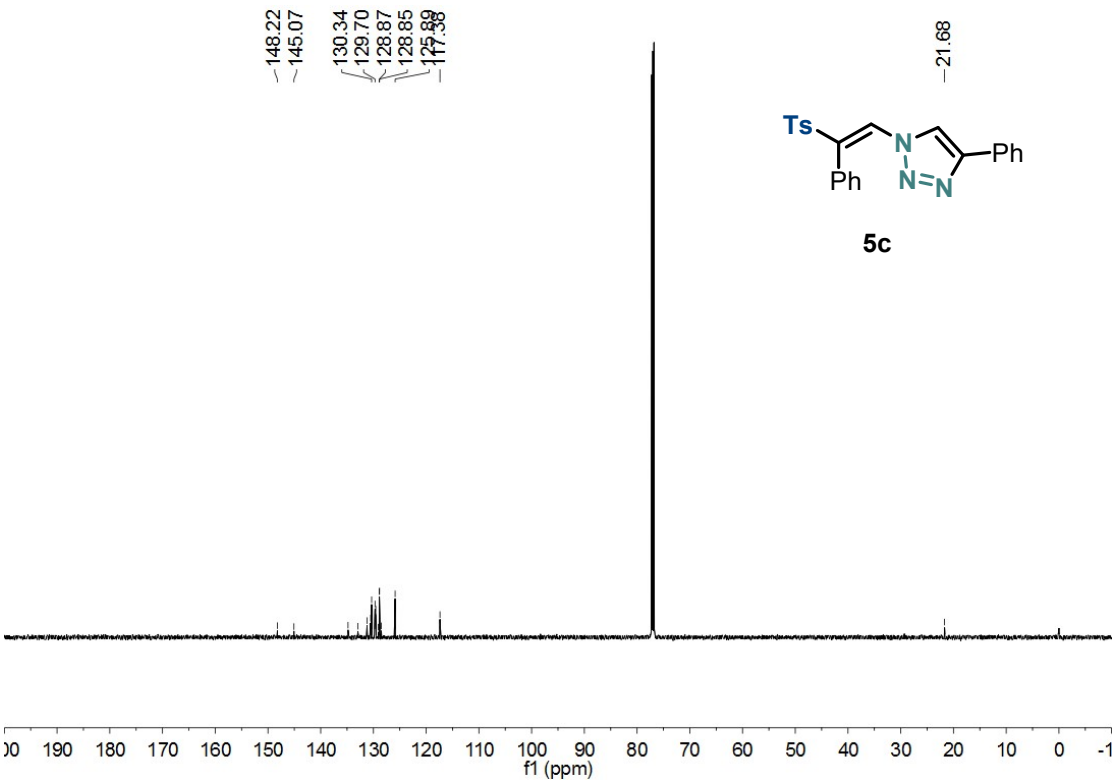

146.67
130.45
130.14
129.83
129.75
129.01
125.55
113.51
63.13
21.81
Tol
O=S=O
N
Ph
5a
f1 (ppm)


8.56
7.53
7.52
7.32
7.31
7.30
7.27
7.24
7.22
7.21
7.20
7.00
6.99
2.40
1.46
1.45
1.43
1.37
1.36
1.35
COOEt
Ts
N
COOEt
Ph
N=N
5b
1.00
2.12
1.03
3.95
2.03
2.02
1.99
3.73
3.09
3.08
f1 (ppm)

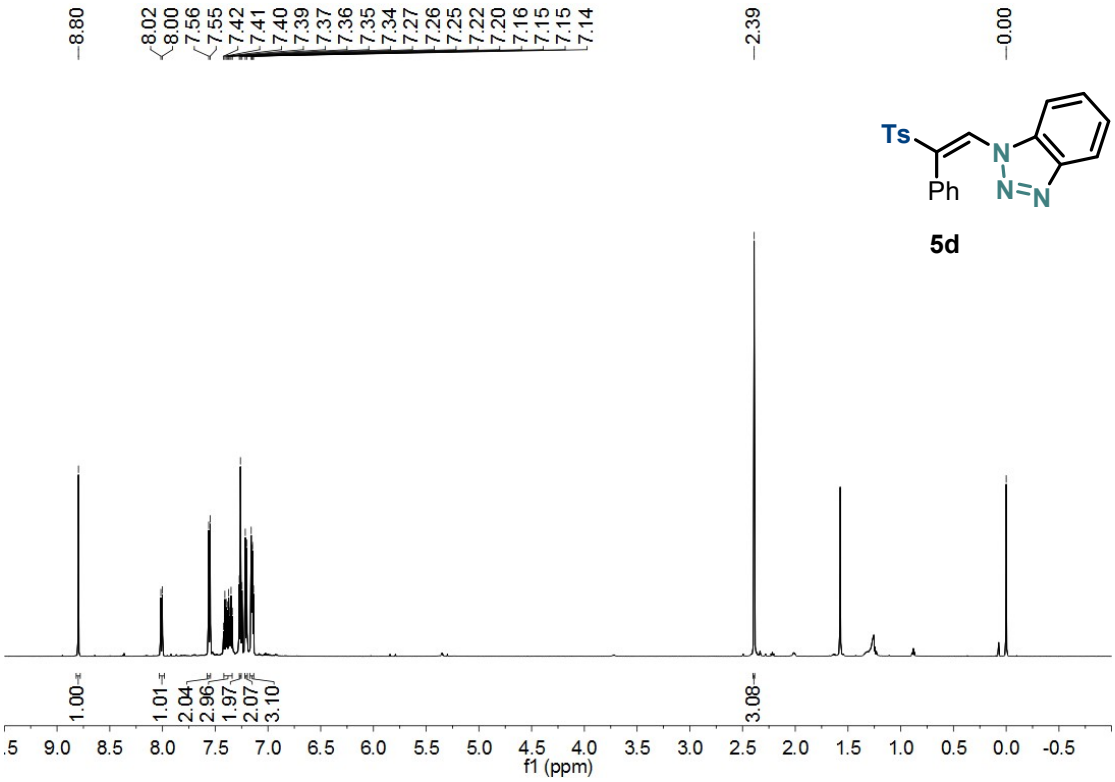

159.30
157.26
145.30
142.94
139.71
134.16
130.98
130.03
129.79
129.67
128.94
128.31
128.12
127.66
63.54
62.09
21.66
14.02
13.85
COOEt
Ts
N
COOEt
Ph
N=N
5b
f1 (ppm)


8.79
7.56
7.54
7.53
7.53
7.53
7.52
7.51
7.45
7.43
7.42
7.35
7.34
7.33
7.31
7.30
7.26
7.25
7.24
7.09
7.08
6.86
6.47
2.42
Ts
Ph
N
N=N
Ph
0.93
4.98
2.01
1.99
1.03
1.94
1.96
0.96
3.00
f1 (ppm)

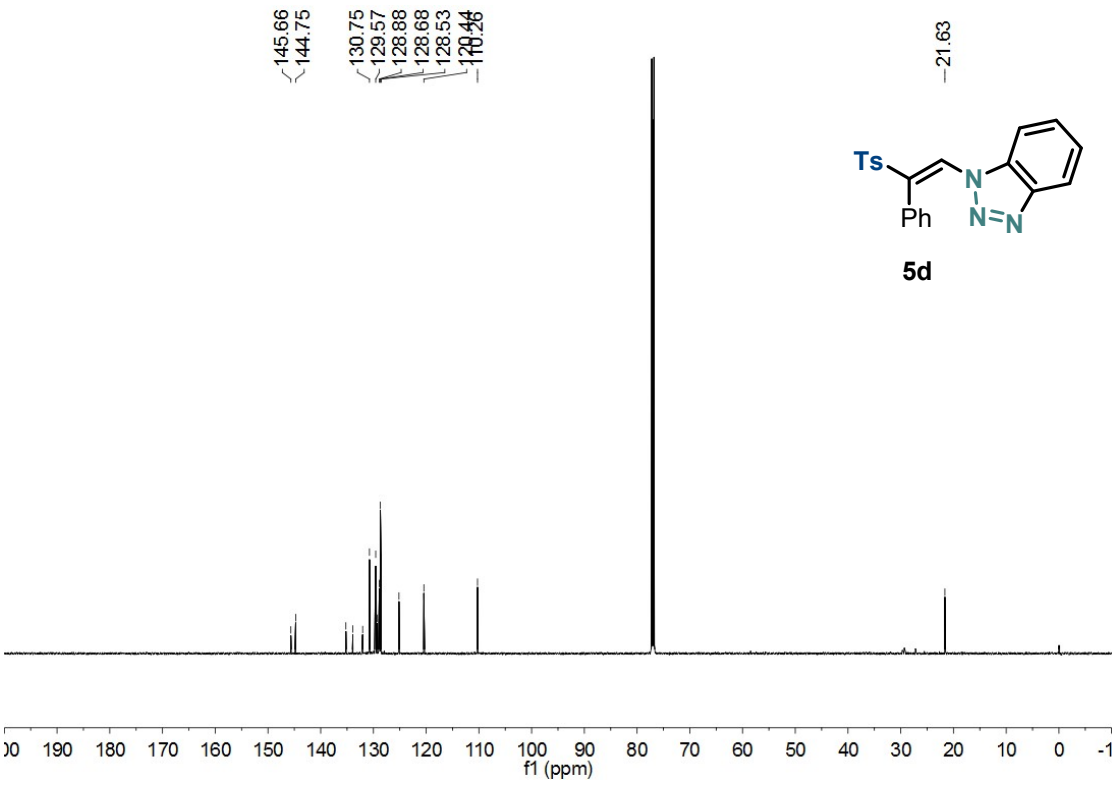
5c


148.22
145.07
130.34
129.70
128.87
128.85
21.68
Ts
Ph
N
N=N
Ph
f1 (ppm)

5c


8.80
8.02
8.00
7.56
7.55
7.42
7.41
7.40
7.39
7.37
7.36
7.35
7.34
7.27
7.26
7.25
7.22
7.20
7.16
7.15
7.15
7.14
2.39
0.00
Ts
Ph
N
N=N
1.00
1.01
2.04
2.96
1.97
2.07
3.10
3.08
f1 (ppm)

5d


145.66
144.75
130.75
129.57
128.88
128.68
128.53
21.63
Ts
Ph
N
N=N
f1 (ppm)

5d

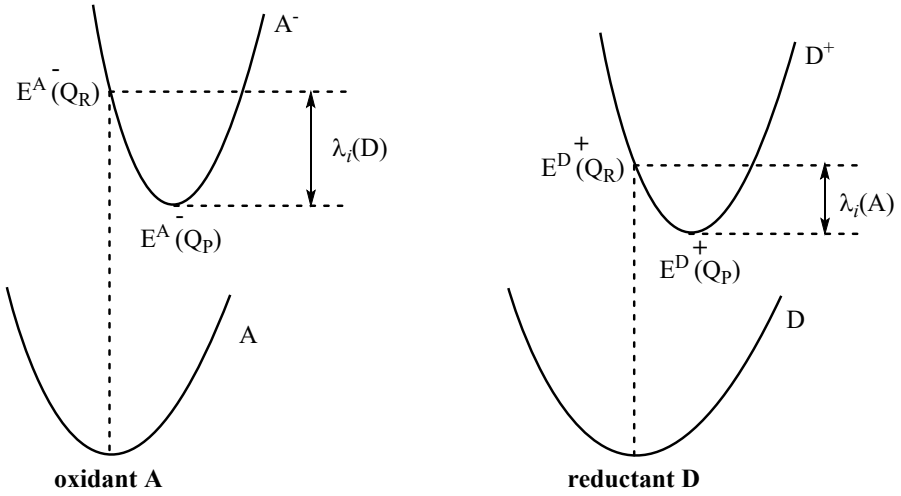
VIII. Mechanistic study using DFT computations

Computational details

All calculations were performed using Gaussian16 suite of programs[2] using the B3LYP functional.[3,4] The I atoms was represented with the Stuttgart-Dresden relativistic effective core potential associated with their adapted basis set.[5,6] All the other atoms C, H, O and S were described with 6-31G(d) basis set.[7,8] The nature of the extrema (minimum) was established with analytical frequencies calculations and geometry optimizations were computed without any symmetry constraints. Intrinsic Reaction Paths (IRPs)[9,10] were traced from the various transition structures to obtain the connected intermediates. The SMD solvation model was used to evaluate solvation energies by a self-consistent reaction field (SCRF) approach based on accurate numerical solutions of the Poisson−Boltzmann equation.[11] DMSO was chosen as solvent. Marcus electron transfer theory was employed to evaluate the single electron transfer (SET) process.[12-14] The radii of the oxidant/reductant was calculated by the Multiwfn program.[15-17] 3D diagrams of the computed species were generated using CYLview visualization software.[18]

Activation Barrier of Single Electron Transfer Step

According to the Marcus equation, the reorganization energy λ ($\lambda = \lambda_i + \lambda_o$) is normally decomposed into internal energy (λ_i) and external energy (λ_o).

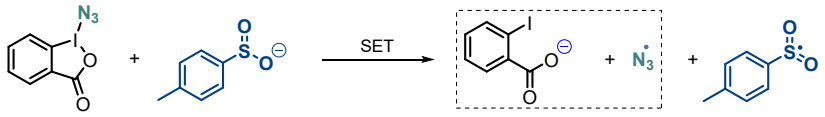


The internal reorganization energy λ_i can be estimated according to the equation:

$$\lambda_i = \lambda_i(D) + \lambda_i(A) = [E^{A^-}(Q_R) - E^{A^-}(Q_P)] + [E^{D^+}(Q_R) - E^{D^+}(Q_P)] \quad \text{(S1)}$$

where Q_R and Q_P are the equilibrium geometries of the reactants and products, respectively.

The single electron transfer (SET) reaction of our system:



I $TolSO_2$-anion $PhICO_2$-anion-N_3-radical $TolSO_2$-radical

Here, the oxidant in the reactant is **3**, while the reductant in the corresponding product is azide radical. Azide radical and o-$IC_6H_4CO_2^-$ are adduct in the SET process, so we treat the adduct **$PhICO_2$-anion-N_3-radical** as the reductant in the corresponding product. The reductant in the reactant is **$TolSO_2$-anion**, while the oxidant in the corresponding product is **$TolSO_2$-radical**. Put their single-point energies into the equation S1, λ_i can be estimated.

λ_i = {[-595.2214927-(-595.2801927)] + [-819.5178329-(-819.5289605)]} ×627.51

= 43.82 kcal/mol

In addition, the external reorganization energy λ_o and the activation barrier may be calculated from equation (S2−S3):

$$\lambda_0 = (332\ kcal/mol)(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R})(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}) \quad \text{(S2)}$$

$$\Delta G^{\neq} = \frac{(\Delta G_r + \lambda)^2}{4\lambda} \quad \text{(S3)}$$

where a_1 is the radii of the oxidant, a_2 is the radii of the reductant, R = a_1 + a_2, ε_{op} is the optical dielectric constant (ε_{op} = 2.25), ε is the static dielectric constant for the DMSO solvent (ε = 48.9), and ΔG_r is the free energy change of the reaction.

Table S1. Estimation of the activation barrier for SET step.

SET step	a_1 (Å)	a_2 (Å)	R (Å)	λ (kcal/mol)	ΔG_r (kcal/mol)	$\Delta G^{\neq}$ (kcal/mol)
	5.306	5.012	10.318	57.48	-12.36	8.85

Cartesian coordinates of all optimized structures

$TolSO_2$-anion

Zero-point correction= 0.125192 (Hartree/Particle)

Thermal correction to Energy= 0.133865

Thermal correction to Enthalpy=	0.134810
Thermal correction to Gibbs Free Energy=	0.090706
Sum of electronic and zero-point Energies=	-819.551988
Sum of electronic and thermal Energies=	-819.543315
Sum of electronic and thermal Enthalpies=	-819.542370
Sum of electronic and thermal Free Energies=	-819.586474

S	-2.22916000	-0.01695600	-0.34036900
O	-2.63477300	-1.26719300	0.44569100
O	-2.62981700	1.30400200	0.32295900
C	3.95276000	0.00931800	0.08898300
C	0.33297400	-1.20880100	-0.10205800
C	1.72724400	-1.20285200	-0.02341800
C	2.44300500	0.00367300	0.03630500
C	1.71487900	1.20295300	0.02484700
C	0.31967300	1.19738900	-0.05634400
C	-0.38147700	-0.00808800	-0.11745400
H	4.33919900	-0.85381500	0.64299300
H	4.33429300	0.91923600	0.56531700
H	4.38779300	-0.03526100	-0.91935500
H	-0.21309400	-2.14893600	-0.13068500
H	2.27162600	-2.14582900	-0.00116800
H	2.24898600	2.15005400	0.08576700
H	-0.23987200	2.12982200	-0.05131700

3

Zero-point correction=	0.105450 (Hartree/Particle)
Thermal correction to Energy=	0.117157
Thermal correction to Enthalpy=	0.118101

Thermal correction to Gibbs Free Energy=	0.065235
Sum of electronic and zero-point Energies=	-595.015339
Sum of electronic and thermal Energies=	-595.003632
Sum of electronic and thermal Enthalpies=	-595.002688
Sum of electronic and thermal Free Energies=	-595.055554

C	-0.62755100	-0.66242400	-0.12045000
C	-1.88751700	-0.12775600	0.09429500
C	-2.96433600	-1.02129800	0.16235000
C	-2.74432900	-2.38977300	0.01780100
C	-1.45201300	-2.88037300	-0.19781800
C	-0.35796100	-2.00883400	-0.27259100
C	-2.06785400	1.35318900	0.25200600
H	-3.95942400	-0.62115800	0.33019400
H	-3.58078700	-3.07990200	0.07323500
H	-1.28383400	-3.94758700	-0.30947000
H	0.64818100	-2.37392100	-0.44326200
O	-3.16523700	1.86418100	0.43364400
O	-0.95368600	2.05747800	0.18225400
I	0.89923800	0.87304300	-0.19269300
N	2.47359800	-0.68585200	-0.65228700
N	3.14394800	-1.00024900	0.32510200
N	3.82202300	-1.34223800	1.18737000

TolSO_2-radical

Zero-point correction=	0.126032 (Hartree/Particle)
Thermal correction to Energy=	0.135595
Thermal correction to Enthalpy=	0.136539
Thermal correction to Gibbs Free Energy=	0.088820

Sum of electronic and zero-point Energies=	-819.402929
Sum of electronic and thermal Energies=	-819.393366
Sum of electronic and thermal Enthalpies=	-819.392422
Sum of electronic and thermal Free Energies=	-819.440141

S	-2.15906600	-0.00033900	-0.24282700
O	-2.67110200	-1.29686000	0.29253500
O	-2.67192400	1.29620300	0.29164100
C	3.92892400	-0.00026900	0.10882100
C	0.31826200	-1.22028300	-0.08261300
C	1.70911500	-1.20667400	-0.01945900
C	2.42525400	0.00106600	0.01570400
C	1.70866400	1.20787500	-0.01891600
C	0.31726900	1.22070700	-0.08216200
C	-0.36128400	0.00021700	-0.08853300
H	4.25039700	-0.06550000	1.15728800
H	4.35652700	0.91706300	-0.30804900
H	4.36098700	-0.85838200	-0.41652600
H	-0.22491100	-2.15870300	-0.11112200
H	2.24816800	-2.15017300	0.00132400
H	2.24712500	2.15161900	0.00227100
H	-0.22626000	2.15892700	-0.11040600

PhICO$_2$-anion-N$_3$-radical

Zero-point correction=	0.103280 (Hartree/Particle)
Thermal correction to Energy=	0.116107
Thermal correction to Enthalpy=	0.117051
Thermal correction to Gibbs Free Energy=	0.058608
Sum of electronic and zero-point Energies=	-595.176913

Sum of electronic and thermal Energies=	-595.164086
Sum of electronic and thermal Enthalpies=	-595.163141
Sum of electronic and thermal Free Energies=	-595.221585

C	0.62158900	0.58183900	-0.13089200
C	1.97000800	0.31716800	0.10284700
C	2.83756800	1.41990000	0.15737000
C	2.37168400	2.72092000	-0.01417100
C	1.01206400	2.94643600	-0.24643800
C	0.12287000	1.87018700	-0.30675300
C	2.55344600	-1.07642500	0.30204100
H	3.88802000	1.21556900	0.33961700
H	3.06367500	3.55733500	0.03308600
H	0.63595300	3.95703700	-0.38128800
H	-0.93566700	2.03093700	-0.48587200
O	3.77767300	-1.18317300	0.50224500
O	1.73930700	-2.05935300	0.25122400
I	-0.79403000	-1.05258100	-0.23208300
N	-3.14090500	0.85670000	-0.68836000
N	-3.69672900	0.87033300	0.36766000
N	-4.25373500	0.88525100	1.40399400

adduct1

Zero-point correction=	0.120337 (Hartree/Particle)
Thermal correction to Energy=	0.131165
Thermal correction to Enthalpy=	0.132109
Thermal correction to Gibbs Free Energy=	0.080236
Sum of electronic and zero-point Energies=	-472.418772
Sum of electronic and thermal Energies=	-472.407944

Sum of electronic and thermal Enthalpies=	-472.407000
Sum of electronic and thermal Free Energies=	-472.458873

C	-2.02296200	1.93985600	0.00159800
C	-0.91424100	1.44128900	0.00122900
C	2.20982500	-0.18917300	-1.21357800
C	0.97610200	0.45200700	-1.22069300
C	0.34479100	0.78271100	0.00066000
C	2.20923300	-0.19233000	1.21328400
C	2.82879000	-0.51074200	-0.00041400
C	0.97550000	0.44880200	1.22149500
H	3.79335000	-1.01054900	-0.00080300
H	2.69191100	-0.43982500	-2.15404700
H	2.69091100	-0.44546700	2.15329500
H	0.48977700	0.70690800	-2.15710200
H	0.48869500	0.70131000	2.15830100
H	-2.96734900	2.44274600	0.00203500
N	-3.20492000	-0.61420500	-0.00134600
N	-2.23073700	-1.29053800	-0.00107000
N	-1.25427500	-1.95092000	-0.00089200

adduct2

Zero-point correction=	0.236044 (Hartree/Particle)
Thermal correction to Energy=	0.254490
Thermal correction to Enthalpy=	0.255434
Thermal correction to Gibbs Free Energy=	0.180069
Sum of electronic and zero-point Energies=	-1127.694164
Sum of electronic and thermal Energies=	-1127.675719
Sum of electronic and thermal Enthalpies=	-1127.674774

Sum of electronic and thermal Free Energies= -1127.750139

S	-0.78595400	1.85420700	-0.35218400
O	-0.03919500	1.63363500	-1.62644100
O	-1.40751200	3.18170700	-0.06221200
C	0.76965300	-0.20190600	2.00197700
C	1.81499600	-0.33394200	1.40193900
C	5.38256900	0.09369700	0.37383900
C	4.18590200	0.24789100	1.07053300
C	3.04592900	-0.48671800	0.68897800
C	4.33297000	-1.52180900	-1.09109600
C	5.46000700	-0.78949000	-0.70692200
C	3.13152700	-1.37505800	-0.40113800
C	-5.07579100	-2.45198600	0.16620600
C	-1.87255200	-0.64029400	-0.84741100
C	-2.85024700	-1.62233100	-0.70744500
C	-4.01440000	-1.38969900	0.04248900
C	-4.17650000	-0.13880900	0.65897700
C	-3.21282600	0.85931300	0.53349800
C	-2.07985600	0.60035300	-0.24050800
H	6.39518700	-0.90688700	-1.24755500
H	6.25663100	0.66456600	0.67500000
H	4.38939700	-2.20903100	-1.93082500
H	4.12293800	0.93346600	1.91030400
H	2.25434900	-1.94264400	-0.69723700
H	-0.14147000	-0.10514800	2.55411300
H	-5.81429000	-2.35610200	-0.64149100
H	-5.61744500	-2.36746500	1.11391100
H	-4.64614800	-3.45656200	0.09700100
H	-0.97612600	-0.83214100	-1.42728300
H	-2.70553500	-2.58679100	-1.18719600

H	-5.06939100	0.05761900	1.24681200
H	-3.34745600	1.82179500	1.01510600

TS1

Zero-point correction=	0.120790 (Hartree/Particle)
Thermal correction to Energy=	0.130617
Thermal correction to Enthalpy=	0.131562
Thermal correction to Gibbs Free Energy=	0.082481
Sum of electronic and zero-point Energies=	-472.416202
Sum of electronic and thermal Energies=	-472.406374
Sum of electronic and thermal Enthalpies=	-472.405430
Sum of electronic and thermal Free Energies=	-472.454511

C	-1.95481000	-1.64947100	0.00108500
C	-0.78043200	-1.27317800	0.00082600
C	2.38995500	0.23535400	1.21537600
C	1.13561400	-0.35960200	1.22488800
C	0.48863000	-0.66404900	0.00042800
C	2.39017100	0.23335600	-1.21565900
C	3.01921100	0.53271200	-0.00033100
C	1.13582900	-0.36161200	-1.22441900
H	4.00098600	0.99756700	-0.00062600
H	2.88285900	0.46997000	2.15422700
H	2.88323800	0.46645300	-2.15480400
H	0.63875200	-0.59496500	2.16071200
H	0.63912000	-0.59848000	-2.15994400
H	-2.76478900	-2.35067700	0.00152300
N	-3.30070600	0.03852000	-0.00040000
N	-2.62819200	1.03448300	-0.00068100

N	-1.96041100	1.99115000	-0.00095500

TS2

Zero-point correction=	0.236299 (Hartree/Particle)
Thermal correction to Energy=	0.253452
Thermal correction to Enthalpy=	0.254396
Thermal correction to Gibbs Free Energy=	0.185684
Sum of electronic and zero-point Energies=	-1127.687917
Sum of electronic and thermal Energies=	-1127.670764
Sum of electronic and thermal Enthalpies=	-1127.669820
Sum of electronic and thermal Free Energies=	-1127.738532

S	0.58611800	-1.63816600	-0.38191000
O	-0.15569500	-1.30168900	-1.62789600
O	1.11813500	-3.01964600	-0.19409300
C	-0.79743700	-1.09134400	1.52150700
C	-1.83315400	-0.50527300	1.18707100
C	-5.20919200	0.05730300	-0.27031400
C	-4.10236800	-0.59405100	0.26191100
C	-2.95733300	0.14814900	0.63810800
C	-4.07197100	2.18997100	-0.06378600
C	-5.19883700	1.44726500	-0.43516100
C	-2.95745400	1.55366300	0.47059600
C	5.20815300	2.30483800	0.23397900
C	1.88079200	0.76809700	-0.83211000
C	2.93112100	1.66782900	-0.66705700
C	4.06934100	1.32856200	0.08255400
C	4.12817200	0.05554700	0.66947800
C	3.08760700	-0.85966000	0.51633200

C	1.97722500	-0.49801400	-0.24887700
H	-6.06682900	1.95038100	-0.85188900
H	-6.08421500	-0.51830700	-0.55863100
H	-4.06467500	3.26857200	-0.19278000
H	-4.10419100	-1.67172000	0.39258600
H	-2.08048000	2.12410100	0.76060600
H	-0.15240000	-1.51443000	2.27016400
H	4.84213300	3.33258200	0.33296600
H	5.86308500	2.27868200	-0.64755300
H	5.82368300	2.06917700	1.10789800
H	1.00647500	1.04014100	-1.41421700
H	2.86637500	2.65079000	-1.12704200
H	5.00011000	-0.22396100	1.25537700
H	3.14552400	-1.84196000	0.97358800

Int1

Zero-point correction=	0.123397 (Hartree/Particle)
Thermal correction to Energy=	0.132920
Thermal correction to Enthalpy=	0.133864
Thermal correction to Gibbs Free Energy=	0.085991
Sum of electronic and zero-point Energies=	-472.443432
Sum of electronic and thermal Energies=	-472.433908
Sum of electronic and thermal Enthalpies=	-472.432964
Sum of electronic and thermal Free Energies=	-472.480837

C	-1.98717800	-1.33765000	-0.00136900
C	-0.72125700	-1.01469000	-0.00106300
C	2.54813800	0.24280300	1.21442800
C	1.25290900	-0.24919500	1.22751200

C	0.56130300	-0.50587800	-0.00053400
C	2.54804500	0.24557500	-1.21394100
C	3.20634700	0.49451100	0.00050600
C	1.25282600	-0.24640500	-1.22804700
H	4.22191300	0.87961300	0.00089700
H	3.05671800	0.43516000	2.15549300
H	3.05657200	0.44005900	-2.15459600
H	0.74380200	-0.44436700	2.16645500
H	0.74365400	-0.43945800	-2.16738900
H	-2.34395200	-2.36525700	-0.00250800
N	-3.11912600	-0.43875700	-0.00044500
N	-2.88241600	0.77436500	0.00086500
N	-2.77638600	1.91008200	0.00196500

Int2

Zero-point correction=	0.238469 (Hartree/Particle)
Thermal correction to Energy=	0.255246
Thermal correction to Enthalpy=	0.256190
Thermal correction to Gibbs Free Energy=	0.189438
Sum of electronic and zero-point Energies=	-1127.701691
Sum of electronic and thermal Energies=	-1127.684914
Sum of electronic and thermal Enthalpies=	-1127.683970
Sum of electronic and thermal Free Energies=	-1127.750722

S	-0.493282	-1.494455	0.346873
O	0.199798	-1.145131	1.601695
O	-0.902887	-2.893790	0.100695
C	0.562174	-0.998898	-1.062416
C	1.713507	-0.436602	-0.875507

C	5.259990	-0.035591	0.099547
C	4.066276	-0.642728	-0.255220
C	2.902305	0.151929	-0.501755
C	4.214525	2.153323	-0.024360
C	5.346695	1.360171	0.217888
C	3.007521	1.573603	-0.380075
C	-5.406651	2.069492	-0.231567
C	-1.977530	0.781803	0.840603
C	-3.098899	1.594113	0.691449
C	-4.186740	1.193622	-0.101041
C	-4.121946	-0.049990	-0.747489
C	-3.009282	-0.877990	-0.609170
C	-1.944028	-0.454650	0.189507
H	6.287862	1.825577	0.495558
H	6.136029	-0.650269	0.287922
H	4.280890	3.234007	0.067777
H	3.997137	-1.721993	-0.347974
H	2.130997	2.185417	-0.568689
H	0.112575	-1.265010	-2.020161
H	-5.141371	3.131521	-0.198791
H	-6.107410	1.884242	0.593912
H	-5.942419	1.872441	-1.165667
H	-1.144450	1.099402	1.459140
H	-3.131425	2.554692	1.199243
H	-4.954186	-0.375841	-1.366121
H	-2.974511	-1.841186	-1.107602

adduct3

Zero-point correction=	0.249641 (Hartree/Particle)
Thermal correction to Energy=	0.271278

Thermal correction to Enthalpy= 0.272223

Thermal correction to Gibbs Free Energy= 0.187711

Sum of electronic and zero-point Energies= -1291.847631

Sum of electronic and thermal Energies= -1291.825994

Sum of electronic and thermal Enthalpies= -1291.825049

Sum of electronic and thermal Free Energies= -1291.909561

C	-5.75500800	-1.17411700	-0.24965700
C	-4.48907700	-1.28180100	-0.80280700
C	-3.34241000	-0.81155300	-0.08545100
C	-3.54718300	-0.24003700	1.21201800
C	-4.82343100	-0.14378400	1.74266800
C	-5.93502300	-0.60740700	1.02177400
H	-6.61528100	-1.53275400	-0.80864500
H	-4.34919200	-1.72081600	-1.78591600
H	-2.68603000	0.12054400	1.76610400
H	-4.96184500	0.29661900	2.72656600
H	-6.93154200	-0.52795200	1.44645300
C	-2.07180600	-0.93156000	-0.61070400
C	-0.88909800	-0.86264600	-1.16122300
H	-0.14484300	-1.65254400	-1.09118200
N	-1.70631200	2.11941400	-2.43040200
N	-1.09857500	1.19315700	-2.16072200
N	-0.34681800	0.23816400	-1.92993200
C	4.44655400	-1.58760700	0.00597400
C	3.28467300	-1.82592200	0.75742500
C	2.34715500	-0.81934800	0.97775800
C	2.59389300	0.44992100	0.44960300
C	3.72556400	0.71728000	-0.32370700
C	4.64830100	-0.30540100	-0.52958600
H	3.11055500	-2.81353400	1.17639200

H	1.45297500	-1.01426500	1.55973200
H	3.89090400	1.70350400	-0.74394400
H	5.53985400	-0.10416800	-1.11773900
C	5.46516200	-2.67778200	-0.20371400
H	6.21960800	-2.65970600	0.59470000
H	4.99942300	-3.66842900	-0.18956600
H	5.99415600	-2.55286900	-1.15410700
S	1.35676900	1.74507300	0.66744600
O	2.04045300	3.06562600	0.52551100
O	0.57020800	1.42945400	1.89788800

adduct4

Zero-point correction=	0.250091 (Hartree/Particle)
Thermal correction to Energy=	0.271503
Thermal correction to Enthalpy=	0.272447
Thermal correction to Gibbs Free Energy=	0.190054
Sum of electronic and zero-point Energies=	-1291.847899
Sum of electronic and thermal Energies=	-1291.826487
Sum of electronic and thermal Enthalpies=	-1291.825543
Sum of electronic and thermal Free Energies=	-1291.907936

C	4.78968900	-1.68559300	0.24634200
C	3.86407500	-0.76872300	0.71812900
C	3.90230300	0.59342000	0.27677900
C	4.92445600	0.97093500	-0.65263100
C	5.83863700	0.03490100	-1.10896800
C	5.78203500	-1.29596400	-0.66662700
H	4.74308000	-2.71634400	0.58768000
H	3.09230700	-1.07028900	1.41944200
H	4.96882800	2.00074800	-0.99364700

H	6.60608200	0.33765300	-1.81643200
H	6.50349200	-2.02198600	-1.03011600
C	3.00031000	1.52082300	0.75843500
C	2.02879300	2.33722100	1.06951400
H	2.05995000	3.01195100	1.92201300
N	0.26664500	1.16821500	-1.52209800
N	0.56395500	1.78172500	-0.60706900
N	0.77303800	2.50344900	0.37266100
C	-5.13975500	0.52468100	-0.22465400
C	-4.05072900	1.20673200	0.34419300
C	-2.80947100	0.59400000	0.48879600
C	-2.66937000	-0.73447000	0.07735600
C	-3.72255100	-1.43744600	-0.50964300
C	-4.95549800	-0.80165200	-0.64349400
H	-4.17717500	2.23268900	0.68033000
H	-1.97768100	1.13074200	0.93242200
H	-3.59186500	-2.46336700	-0.83673900
H	-5.78805900	-1.34643500	-1.08041200
C	-6.46752700	1.21568600	-0.39787900
H	-6.42876600	1.92665400	-1.23398800
H	-7.26771800	0.49929400	-0.60670900
H	-6.73700700	1.78749700	0.49723400
S	-1.05168400	-1.52493200	0.19519300
O	-1.25854900	-3.00348100	0.23707200
O	-0.27849800	-0.83788400	1.27261500

TS3-*trans*

Zero-point correction=	0.250685 (Hartree/Particle)
Thermal correction to Energy=	0.270558
Thermal correction to Enthalpy=	0.271503

Thermal correction to Gibbs Free Energy= 0.196795

Sum of electronic and zero-point Energies= -1291.837208

Sum of electronic and thermal Energies= -1291.817335

Sum of electronic and thermal Enthalpies= -1291.816390

Sum of electronic and thermal Free Energies= -1291.891098

C	-4.11489400	-1.70946300	-1.34335700
C	-3.10320400	-0.76733600	-1.44536700
C	-2.08809300	-0.67207200	-0.44152300
C	-2.14857200	-1.57885200	0.65527800
C	-3.17204900	-2.51177100	0.74133300
C	-4.15882300	-2.58695900	-0.25102500
H	-4.87816100	-1.76143800	-2.11507900
H	-3.06826300	-0.08837100	-2.29207600
H	-1.39399500	-1.53214400	1.43180700
H	-3.20500400	-3.19105700	1.58883100
H	-4.95378400	-3.32336800	-0.17548900
C	-1.04388800	0.25533200	-0.63637800
C	-0.83461400	1.44120100	-1.26711200
H	0.05571200	1.62854400	-1.86055200
N	-3.55506500	2.74644300	0.19472800
N	-2.60831000	2.60612300	-0.42013400
N	-1.57941800	2.61908000	-1.12229000
C	4.41172000	-0.63873300	-0.76013800
C	3.67063200	-1.58702200	-0.03849600
C	2.49142500	-1.23548500	0.61702100
C	2.05292600	0.08858100	0.55883900
C	2.76253100	1.05323800	-0.15991000
C	3.93864800	0.68210000	-0.80938900
H	4.01923500	-2.61555000	0.00990900
H	1.92842600	-1.97854600	1.17242600

H	2.41149400	2.07907300	-0.19777500
H	4.49869700	1.43165600	-1.36317900
C	5.69686000	-1.02096900	-1.45012500
H	6.56471100	-0.77667900	-0.82259400
H	5.73505500	-2.09489300	-1.65865600
H	5.81891700	-0.47941900	-2.39439400
S	0.48686100	0.53668700	1.34255500
O	0.52318000	2.00924000	1.58429100
O	0.31595900	-0.37887300	2.51719700

TS3-*cis*

Zero-point correction=	0.250743 (Hartree/Particle)
Thermal correction to Energy=	0.270507
Thermal correction to Enthalpy=	0.271451
Thermal correction to Gibbs Free Energy=	0.197867
Sum of electronic and zero-point Energies=	-1291.837799
Sum of electronic and thermal Energies=	-1291.818035
Sum of electronic and thermal Enthalpies=	-1291.817091
Sum of electronic and thermal Free Energies=	-1291.890675

C	-1.81161100	3.17658200	0.39783300
C	-1.45214200	1.84781200	0.57331000
C	-2.16507300	0.80885900	-0.08772800
C	-3.25399200	1.18331400	-0.93356100
C	-3.59384800	2.51652900	-1.10687800
C	-2.87648000	3.52222600	-0.44460800
H	-0.64230900	1.59980600	1.24853700
C	-1.81800300	-0.55829600	-0.00087400
C	-2.53634300	-1.71768000	0.05711200
N	-0.41698000	-3.18755700	-2.07178200

N	-1.25407500	-2.97548600	-1.33337100
N	-2.21670700	-2.92717100	-0.54169800
C	3.79154800	0.93290000	-0.73885500
C	3.17633600	-0.21417900	-1.26407500
C	2.10032600	-0.81799800	-0.61595000
C	1.63443500	-0.26959900	0.58119300
C	2.21664800	0.87929800	1.12073200
C	3.29471700	1.46659200	0.46027700
C	4.97333700	1.56175600	-1.43268700
S	0.20036100	-1.01853000	1.39789500
O	0.18133200	-0.49690100	2.80060700
O	0.31266700	-2.49271500	1.18435000

Int3

Zero-point correction=	0.255857 (Hartree/Particle)
Thermal correction to Energy=	0.275106
Thermal correction to Enthalpy=	0.276050
Thermal correction to Gibbs Free Energy=	0.203858
Sum of electronic and zero-point Energies=	-1291.931012
Sum of electronic and thermal Energies=	-1291.911762
Sum of electronic and thermal Enthalpies=	-1291.910818
Sum of electronic and thermal Free Energies=	-1291.983011

C	-1.57625200	-2.74046400	-0.59920000
C	-1.19855800	-1.40743900	-0.76466600
C	-1.48301400	-0.45991500	0.23389700
C	-2.13555700	-0.87460400	1.40732300
C	-2.50750000	-2.20882200	1.56936000
C	-2.23128800	-3.14295800	0.56687700
H	-1.35752700	-3.46290500	-1.38071300

H	-0.68732600	-1.09295000	-1.67020300
H	-2.35474700	-0.14841000	2.18322300
H	-3.01883600	-2.51816000	2.47685700
H	-2.52542800	-4.18122600	0.69491900
C	-1.09939300	0.95918800	0.03385700
C	-1.68461200	1.85601900	-0.78518300
H	-1.27755600	2.85585000	-0.87868200
N	-4.25826600	-0.16361700	-1.70611700
N	-3.50545000	0.67717900	-1.57495600
N	-2.81647400	1.71466100	-1.58799300
C	3.89794500	-0.80703000	-0.64023200
C	3.20183600	-1.23794600	0.50086900
C	2.11508300	-0.52180000	0.99608900
C	1.71849200	0.64880900	0.34232600
C	2.39270100	1.10261200	-0.79365100
C	3.47780500	0.37140300	-1.27449100
H	3.51705400	-2.14533800	1.01009100
H	1.59105300	-0.85845500	1.88407100
H	2.08378200	2.01704200	-1.28967700
H	4.00930800	0.72437600	-2.15431000
C	5.06709300	-1.60040000	-1.16609500
H	5.81929000	-1.76021900	-0.38410500
H	4.74544200	-2.59265100	-1.50751100
H	5.54960600	-1.09347500	-2.00705200
S	0.31834300	1.58125400	0.96337900
O	0.52092900	3.00257300	0.60985300
O	0.12220100	1.21480100	2.38139600

Int4

Zero-point correction= 0.255944 (Hartree/Particle)

Thermal correction to Energy=	0.275047
Thermal correction to Enthalpy=	0.275991
Thermal correction to Gibbs Free Energy=	0.205497
Sum of electronic and zero-point Energies=	-1291.922138
Sum of electronic and thermal Energies=	-1291.903035
Sum of electronic and thermal Enthalpies=	-1291.902091
Sum of electronic and thermal Free Energies=	-1291.972585

C	-3.71497300	1.89512700	0.60680000
C	-2.92740800	0.75793500	0.78360300
C	-2.07475200	0.31791700	-0.24436100
C	-2.03228300	1.04416000	-1.44732100
C	-2.82606500	2.17896300	-1.62194000
C	-3.66725800	2.60896200	-0.59414200
H	-4.37449800	2.21952400	1.40733500
H	-2.97614200	0.20397300	1.71381800
H	-1.36885800	0.71733800	-2.24310600
H	-2.78097200	2.72804500	-2.55860400
H	-4.28343300	3.49419900	-0.72718400
C	-1.24087900	-0.91111900	-0.11102600
C	-1.44385300	-1.92940000	-0.98476800
H	-2.30590900	-1.81904800	-1.63652700
N	1.33080500	-3.97600500	-0.86699500
N	0.31243700	-3.48603700	-0.97840000
N	-0.84908900	-3.15527500	-1.26172200
C	3.32708600	1.86595100	-0.30461000
C	3.37531300	0.48591700	-0.56063500
C	2.37080800	-0.36693000	-0.11116800
C	1.30111200	0.16624200	0.61454400
C	1.22886100	1.53462800	0.88877100
C	2.24329800	2.37209600	0.42778400

H	4.21374700	0.07292400	-1.11568800
H	2.42862000	-1.43140300	-0.31233900
H	0.40406900	1.93727300	1.46658200
H	2.19438900	3.43562200	0.64635500
C	4.40806600	2.78053300	-0.82131000
H	4.43057400	3.72521400	-0.26919000
H	5.39527000	2.31120800	-0.74918400
H	4.24072200	3.01982100	-1.88019700
S	-0.00628800	-0.91241700	1.19948000
O	-0.60878900	-0.27845200	2.38790100
O	0.52897800	-2.28413200	1.32394400

TS4

Zero-point correction=	0.255386 (Hartree/Particle)
Thermal correction to Energy=	0.273926
Thermal correction to Enthalpy=	0.274870
Thermal correction to Gibbs Free Energy=	0.205130
Sum of electronic and zero-point Energies=	-1291.923079
Sum of electronic and thermal Energies=	-1291.904539
Sum of electronic and thermal Enthalpies=	-1291.903595
Sum of electronic and thermal Free Energies=	-1291.973335

C	1.27419500	2.94392500	-0.97910900
C	1.12150500	1.55898100	-1.03641700
C	1.32197600	0.77535600	0.11284600
C	1.67071300	1.40271600	1.32006600
C	1.82174600	2.78900500	1.37079900
C	1.62388600	3.56198000	0.22423300
H	1.11594000	3.53952400	-1.87401800
H	0.84321800	1.07893300	-1.96998400

H	1.82668800	0.80488900	2.21138100
H	2.09743300	3.26431100	2.30824600
H	1.74200800	4.64132700	0.26791700
C	1.16376000	-0.69655400	0.02477500
C	1.88297700	-1.53401600	-0.73302900
H	1.65772000	-2.59539800	-0.78711000
N	5.17566800	-0.87213800	-0.90949600
N	4.07380400	-1.00043100	-1.16912600
N	2.92255300	-1.08854200	-1.60276400
C	-4.02211900	0.35702700	-0.65069000
C	-3.40823900	0.88788000	0.49201600
C	-2.23197000	0.33811900	1.00202700
C	-1.66562700	-0.76273000	0.35777300
C	-2.25498000	-1.31482600	-0.78507300
C	-3.42688200	-0.75080000	-1.27874300
H	-3.85576200	1.74242400	0.99241500
H	-1.76915700	0.75275000	1.89096700
H	-1.80969400	-2.17478700	-1.27489600
H	-3.89101900	-1.17816400	-2.16404200
C	-5.29805700	0.94703900	-1.19489400
H	-5.57825700	1.85878900	-0.65892600
H	-5.19795600	1.19012900	-2.25956700
H	-6.12747200	0.23357500	-1.10655600
S	-0.15517400	-1.48014000	0.99871100
O	-0.15709900	-2.92478900	0.69054400
O	0.00554900	-1.04607300	2.40133300

4a

Zero-point correction=	0.255911 (Hartree/Particle)
Thermal correction to Energy=	0.275139

Thermal correction to Enthalpy= 0.276084

Thermal correction to Gibbs Free Energy= 0.204451

Sum of electronic and zero-point Energies= -1291.934206

Sum of electronic and thermal Energies= -1291.914978

Sum of electronic and thermal Enthalpies= -1291.914034

Sum of electronic and thermal Free Energies= -1291.985667

C	2.14332200	-1.23121700	-0.11729300
C	1.25337400	-0.35277400	0.38526700
C	-1.56188600	-0.74688800	0.49805800
C	-1.95905900	-1.62082700	-0.52000300
C	-3.13176600	-1.35488300	-1.21946300
C	-3.91724600	-0.22796300	-0.92133300
C	-3.49459800	0.62900000	0.10385200
C	-2.32111000	0.37987900	0.81649000
C	-5.18837000	0.03893200	-1.68658500
C	1.23996900	1.10978000	0.14447100
C	1.32050400	2.03095400	1.20299000
C	1.31707600	3.40199500	0.94434700
C	1.23322200	3.87214000	-0.36851800
C	1.15115800	2.96347800	-1.42657700
C	1.15102100	1.59205700	-1.17359600
N	4.00517400	-1.65918200	-1.31190100
N	3.22794400	-0.79020900	-0.88042600
N	4.79724200	-2.32970200	-1.77525300
O	-0.10685000	-0.34332900	2.67777600
O	0.15737900	-2.54456400	1.42783900
S	-0.04803700	-1.08074200	1.39831600
H	2.05050600	-2.29684200	0.07066500
H	1.38995500	1.67022700	2.22324200
H	1.38503000	4.10353100	1.77150600

H	1.23136500	4.94073600	-0.56614800
H	1.08170300	3.32117400	-2.45033100
H	1.07644100	0.88758000	-1.99668700
H	-2.00802500	1.04608800	1.61306400
H	-1.36562100	-2.49854900	-0.75488800
H	-3.44645600	-2.03329900	-2.00855800
H	-4.09085400	1.50333800	0.35116100
H	-5.92586500	-0.75464200	-1.51071200
H	-5.63967200	0.99137000	-1.39310900
H	-5.00031600	0.06596000	-2.76676100