Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-Assisted Wittig-Type Olefination of Aldehydes with *p*-Toluenesulfonylmethyl Isocyanide

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I. General information

All reagents were purchased from commercial sources and used without treatment unless otherwise indicated. The products were purified by column chromatography over silica gel. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 25 °C on a Varian spectrometer at 400 MHz, 101 MHz and 376 MHz, respectively, and TMS was used as the internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High-resolution mass spectra (HRMS) were recorded on Bruck microTof using the ESI-TOF method.

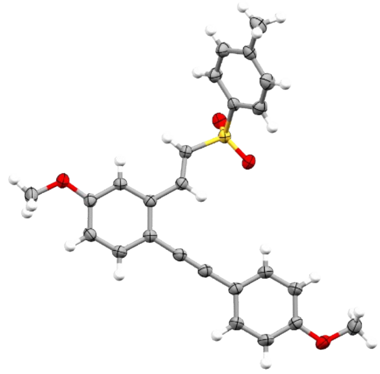
II. Computational details

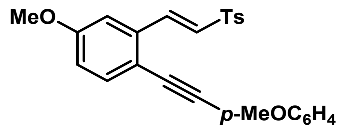
All the calculations in this work were performed based on density functional theory (DFT) in the Gaussian G16 package (Revision B.01).[1] Geometry optimizations and frequencies were calculated with the B3LYP,[2] dispersion-corrected with the D3 version of Grimme's dispersion with Becke-Johnson damping (B3LYP-D3(BJ))[3] and Stuttgart-Dresden effective core potential SDD[4] for Cu and basis set 6-31+G(d, p) for rest of the atoms.[5] All of the optimized geometries had been characterized as minima (zero imaginary frequencies) or transition state structures (a single imaginary frequency) at the same level of theory. Intrinsic reaction coordinate (IRC)[6] calculations were also carried out to inspect whether the transition structures connected the proposed reactant and product.

III. Crystallography

The structures of the *N*-fused heterocyclic scaffolds were further established by X-ray diffraction. Single-crystal X-ray diffraction data for the reported compounds was recorded at a temperature of 296(2) K on an Oxford Diffraction Gemini R Ultra diffractometer using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by the Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.[7] Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement are summarized in Table S1.

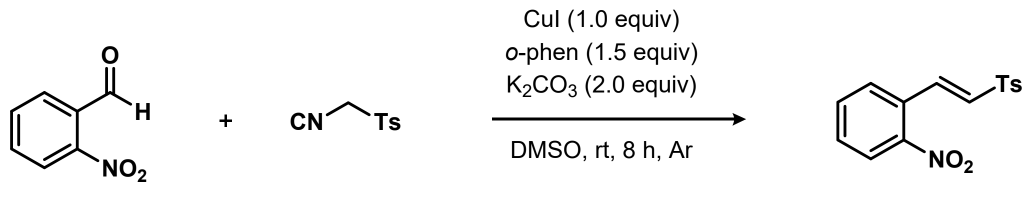
Table S1. Crystal structure and refinement data for compound **3aa** (thermal ellipsoids at 30% probability).





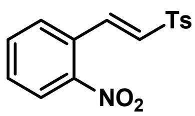
Empirical formula	$C_{18}H_{17}NO_3$
Temperature	296(2) K
Wavelength	0.71073 Å
Space group	P2(1)/c
Unit cell dimensions	a = 15.137(2) Å b = 16.348(2) Å c = 8.7649(13) Å alpha = 90.00 deg. beta = 97.271(2) deg. gamma = 90.00 deg.
Volume	2151.5(5) Å^3
Z	4
Calculated density	1.292 Mg/m^3
Absorption coefficient	0.179 mm^{-1}
F(000)	880
Crystal size	0.122 x 0.103 x 0.092 mm
Theta range for data collection	2.65 to 25.00 deg.
Reflections collected / unique	10685 / 3788 [R(int) = 0.0203]
Data / restraints / parameters	3788/ 0 / 271
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1197
R indices (all data)	R1 = 0.0545, wR2 = 0.1285

IV. Synthesis and analytical data of compound 3

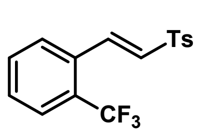


Typical synthetic procedure (with 3a as an example): To a 25 mL Schlenk tube equipped with a magnetic stir bar was added 2-nitrobenzaldehyde **1a** (91 mg, 0.6 mmol), TosMIC **2** (98 mg, 0.5 mmol), DMSO (2.0 mL), K_2CO_3 (138 mg, 1.0 mmol), CuI (95 mg, 0.5 mmol) and *o*-phen (135 mg, 0.75 mmol). The reaction mixture was stirred at 25 °C for about 10 h. The resulting mixture was concentrated and the residue was taken up in CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 10:1) afforded **3a** as pale yellow solid in 88% yield (133 mg).

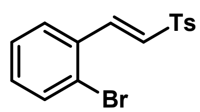
Gram-scale synthesis: To a 50 mL Schlenk tube equipped with a magnetic stir bar was added 2-nitrobenzaldehyde **1a** (0.91 g, 6 mmol), TosMIC **2** (0.98 g, 5 mmol), CuI (0.95 g, 5 mmol), DMSO (20 mL), K_2CO_3 (1.38 g, 10 mmol), and *o*-phen (1.35 g, 7.5 mmol). The reaction mixture was stirred at 25 °C for about 10 h. The resulting mixture was concentrated and the residue was taken up in CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 10:1) afforded **3a** as pale yellow solid in 79% yield (1.2 g).



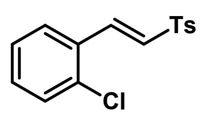
(*E*)-1-Nitro-2-(2-tosylvinyl)benzene (3a):[8] Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 86% (100 mg); pale yellow soild, mp 119–120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.15-8.10 (m, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.69–7.65 (m, 1H), 7.60–7.53 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 15.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 147.9, 144.9, 138.6, 136.8, 133.9, 132.5, 130.9, 130.1, 129.6, 129.1, 128.0, 125.2, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{13}NNaO_4S$ [M + Na]$^+$: 326.0457, found 326.0443.



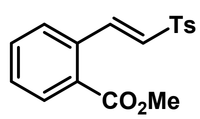
(*E*)-1-(2-Tosylvinyl)-2-(trifluoromethyl)benzen (3b): Column chromatography (silica gel; petroleum ether/ethyl acetate 12:1); yield: 91% (148 mg); white soild, mp 106–107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.02 (dd, *J* = 15.6, 2.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.60–7.49 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 15.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 144.7, 137.8 (q, $J_{C\text{–}F}$ = 2.3 Hz), 137.0, 132.2, 131.4 (q, $J_{C\text{–}F}$ = 2.0 Hz), 130.3, 130.0, 129.5, 128.9 (q, $J_{C\text{–}F}$ = 30.5 Hz), 128.3, 127.9, 126.3 (q, $J_{C\text{–}F}$ = 5.5 Hz), 123.7 (d, $J_{C\text{–}F}$ = 272 Hz), 21.6; ^{19}F NMR ($CDCl_3$, 376 MHz): δ_F –58.9; HRMS (ESI-TOF, *m/z*): Calcd for $C_{16}H_{13}F_3NaO_2S$ $[M + Na]^+$: 349.0481, found 349.0469.



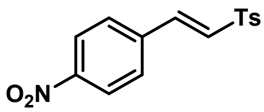
(*E*)-1-Bromo-2-(2-tosylvinyl)benzene (3c):[9] Column chromatography (silica gel; petroleum ether/ethyl acetate 12:1); yield: 82% (137 mg); white soild, mp 119–120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.15–8.10 (m, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.69–7.65 (m, 1H), 7.60–7.53 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 15.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 147.8, 144.9, 138.6, 136.8, 133.9, 132.5, 130.9, 130.1, 129.5, 129.1, 128.0, 125.2, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{13}BrNaO_2S$ $[M + Na]^+$: 358.9712, found 358.9716.



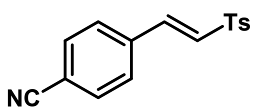
(*E*)-1-Chloro-2-(2-tosylvinyl)benzene (3d):[10] Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 79% (115 mg); white soild, mp 105–106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.04 (d, *J* = 15.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.33-7.31 (m, 1H), 7.27–7.24 (m, 1H), 6.87 (d, *J* = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 144.6, 137.9, 137.3, 135.3, 131.8, 130.8, 130.4, 130.35, 130.0, 128.2, 127.9, 127.2, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{13}ClNaO_2S$ $[M + Na]^+$: 315.0217, found 315.0219.



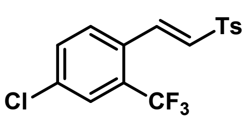
(*E*)-Methyl 2-(2-tosylvinyl)benzoate (3e): Column chromatography (silica gel; petroleum ether/ethyl acetate 8:1); yield: 88% (139 mg); white soild, mp 115–116 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.43 (d, *J* = 15.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.58–7.42 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 3.94 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 166.7, 144.4, 142.0, 137.5, 134.4, 132.5, 131.0, 130.1, 130.0, 129.9, 128.2, 127.9, 52.5, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{17}H_{16}NaO_4S$ [M + Na]$^+$: 339.0662, found 339.0675.



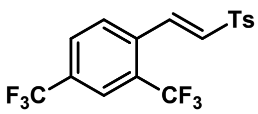
(*E*)-1-Methyl-4-((4-nitrostyryl)sulfonyl)benzene (3f):[8] Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 83% (126 mg); pale yellow soild, mp 185–186 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.24 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 15.5 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 15.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 147.9, 144.0, 137.7, 137.5, 135.7, 131.0 129.1, 128.1, 126.9, 123.2, 20.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{13}NNaO_4S$ [M + Na]$^+$: 326.0457, found 326.0463.



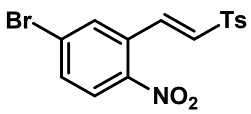
(*E*)-4-(2-Tosylvinyl)benzonitrile (3g):[11] Column chromatography (silica gel; petroleum ether/ethyl acetate 9:1); yield: 72% (102 mg); yellow soild, mp 123–125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.83 (d, *J* = 8.0 Hz, 2H), 7.73–7.53 (m, 5H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 145.0, 139.2, 136.8, 136.7, 132.7, 131.3, 130.1, 128.8, 127.9, 118.0, 114.2, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{13}NNaO_4S$ [M + Na]$^+$: 306.0559, found 306.0563.



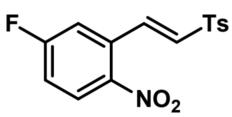
(*E*)-4-Chloro-1-(2-tosylvinyl)-2-(trifluoromethyl)benzene (3h): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 85% (153 mg); white soild, mp 151–152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.92 (d, *J* = 15.6 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.83 (*J* = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 145.0, 138.6, 137.6, 136.2, 133.5, 133.3, 130.1, 128.4, 127.9, 127.9 (q, $J_{C–F}$ = 11.1 Hz), 127.2 (d, $J_{C–F}$ = 31 Hz), 123.2 (d, $J_{C–F}$ = 273 Hz), 119.2, 21.6; ^{19}F NMR ($CDCl_3$, 376 MHz): δ_F –58.8; HRMS (ESI-TOF, *m/z*): Calcd for $C_{16}H_{12}ClF_3NaO_2S$ [M + Na]$^+$: 383.0091, found 383.0099.



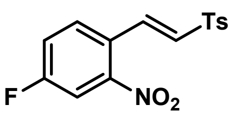
(*E*)-1-(2-Tosylvinyl)-2,4-bis(trifluoromethyl)benzene (3i): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 68% (142 mg); white solid, mp 164–165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.00 (d, J = 16.4 Hz, 1H), 7.96 (s, 1H), 7.84–7.82 (m, 3H), 7.71 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 15.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 145.2, 136.4, 136.1, 135.2, 134.7, 132.8, 131.8, 131.1 (q, $J_{C–F}$ = 213 Hz), 129.2, 129.1 (d, $J_{C–F}$ = 212 Hz), 126.9, 123.6 (q, $J_{C–F}$ = 10 Hz), 122.9 (d, $J_{C–F}$ = 212 Hz), 118.8, 21.7; ^{19}F NMR ($CDCl_3$, 376 MHz): δ_F –59.4, –63.1; HRMS (ESI-TOF, *m/z*): Calcd for $C_{17}H_{12}F_6NaO_2S$ [M + Na]$^+$: 417.0354, found 417.0366.



(*E*)-4-Bromo-1-nitro-2-(2-tosylvinyl)benzene (3j): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 92% (175 mg); pale yellow soild, mp 171–172 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.07 (d, J = 15.2 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.73–7.65 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.76 (q, J = 15.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 146.4, 145.1, 137.2, 136.5, 133.8, 133.6, 132.4, 131.0, 130.2, 128.9, 128.1, 126.7, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}BrNNaO_4S$ [M + Na]$^+$: 403.9563, found 403.9571.

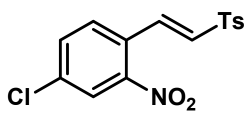


(*E*)-4-Fluoro-1-nitro-2-(2-tosylvinyl)benzene (3k): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 86% (138 mg); pale yellow soild, mp 132–133 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.19 (dd, J = 9.2, 4.8 Hz, 1H), 8.12 (d, J = 15.2 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.31–7.17 (m, 2H), 6.75 (d, J = 15.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 164.9 (d, $J_{C–F}$ = 258 Hz), 145.1, 137.5, 136.5, 133.6, 132.5, 132.4, 130.2, 128.2 (d, $J_{C–F}$ = 9.6 Hz), 128.1, 117.7 (d, $J_{C–F}$ = 23 Hz), 116.6 (d, $J_{C–F}$ = 24 Hz), 21.7; ^{19}F NMR ($CDCl_3$, 376 MHz): δ_F –101.5; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}FNNaO_4S$ [M + Na]$^+$: 344.0363, found 344.0377.

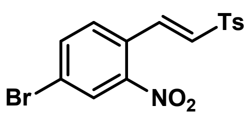


(*E*)-4-Fluoro-2-nitro-1-(2-tosylvinyl)benzene (3l): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 81% (130 mg); pale yellow soild, mp 149–150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.07 (d, J = 19.6 Hz, 1H), 7.98–7.80 (m, 3H), 7.62–7.51 (m, 1H), 7.48–7.32 (m, 3H), 6.74 (d, J = 19.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR

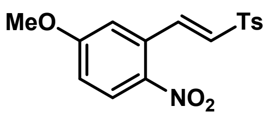
(CDCl$_3$, 101 MHz): δ_C 162.9 (d, J_{C-F} = 254 Hz), 145.0, 137.4, 136.6, 132.8, 131.3 (d, J_{C-F} = 8.0 Hz), 130.1, 128.1, 125.4 (d, J_{C-F} = 4.0 Hz), 121.5, 121.3, 113.0 (d, J_{C-F} = 27 Hz), 21.7; ^{19}F NMR (CDCl$_3$, 376 MHz): δ_F –105.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}FNNaO_4S$ [M + Na]$^+$: 344.0363, found 344.0372.



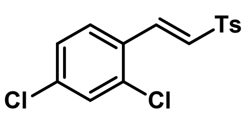
(*E*)-4-Chloro-2-nitro-1-(2-tosylvinyl)benzene (3m): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 80% (134 mg); pale yellow soild, mp 157–158 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 8.10 (d, *J* = 2.0 Hz, 1H), 8.04 (d, *J* = 15.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 6.21 (dd, *J* = 2.0 and 8.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 15.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ_C 148.1, 145.0, 137.2, 137.0, 136.5, 134.0, 133.1, 130.6, 130.1, 128.1, 127.5, 125.4, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}ClNNaO_4S$ [M + Na]$^+$: 360.0068, found 360.0083.



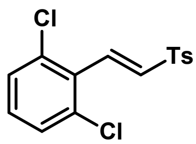
(*E*)-4-Bromo-2-nitro-1-(2-tosylvinyl)benzene (3n): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 93% (176 mg); pale yellow soild, mp 173–174 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 8.25 (s, 1H), 8.02 (d, *J* = 15.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.77 (dd, *J* = 1.6 and 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.77 (dd, *J* = 2.0 and 15.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ_C 148.1, 145.1, 137.3, 136.9, 136.5, 133.1, 130.7, 130.2, 128.3, 128.1, 127.9, 124.5, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}BrNNaO_4S$ [M + Na]$^+$: 403.9563, found 403.9567.



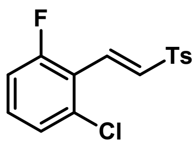
(*E*)-4-Methoxy-1-nitro-2-(2-tosylvinyl)benzene (3o): Column chromatography (silica gel; petroleum ether/ethyl acetate 8:1); yield: 95% (158 mg); pale yellow soild, mp 164–165 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 8.23–8.15 (m, 2H), 7.92–7.86 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.78 (dd, *J* = 2.8 and 9.2 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.69 (d, *J* = 15.2 Hz, 1H), 3.91 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ_C 163.7, 144.9, 140.6, 140.0, 136.8, 132.3, 132.2, 130.1, 128.1, 127.9, 115.4, 114.5, 56.2, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{16}H_{15}NNaO_5S$ [M + Na]$^+$: 356.0563, found 356.0573.



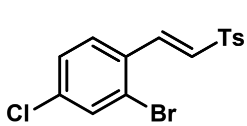
(*E*)-2,4-Dichloro-1-(2-tosylvinyl)benzene (3p):[12] Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 89% (145 mg); white soild, mp 139–140 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.98 (d, J = 15.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.46–7.43 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.25 (dd, J = 8.4, 2.0 Hz, 1H), 6.87 (d, J = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 144.7, 137.2, 137.1, 136.6, 135.9, 130.8, 130.2, 130.1, 129.4, 128.9, 127.9, 127.7, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}Cl_2NaO_2S$ [M + Na]$^+$: 348.9827, found 348.9839.



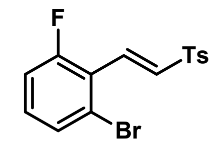
(*E*)-1,3-Dichloro-2-(2-tosylvinyl)benzene (3q):[13] Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 67% (109 mg); white soild, mp 127–128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.85 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 15.6 Hz, 1H), 7.37–7.34 (m, 4H), 7.24–7.20 (m, 1H), 7.14 (d, J = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 144.7, 137.0, 135.7, 135.23, 135.2, 130.6, 130.0, 129.7, 128.9, 127.9, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}Cl_2NaO_2S$ [M + Na]$^+$: 348.9827, found 348.9836.



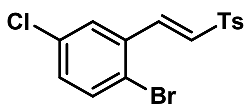
(*E*)-1-Chloro-3-fluoro-2-(2-tosylvinyl)benzene (3r): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 73% (117 mg); white soild, mp 112–113 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.89 (d, J = 16 Hz, 1H), 7.85–7.83 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.25–7.19 (m, 1H), 7.16 (d, J = 15.6 Hz, 1H), 7.10–7.05 (m, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 161.7 (d, $J_{C–F}$ = 256.6 Hz), 144.6, 137.1, 134.40 (d, $J_{C–F}$ = 15.5 Hz), 134.38 (d, $J_{C–F}$ = 2.2 Hz), 132.1 (d, $J_{C–F}$ = 10.2 Hz), 130.0, 129.5 (d, $J_{C–F}$ = 3.4 Hz), 127.9, 126.5 (d, $J_{C–F}$ = 3.8 Hz), 121.3 (d, $J_{C–F}$ = 15.4 Hz), 115.6 (d, $J_{C–F}$ = 23.0 Hz), 21.6; ^{19}F NMR ($CDCl_3$, 376 MHz): δ_F –106.5; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}FNNaO_4S$ [M + Na]$^+$: 344.0363, found 344.0369.



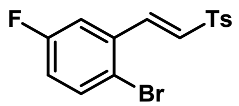
(*E*)-2-Bromo-4-chloro-1-(2-tosylvinyl)benzene (3s): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 81% (149 mg); white soild, mp 144–145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.95 (d, J = 15.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.29 (dd, J = 8.4, 2.0 Hz, 1H), 6.83 (d, J = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 144.7, 139.0, 137.2, 137.0, 133.2, 131.1, 130.9, 130.1, 128.8, 128.2, 127.9, 125.7, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}BrClNaO_2S$ [M + Na]$^+$: 392.9322, found 392.9339.



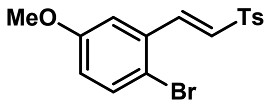
(*E*)-1-Bromo-3-fluoro-2-(2-tosylvinyl)benzene (3t): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 84% (149 mg); white soild, mp 131–132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.89 (d, *J* = 16.0 Hz, 1H), 7.85–7.83 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25–7.19 (m, 1H), 7.16 (d, *J* = 15.6 Hz, 1H), 7.10–7.05 (m, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 161.9 (d, $J_{C–F}$ = 256.0 Hz), 144.6, 137.1, 136.3 (d, $J_{C–F}$ = 4.8 Hz), 134.2 (d, $J_{C–F}$ = 15.1 Hz), 131.8 (d, $J_{C–F}$ = 10.6 Hz), 131.6 (d, $J_{C–F}$ = 1.5 Hz), 130.0, 127.9, 126.1 (d, $J_{C–F}$ = 3.4 Hz), 119.6 (d, $J_{C–F}$ = 13.5 Hz), 114.9 (d, $J_{C–F}$ = 23.0 Hz), 21.6; ^{19}F NMR ($CDCl_3$, 376 MHz): δ_F –105.8; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}BrFNaO_2S$ [M + Na]$^+$: 376.9618, found 376.9619.



(*E*)-1-Bromo-4-chloro-2-(2-tosylvinyl)benzene (3u): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 80% (148 mg); white soild, mp 140–141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.93 (d, *J* = 15.6 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.81 (d, *J* = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 147.8, 144.9, 138.6, 136.8, 133.9, 132.5, 130.9, 130.1, 129.5, 129.1, 128.0, 125.2, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}BrClNaO_2S$ [M + Na]$^+$: 392.9322, found 392.9336.

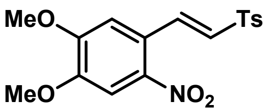


(*E*)-1-Bromo-4-fluoro-2-(2-tosylvinyl)benzene (3v): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 85% (150 mg); white soild, mp 128–129 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.94 (d, *J* = 15.6 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.59 (dd, *J* = 8.8, 5.2 Hz, 1H),7.36 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.03–6.97 (m, 1H), 6.80 (d, *J* = 15.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 161.8 (d, $J_{C–F}$ = 247.0 Hz), 144.9, 139.3, 136.8, 134.9 (d, $J_{C–F}$ = 12.0 Hz), 134.3, 134.2, 131.7, 129.0 (d, $J_{C–F}$ = 213 Hz), 119.7, 119.2 (d, $J_{C–F}$ = 22.0 Hz), 119 (d, $J_{C–F}$ = 24.0 Hz), 21.6; ^{19}F NMR ($CDCl_3$, 376 MHz): δ_F –113.2; HRMS (ESI-TOF, *m/z*): Calcd for $C_{15}H_{12}BrFNaO_2S$ [M + Na]$^+$: 376.9618, found 376.9624.

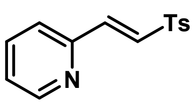


(*E*)-1-Bromo-4-methoxy-2-(2-tosylvinyl)benzene (3w): Column chromatography (silica gel; petroleum ether/ethyl acetate 9:1); yield: 90% (165 mg); white soild, mp 153–154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.95 (d,

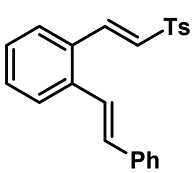
J = 15.2 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 3.2 Hz, 1H), 6.85–6.77 (m, 2H), 3.78 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 159.0, 144.6, 140.6, 137.2, 134.2, 133.2, 130.6, 130.0, 127.9, 118.3, 116.1, 113.0, 55.6, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{16}H_{15}BrNaO_3S$ [M + Na]$^+$: 388.9817, found 388.9834.



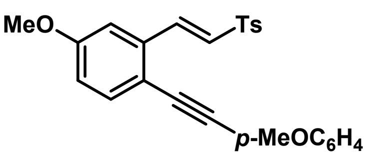
(*E*)-1,2-Dimethoxy-4-nitro-5-(2-tosylvinyl)benzene (3x): Column chromatography (silica gel; petroleum ether/ethyl acetate 8:1); yield: 91% (165 mg); pale yellow soild, mp 169–170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.18 (d, J = 15.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.67 (s, 1H), 7.37 (d, J = 8.4 Hz, 2H), 6.87 (s, 1H), 6.70 (d, J = 15.2 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 153.4, 150.2, 144.8, 140.8, 139.5, 136.9, 131.2, 130.1, 128.0, 123.5, 110.3, 107.9, 56.7, 56.6, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{17}H_{17}NNaO_6S$ [M + Na]$^+$: 386.0669, found 386.0673.



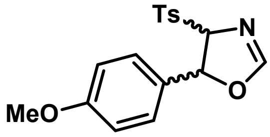
(*E*)-2-(2-Tosylvinyl)pyridine (3y):[10] Column chromatography (silica gel; petroleum ether/ethyl acetate 9:1); yield: 93% (120 mg); white soild, mp 92–93 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.60 (d, J = 4.8 Hz, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.73 (t, J = 3.6 Hz, 1H), 7.62 (d, J = 14.8 Hz, 1H), 7.47–7.37 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.31–7.25 (m, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 151.1, 150.3, 144.6, 140.0, 137.2, 137.0, 132.1, 130.0, 127.9, 125.4, 124.9, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{14}H_{13}NaO_2S$ [M + Na]$^+$: 282.0559, found 282.0567.



1-((*E*)-Styryl)-2-((*E*)-2-tosylvinyl)benzene (3z): Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 82% (157 mg); white soild, mp 109–110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.05 (d, J = 15.2 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 2H), 7.47–7.23 (m, 9H), 6.94 (d, J = 16.0 Hz, 1H), 6.80 (d, J = 15.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 144.4, 139.8, 138.0, 137.6, 136.7, 133.5, 130.7, 130.6, 130.0, 129.7, 128.8, 128.3, 127.74, 127.7, 127.3, 126.8, 124.9, 21.6; HRMS (ESI-TOF, *m/z*): Calcd for $C_{23}H_{20}NaO_2S$ [M + Na]$^+$: 383.4602, found 383.4619.

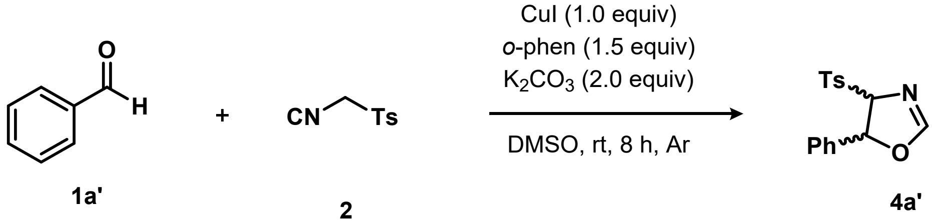


(*E*)-4-Methoxy-1-((4-methoxyphenyl)ethynyl)-2-(2-tosylvinyl)benzene (3aa): Column chromatography (silica gel; petroleum ether/ethyl acetate 8:1); yield: 87% (181 mg); white soild,

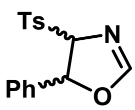


mp 101–102 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.20 (d, J = 15.6 Hz, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.49–7.43 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 15.6 Hz, 1H), 6.97 (d, J = 2.8 Hz, 1H), 6.93-6.87 (m, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 163.7, 144.9, 140.6, 140.0, 136.8, 132.2, 132.2, 130.1, 128.1, 127.9, 115.4, 114.5, 56.2, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{25}H_{22}NaO_4S$ [M + Na]$^+$: 441.1131, found 441.1139.

V. Synthesis and analytical data of compound 4



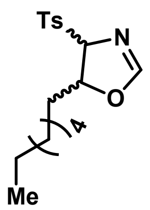
Typical synthetic procedure (with benzaldehyde as an example): To a 25 mL Schlenk tube equipped with a magnetic stir bar was added benzaldehyde **1a'** (61 μL, 0.6 mmol), TosMIC **2** (98 mg, 0.5 mmol), DMSO (2.0 mL), K_2CO_3 (138 mg, 1.0 mmol), CuI (95 mg, 0.5 mmol) and *o*-phen (135 mg, 0.75 mmol). The reaction mixture was stirred at 25 °C for about 10 h. The resulting mixture was concentrated and the residue was taken up in CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 10:1) afforded 5-phenyl-4-tosyl-4,5-dihydrooxazole **4a'** as a white solid in 91% yield (137 mg).



5-Phenyl-4-tosyl-4,5-dihydrooxazole (4a'):[14] Column chromatography (silica gel; petroleum ether/ethyl acetate 10:1); yield: 91% (137 mg); white soild, mp 172–173 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.84 (d, J = 7.6 Hz, 2H), 7.47–7.29 (m, 7H), 7.22 (s, 1H), 6.05 (d, J = 6.0 Hz, 1H), 5.04 (d, J = 6.0 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.2, 159.5, 145.7, 133.2, 129.9, 129.8, 129.7, 129.5, 129.1, 126.9, 114.5, 92.4, 79.4, 55.3, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{16}H_{16}NO_3S$ [M + H]$^+$: 302.0845, found 302.0856.

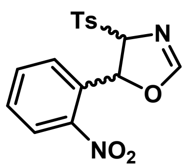
5-(4-Methoxyphenyl)-4-tosyl-4,5-dihydrooxazole (4b'):[14] Column chromatography (silica gel; petroleum ether/ethyl acetate 8:1); yield: 87% (144 mg); white soild, mp 156–157 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.83 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.19 (s, 1H), 6.90

(d, J = 8.0 Hz, 2H), 5.99 (d, J = 6.0 Hz, 1H), 5.02 (d, J = 6.0 Hz, 1H), 3.81 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 160.3, 159.6, 145.7, 133.3, 130.0, 129.96, 129.9, 129.8, 129.6, 129.5, 127.0, 126.9, 114.6, 114.1, 92.5, 79.5, 55.5, 21.8; HRMS (ESI-TOF, *m/z*): Calcd for $C_{17}H_{17}NO_4S$ [M + H]$^+$: 332.0951, found 332.0958.



5-Heptyl-4-tosyl-4,5-dihydrooxazole (4c'):[15] Column chromatography (silica gel; petroleum ether/ethyl acetate 5:1); yield: 92% (148 mg); white soild, mp 125–127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.81 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 6.99 (s, 1H), 5.03 (q, J = 2.8 Hz, 1H), 4.76 (d, J = 5.2 Hz, 1H), 2.46 (s, 3H), 1.63–1.56 (m, 2H), 1.49–1.18 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 159.6, 145.5, 133.1, 129.8, 129.5, 89.7, 79.1, 35.0, 31.6, 29.0, 24.3, 22.5, 21.7, 14.0; HRMS (ESI-TOF, *m/z*): Calcd for $C_{17}H_{25}NO_3SNa$ [M + Na]$^+$: 346.1447, found 346.1452.

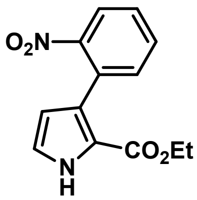
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added 2-nitrobenzaldehyde **1a** (91 mg, 0.6 mmol), TosMIC **2** (98 mg, 0.5 mmol), CuI (95 mg, 0.5 mmol), DMF (2.0 mL) and K_2CO_3 (138 mg, 1.0 mmol). The reaction mixture was stirred at 25 °C for about 10 h. The resulting mixture was concentrated and the residue was taken up in CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 5:1) afforded **4a** as yellow solid in 84% yield (154 mg).



5-(2-Nitrophenyl)-4-tosyl-4,5-dihydrooxazole (4a):[16] Column chromatography (silica gel; petroleum ether/ethyl acetate 5:1); yield: 84% (145 mg); yellow soild, mp 187–188 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 7.91 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.62–7.49 (m, 4H), 7.39 (d, J = 8.0 Hz, 2H), 7.10 (t, J = 1.6 Hz, 1H), 6.40 (d, J = 7.2 Hz, 1H), 5.37–5.27 (m, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 159.0, 148.1, 145.9, 133.4, 132.8,9, 130.7, 130.4, 129.9, 129.7, 129.6, 129.5, 125.2, 91.7, 76.9, 21.7; HRMS (ESI-TOF, *m/z*): Calcd for $C_{16}H_{14}N2O_5SNa$ [M + Na]$^+$: 369.0516, found 369.0531.

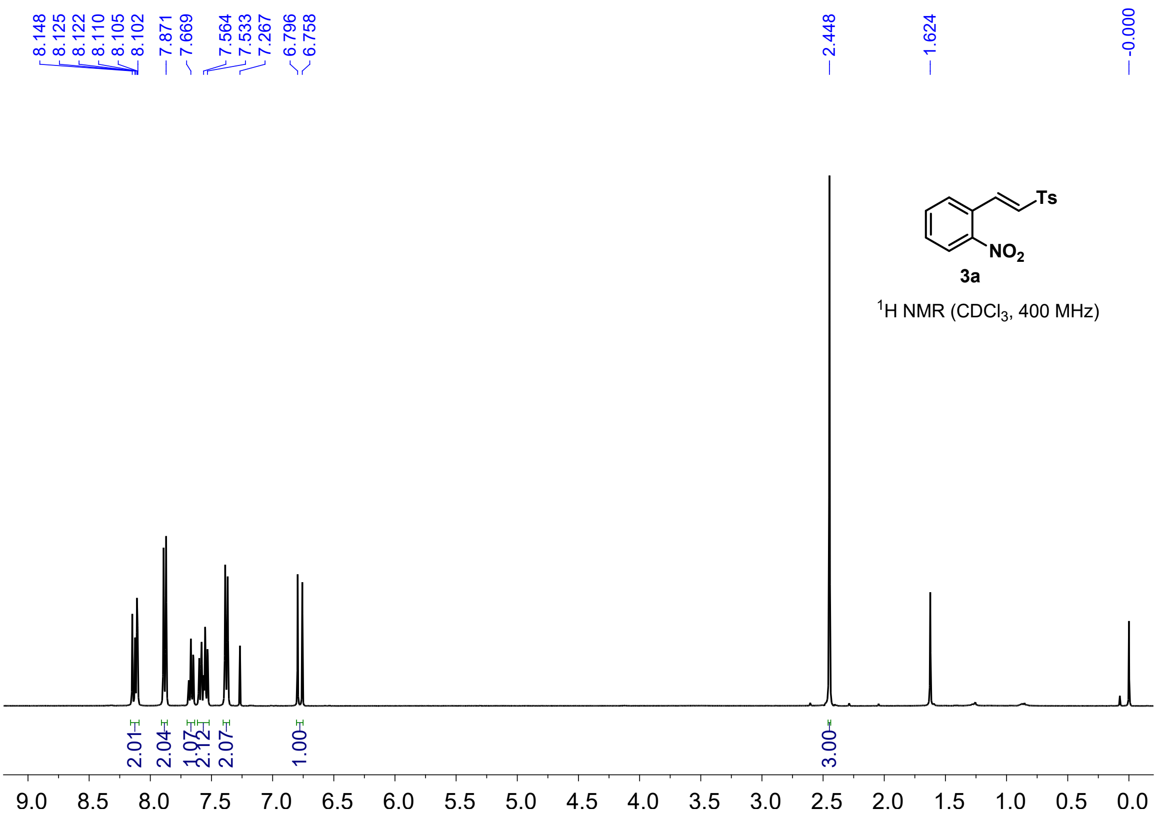
VI. Synthesis and analytical data of pyrrole 5

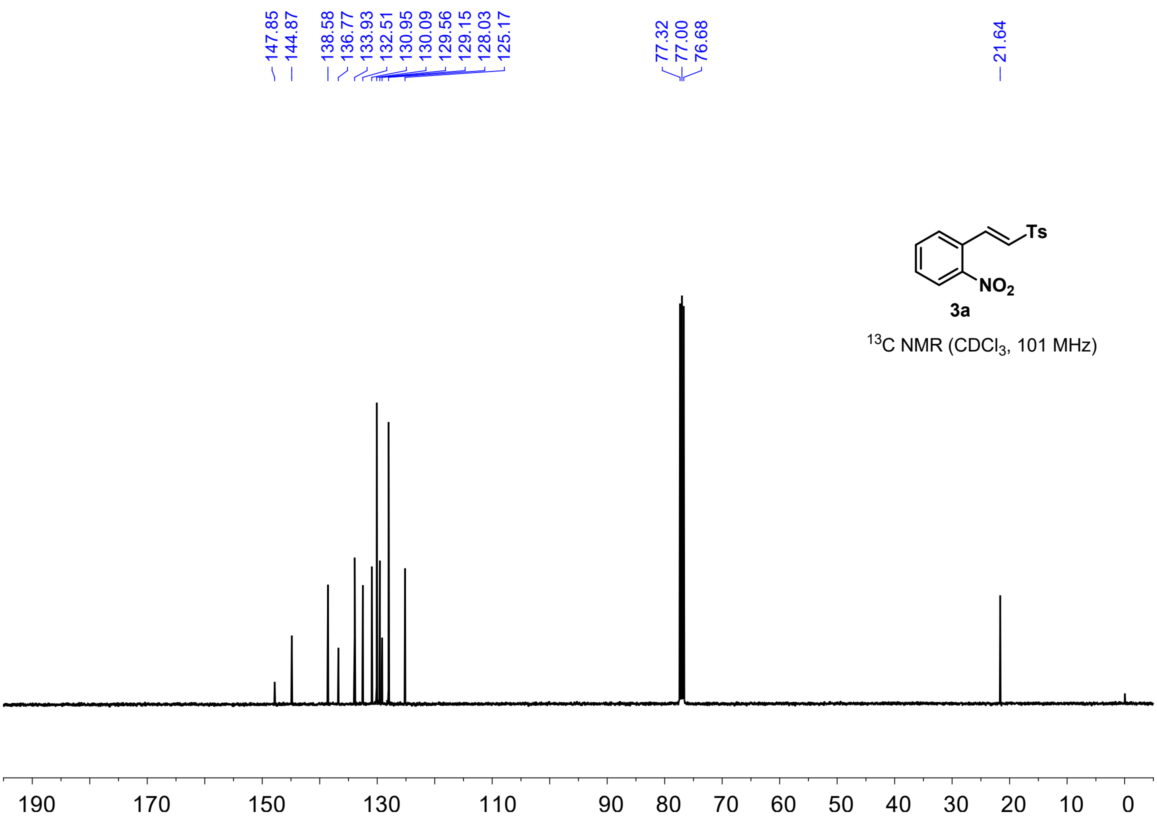
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added **3a** (1.2 g, 3.96 mmol), ethyl isocyanate (5.94 mmol, 0.65 mL), 1,4-dioxane (20 mL). The reaction mixture was stirred at 80 °C for about 6 h. The resulting mixture was concentrated and the residue was taken up in CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether/ethyl acetate 10:2) afforded **5a** as yellow solid in 83% yield (0.86 g).

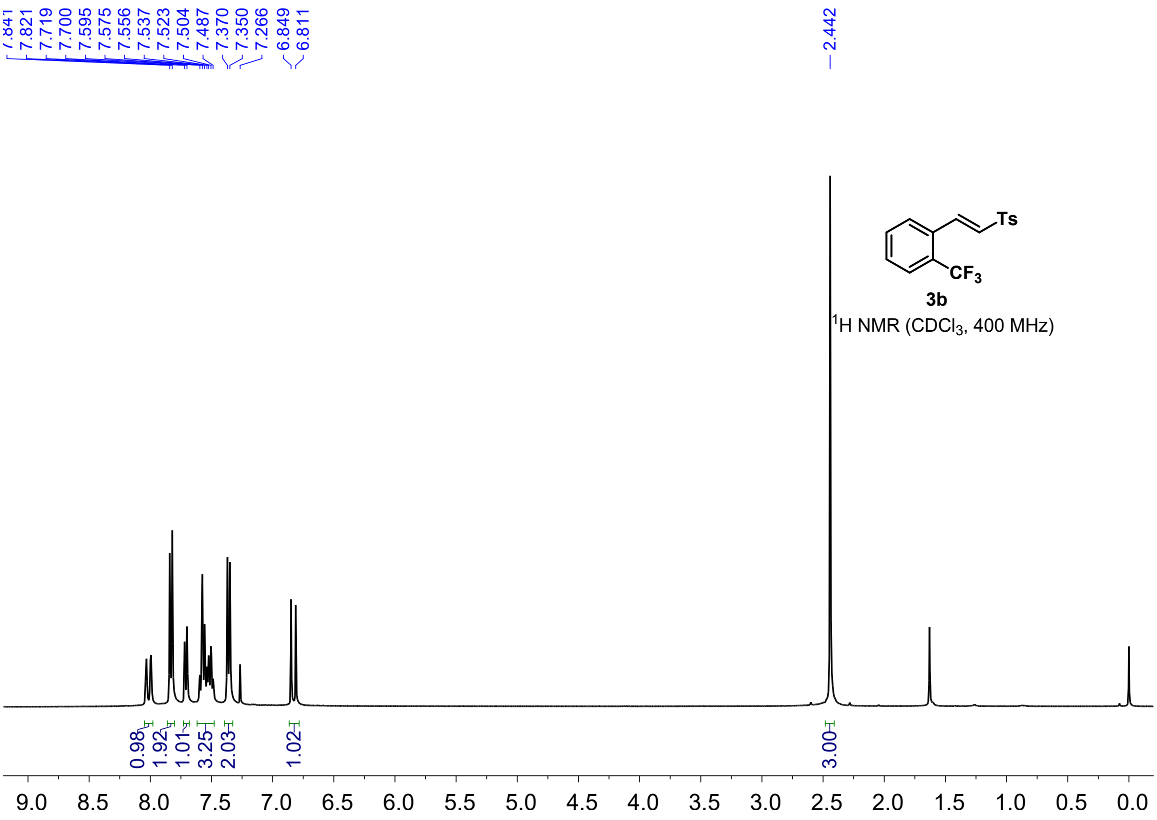


Ethyl 3-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate (5): Column chromatography (silica gel; petroleum ether/ethyl acetate 5:1); yield: 82% (107 mg); yellow soild, mp 141–142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 9.47 (s, 1H), 7.68 (d, *J* = 4.8 Hz, 1H), 7.57–7.48 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.99 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ_C 160.9, 149.1, 131.8, 131.2, 128.7, 127.3, 123.8, 123.6, 121.4, 120.9, 114.4, 60.7, 14.4; HRMS (ESI-TOF, *m/z*): Calcd for $C_{13}H_{12}N_2NaO_4$ [M + Na]$^+$: 283.0689, found 283.0689.

VII. NMR spectra



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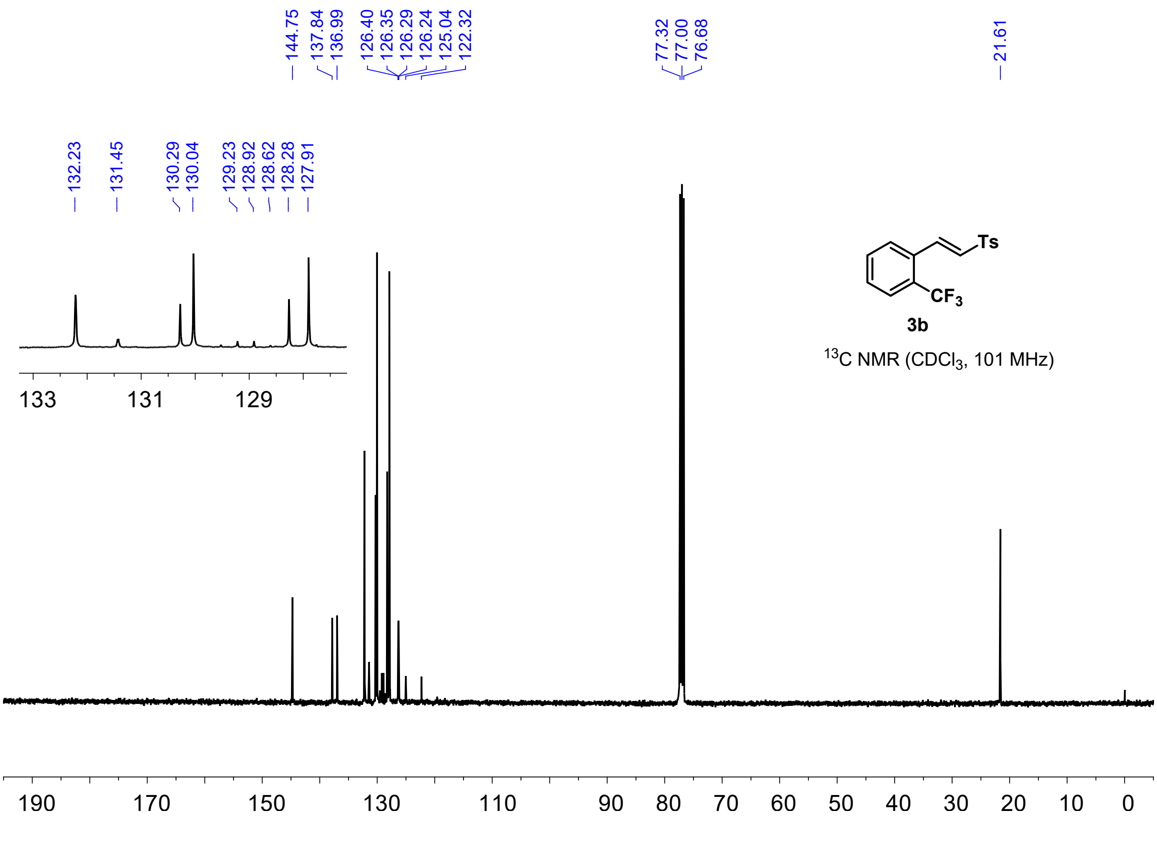
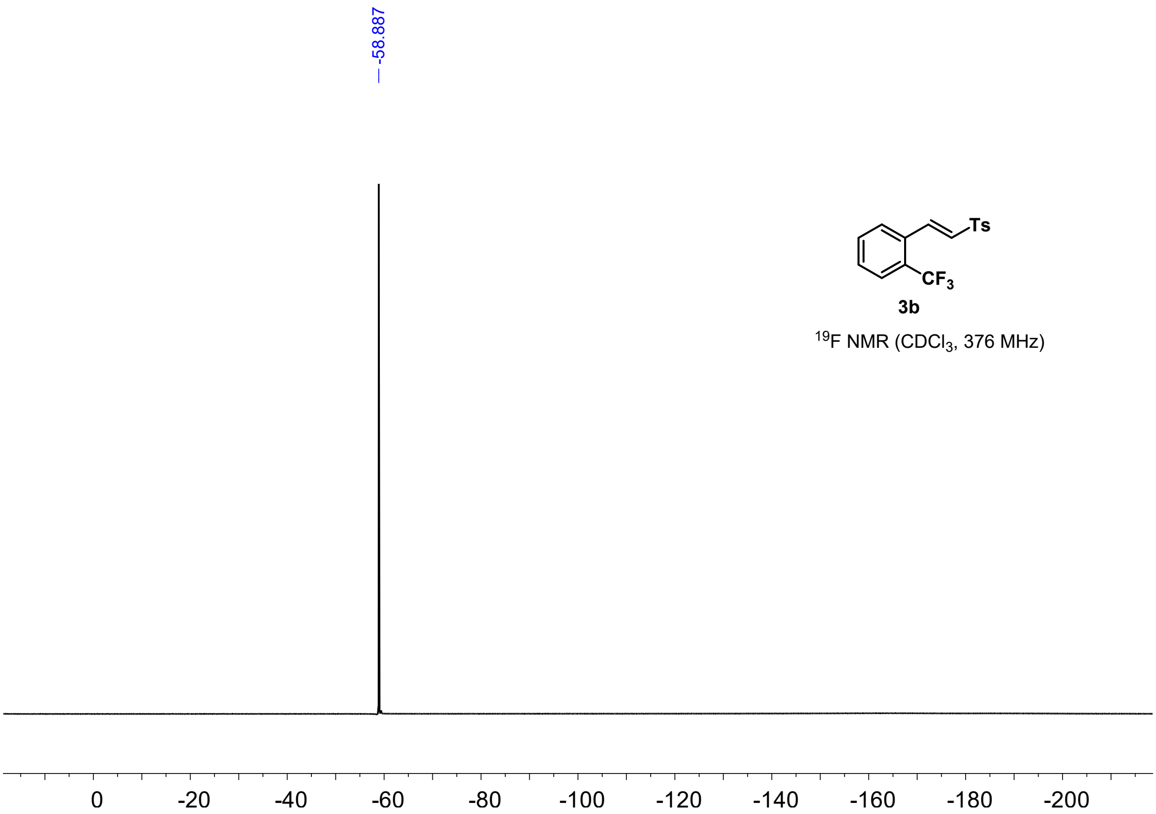
7.821
7.719
7.700
7.595
7.575
7.556
7.537
7.523
7.504
7.487
7.370
7.350
7.266
6.849
6.811
2.442
Ts
CF3
3b
1H NMR (CDCl3, 400 MHz)
0.98
1.92
1.01
3.25
2.03
1.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


144.75
137.84
136.99
126.40
126.35
126.29
126.24
125.04
122.32
77.32
77.00
76.68
21.61
132.23
131.45
130.29
130.04
129.23
128.92
128.62
128.28
127.91
133 131 129
Ts
CF3
3b
13C NMR (CDCl3, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0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Ts
CF3
3b
19F NMR (CDCl3, 376 MHz)
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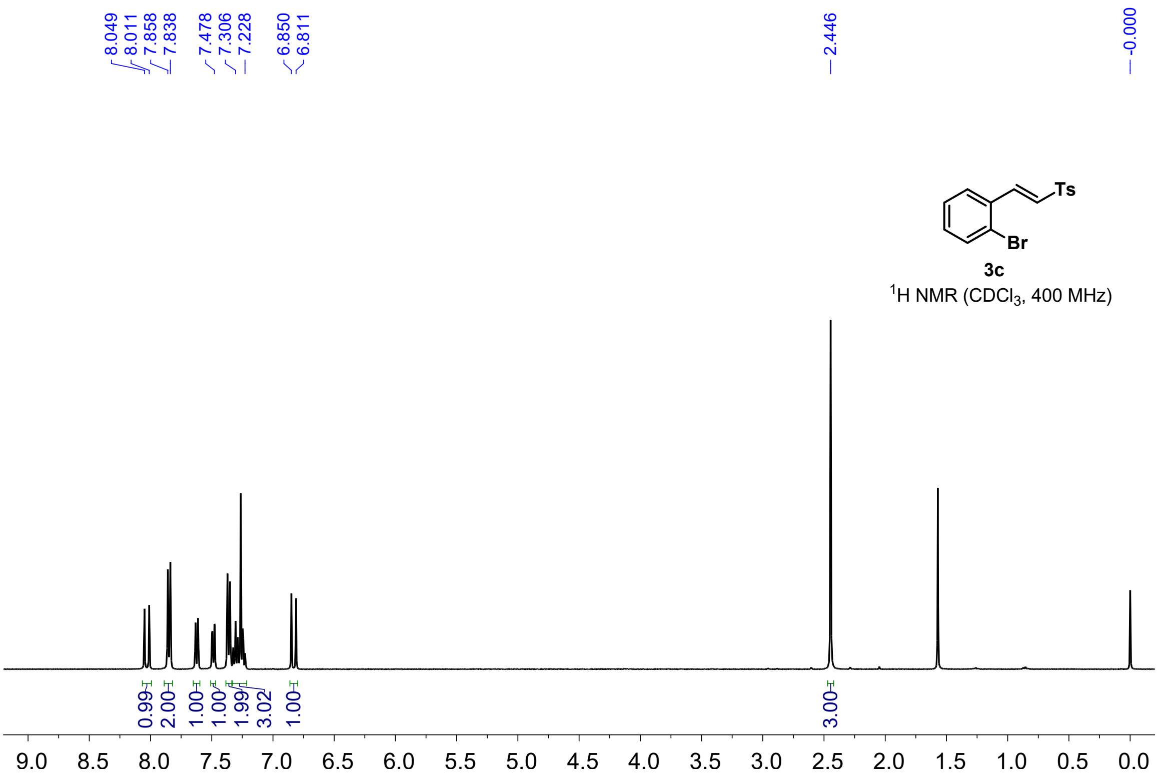
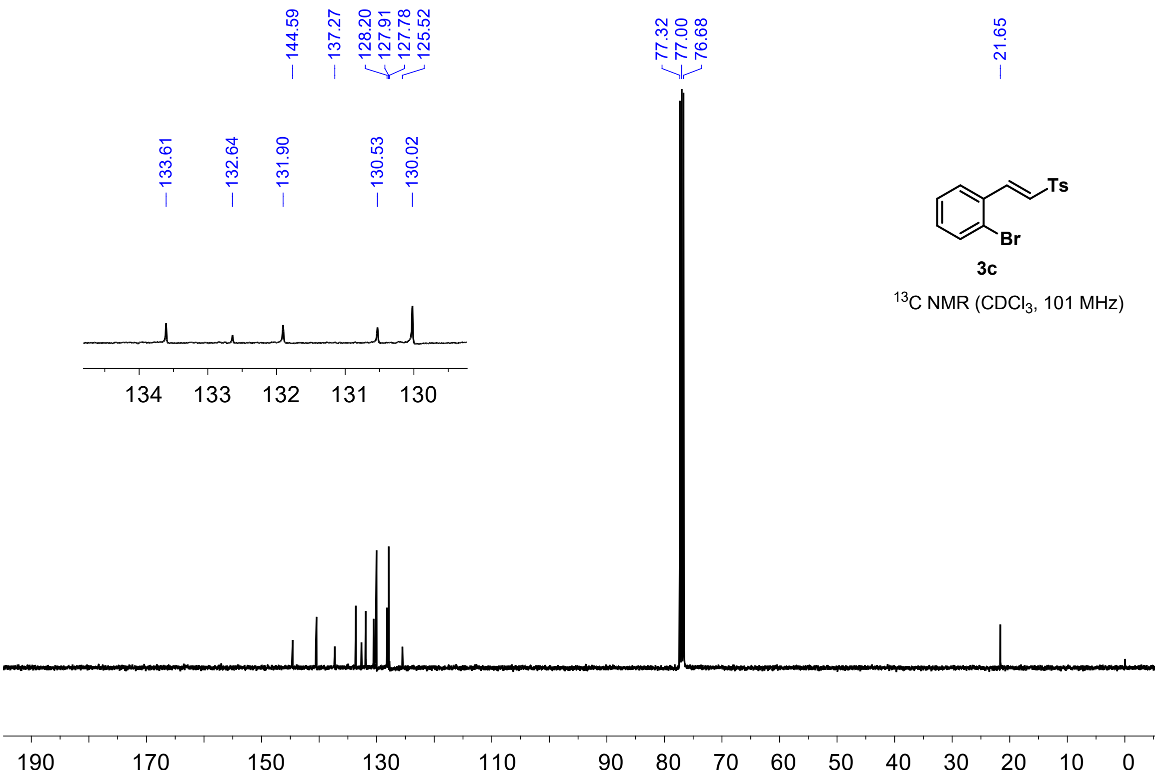
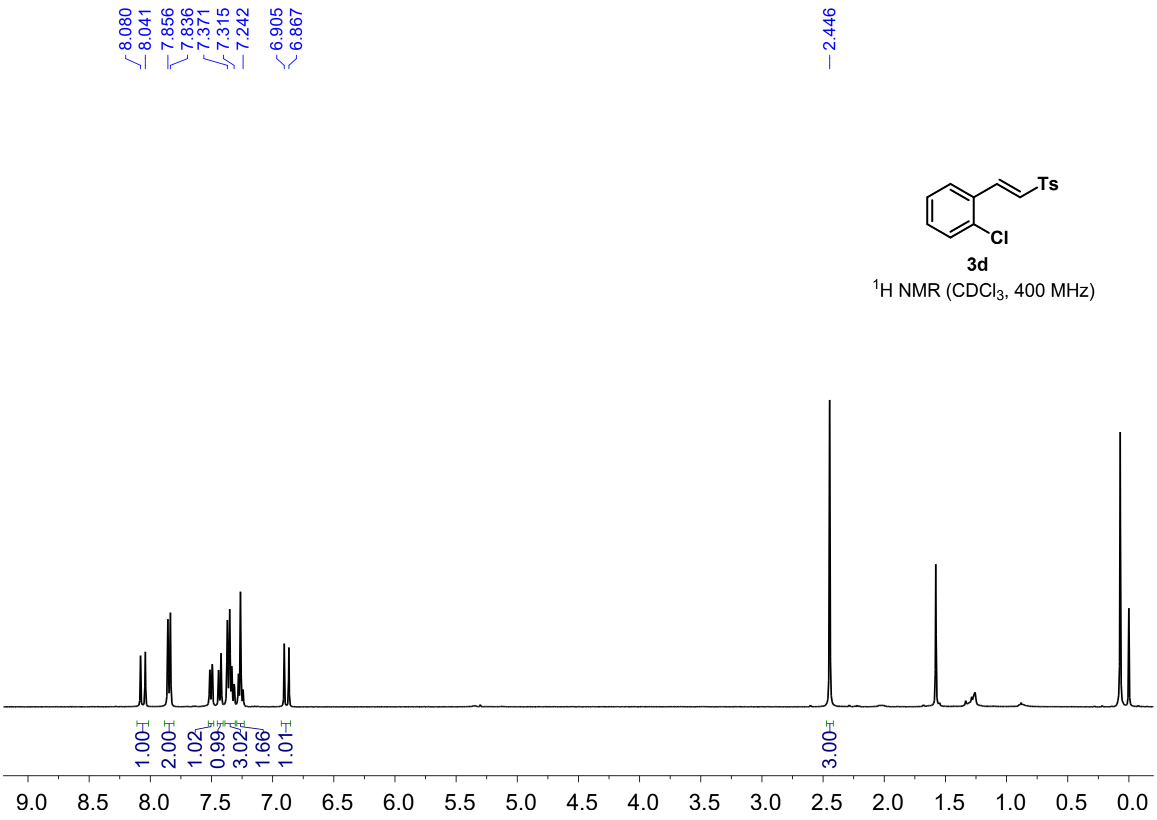
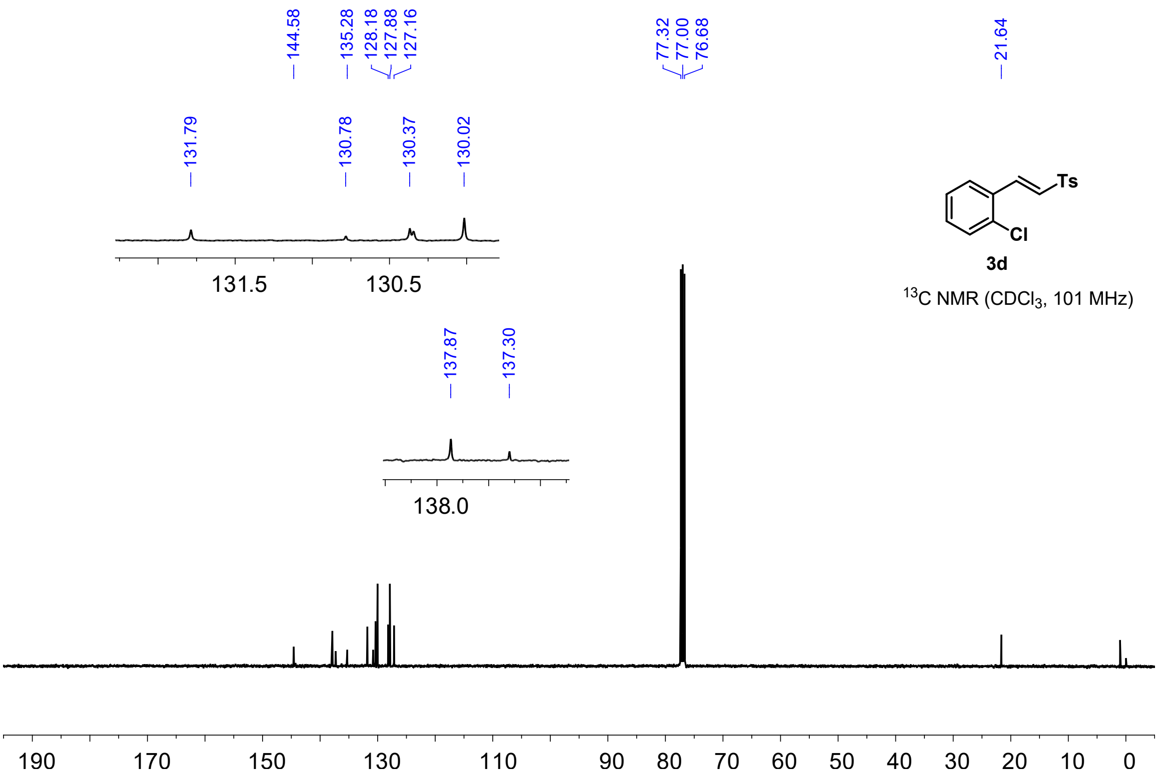
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200


8.049
8.011
7.858
7.838
7.478
7.306
7.228
6.850
6.811
2.446
-0.000
Ts
Br
3c
^{1}H NMR (CDCl$_3$, 400 MHz)
0.99
2.00
1.00
1.00
1.99
3.02
1.00
3.00
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


144.59
137.27
128.20
127.91
127.78
125.52
77.32
77.00
76.68
21.65
133.61
132.64
131.90
130.53
130.02
Ts
Br
3c
^{13}C NMR (CDCl$_3$, 101 MHz)
134 133 132 131 130
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0



8.080
8.041
7.856
7.836
7.371
7.315
7.242
6.905
6.867
2.446
Ts
Cl
3d
1H NMR (CDCl3, 400 MHz)
1.00
2.00
1.02
0.99
3.02
1.66
1.01
3.00
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



144.58
135.28
128.18
127.88
127.16
77.32
77.00
76.68
21.64
131.79
130.78
130.37
130.02
131.5
130.5
Ts
Cl
3d
13C NMR (CDCl3, 101 MHz)
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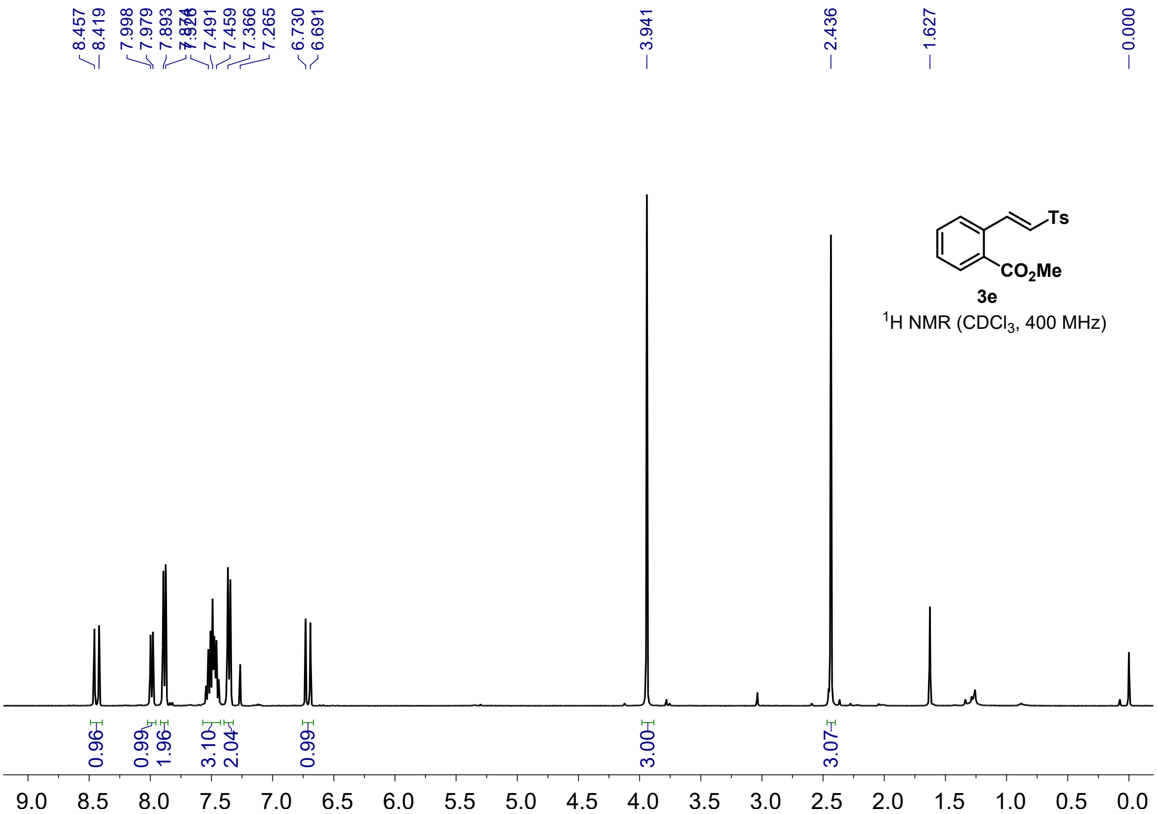
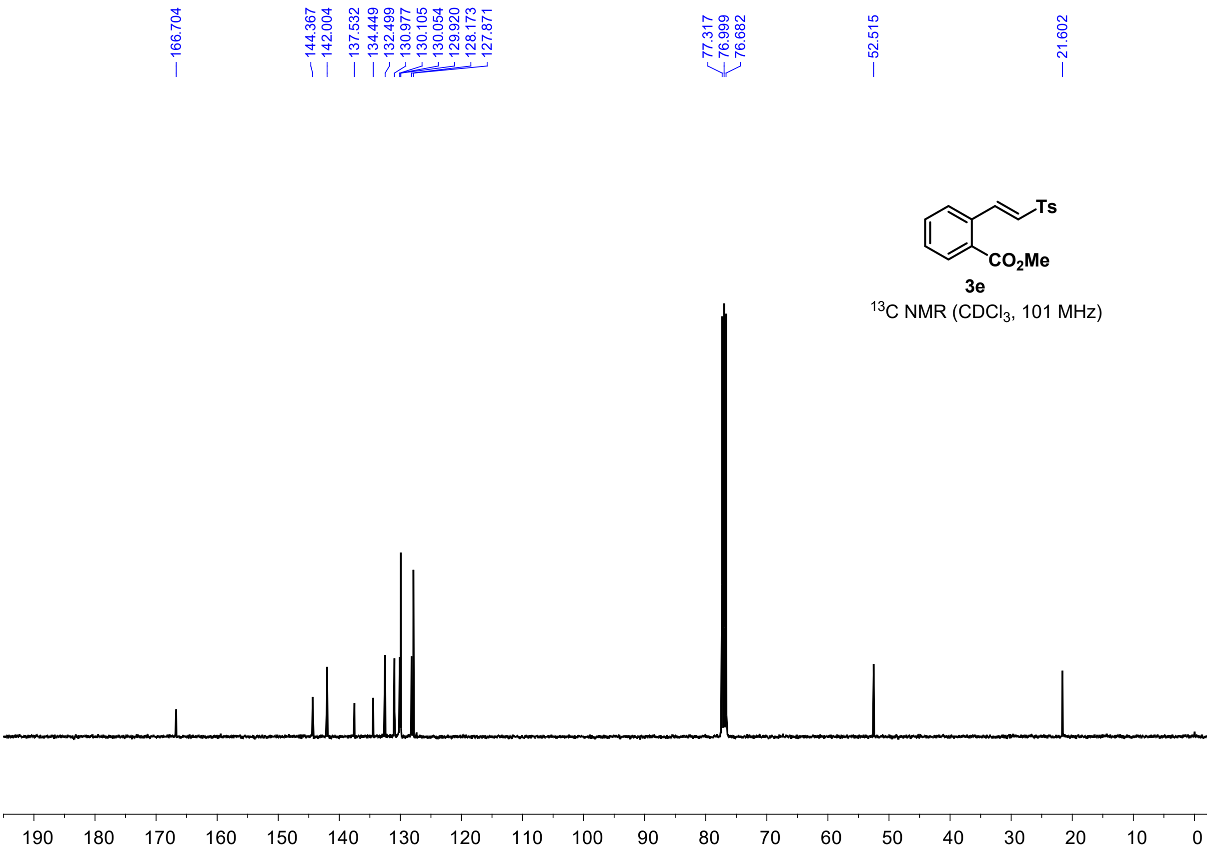
137.30
138.0
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0



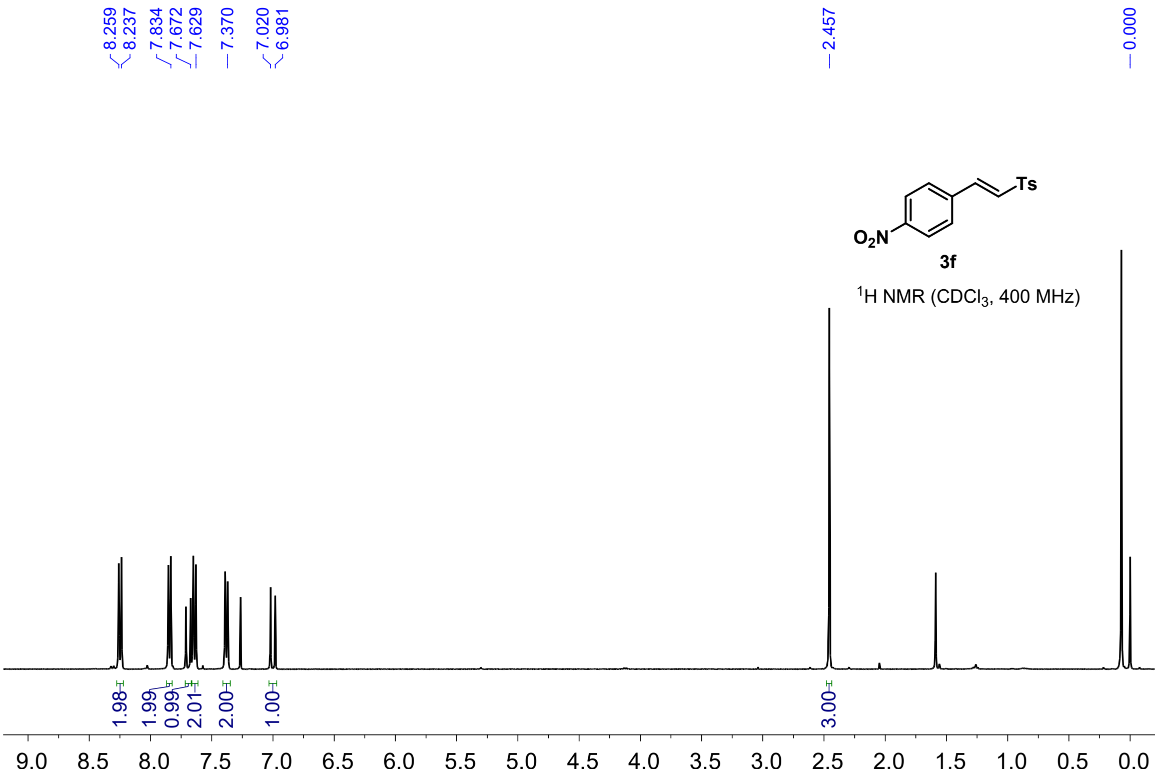
3e

^1H NMR ($CDCl_3$, 400 MHz)



3e

^{13}C NMR ($CDCl_3$, 101 MHz)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8.237
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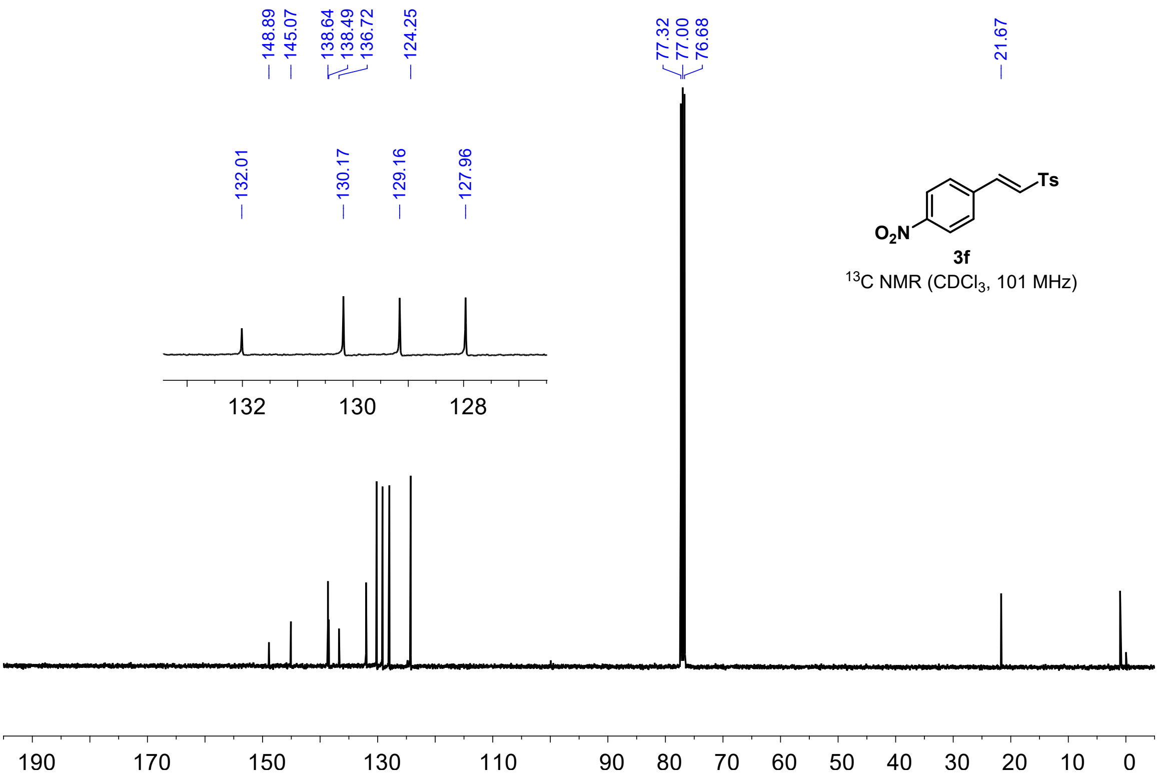
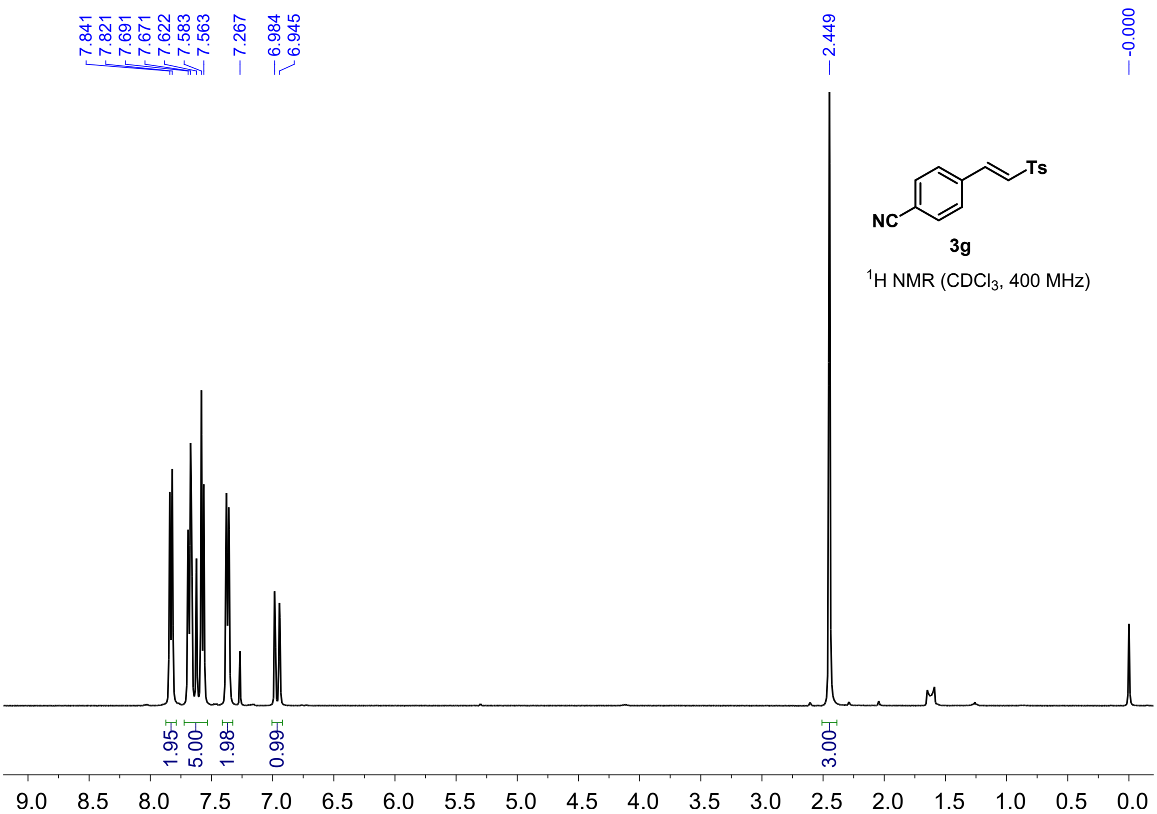
7.672
7.629
7.370
7.020
6.981
2.457
0.000
Ts
O2N
3f
1H NMR (CDCl3, 400 MHz)
1.98
1.99
0.99
2.01
2.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


148.89
145.07
138.64
138.49
136.72
124.25
77.32
77.00
76.68
21.67
132.01
130.17
129.16
127.96
Ts
O2N
3f
13C NMR (CDCl3, 101 MHz)
132 130 128
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0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7.821
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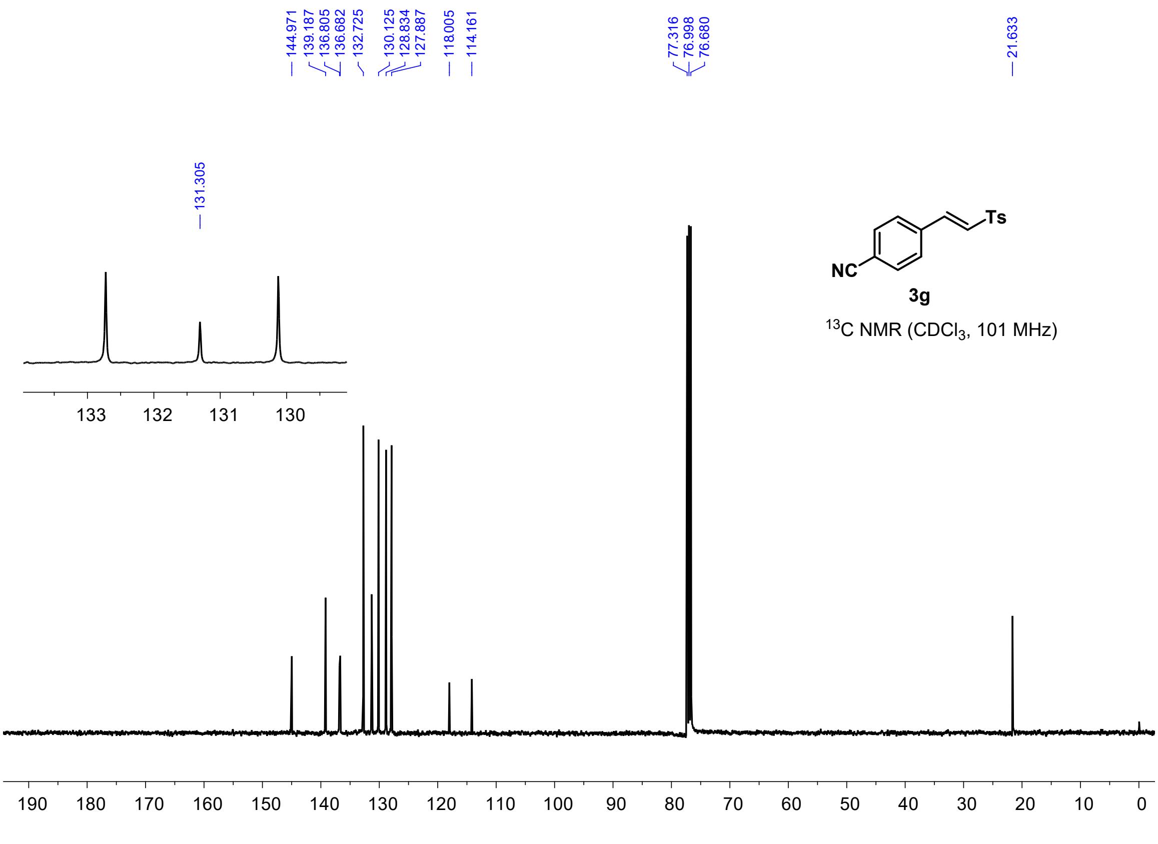
7.671
7.622
7.583
7.563
7.267
6.984
6.945
2.449
0.000
Ts
NC
3g
^{1}H NMR (CDCl$_3$, 400 MHz)
1.95
5.00
1.98
0.99
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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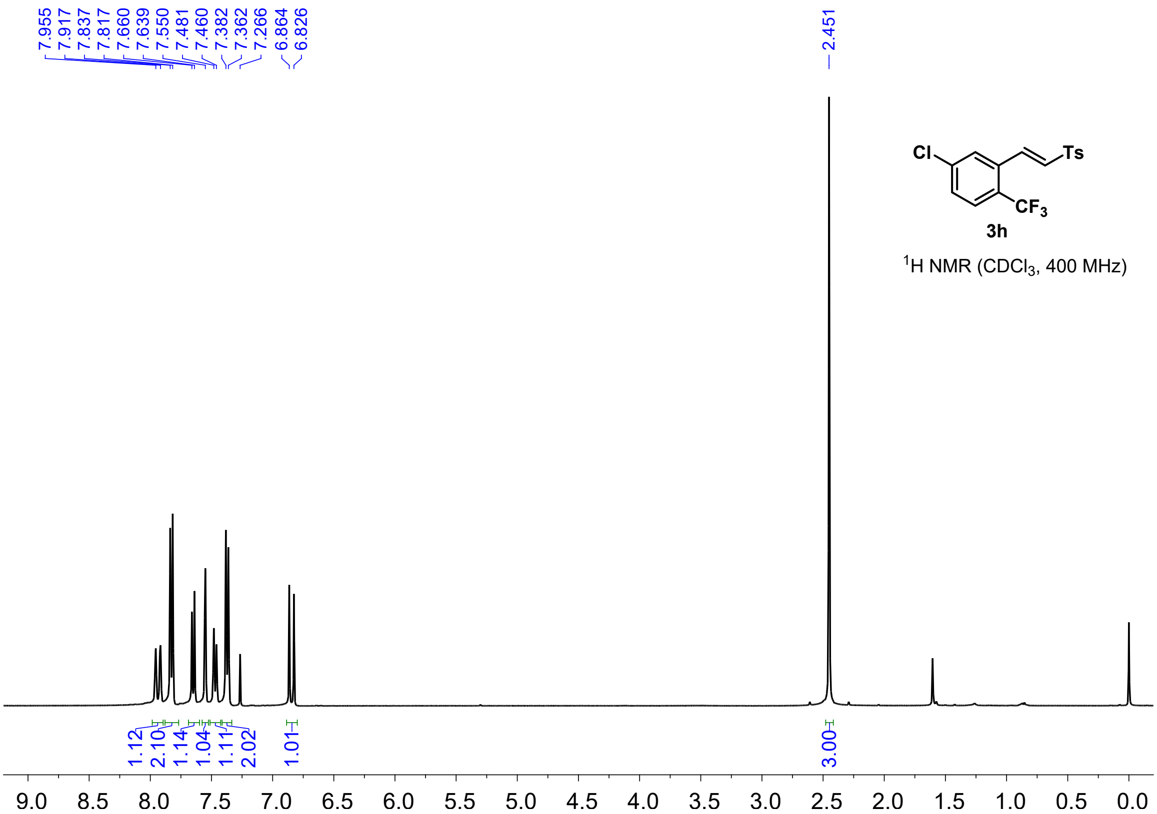
139.187
136.805
136.682
132.725
130.125
128.834
127.887
118.005
114.161
77.316
76.998
76.680
21.633
131.305
133 132 131 130
Ts
NC
3g
^{13}C NMR (CDCl$_3$, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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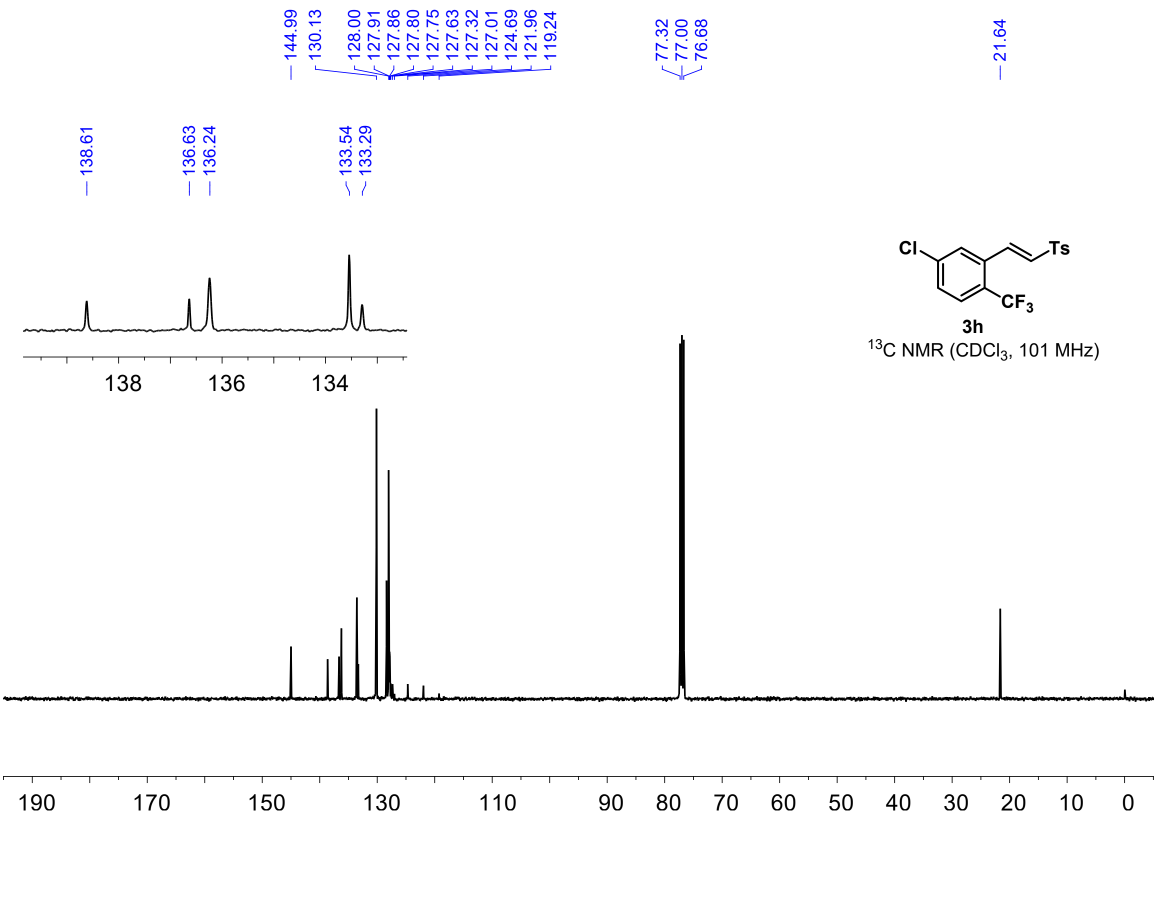
7.917
7.837
7.817
7.660
7.639
7.550
7.481
7.460
7.382
7.362
7.266
6.864
6.826
2.451
Cl
Ts
CF3
3h
1H NMR (CDCl3, 400 MHz)
1.12
2.10
1.14
1.04
1.11
2.02
1.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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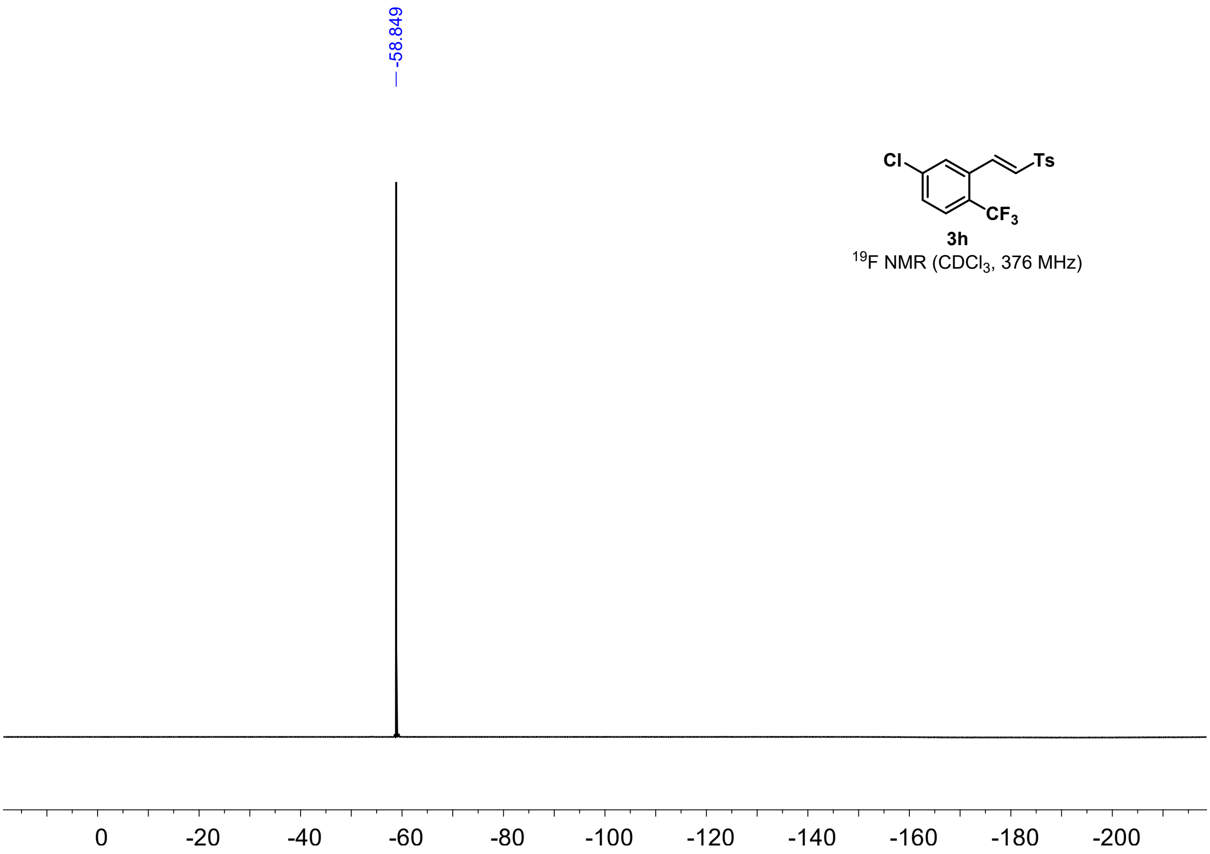
127.86
127.80
127.75
127.63
127.32
127.01
124.69
121.96
119.24
77.32
77.00
76.68
21.64
138.61
136.63
136.24
133.54
133.29
138 136 134
Cl
Ts
CF3
3h
13C NMR (CDCl3, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0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Cl
Ts
CF3
3h
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-60
-80
-100
-120
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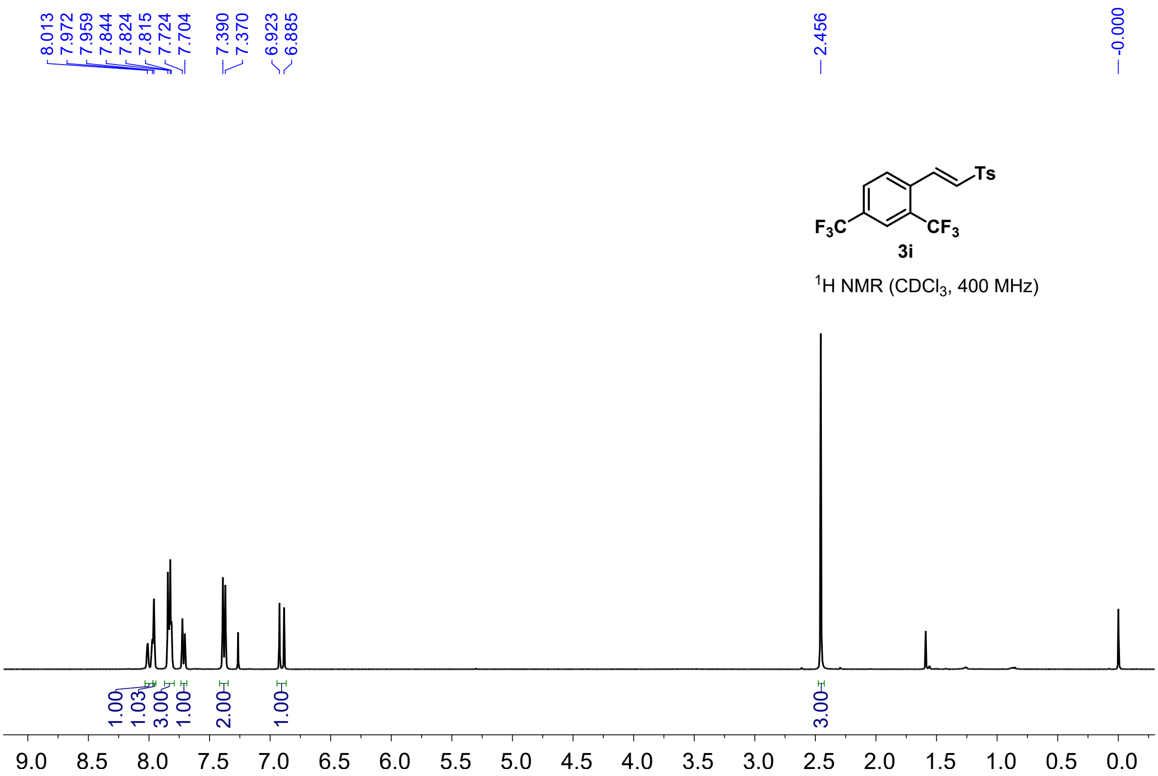
-160
-180
-200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7.724
7.704
7.390
7.370
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6.885
2.456
-0.000
Ts
F3C
CF3
3i
1H NMR (CDCl3, 400 MHz)
1.00
1.03
3.00
1.00
2.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
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2.0
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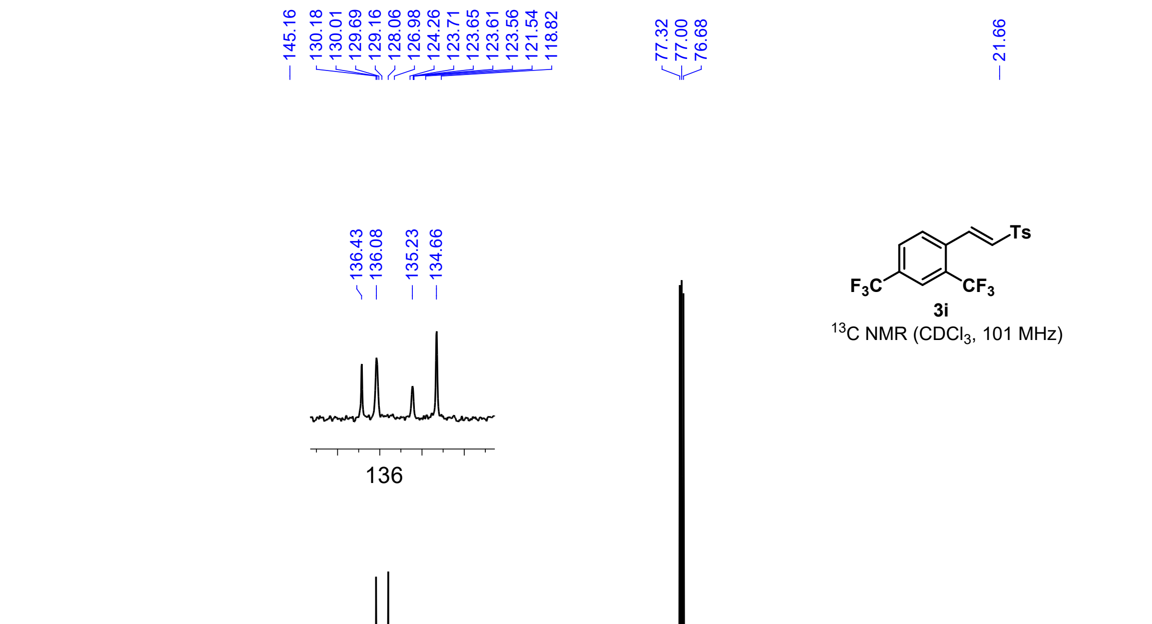
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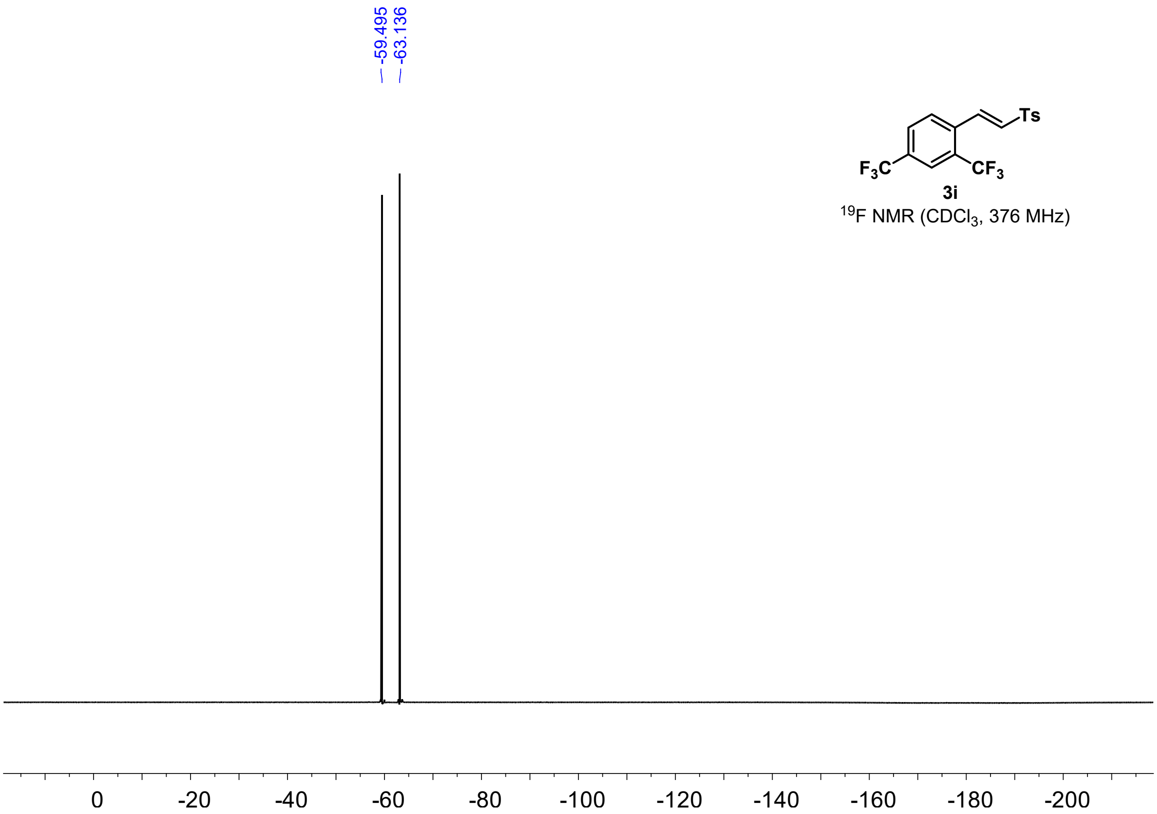
121.54
118.82
77.32
77.00
76.68
21.66
136.43
136.08
135.23
134.66
136
Ts
F3C
CF3
3i
13C NMR (CDCl3, 101 MHz)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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CF3
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19F NMR (CDCl3, 376 MHz)
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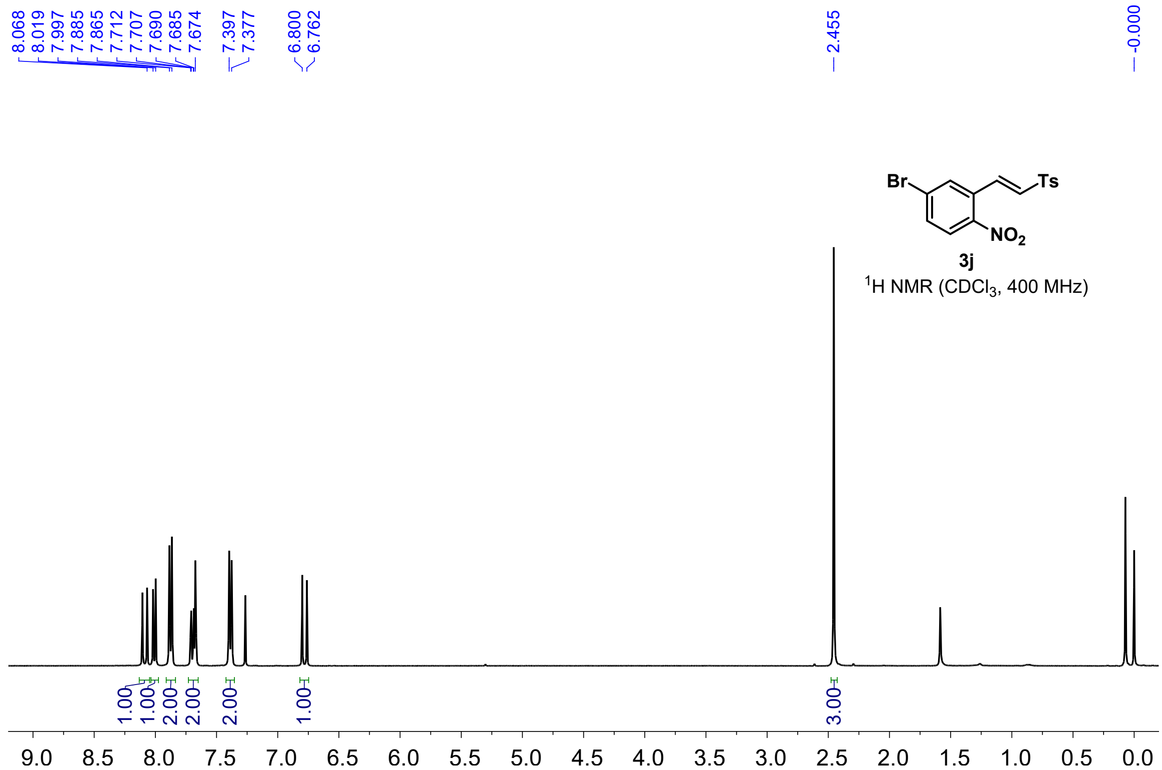
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7.690
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7.674
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7.377
6.800
6.762
2.455
-0.000
Br
Ts
NO2
3j
1H NMR (CDCl3, 400 MHz)
1.00
1.00
2.00
2.00
2.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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2.0
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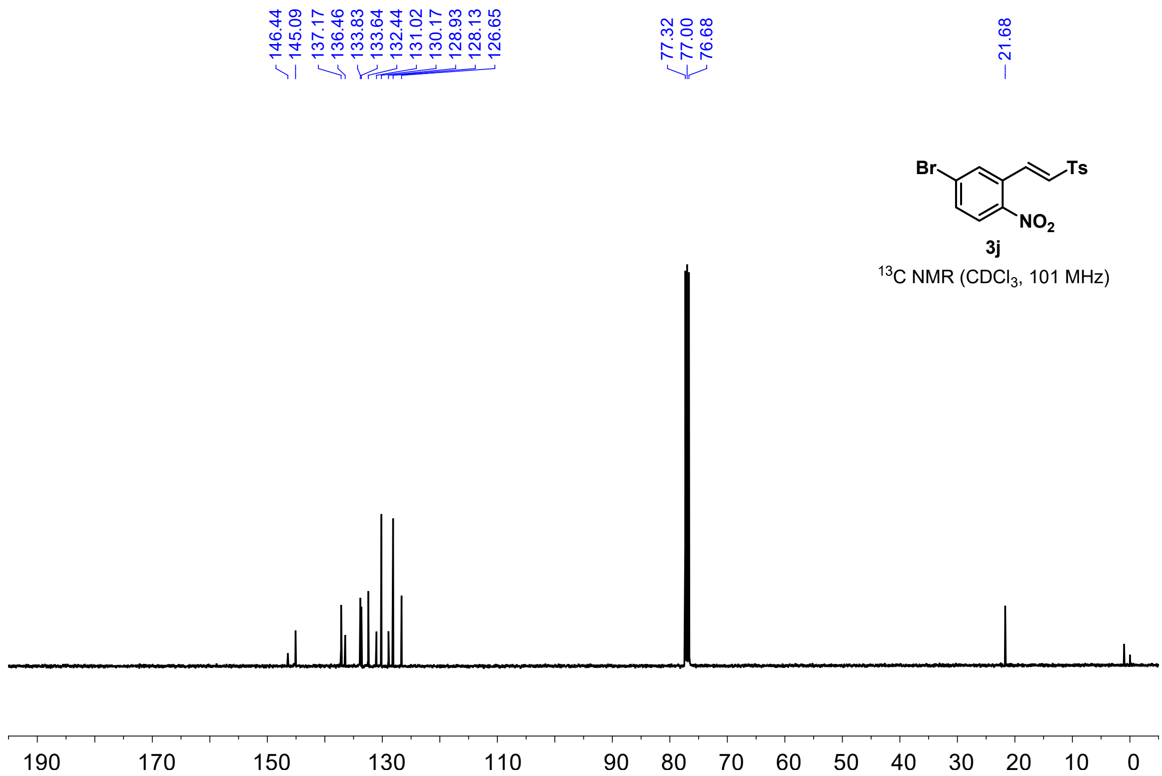
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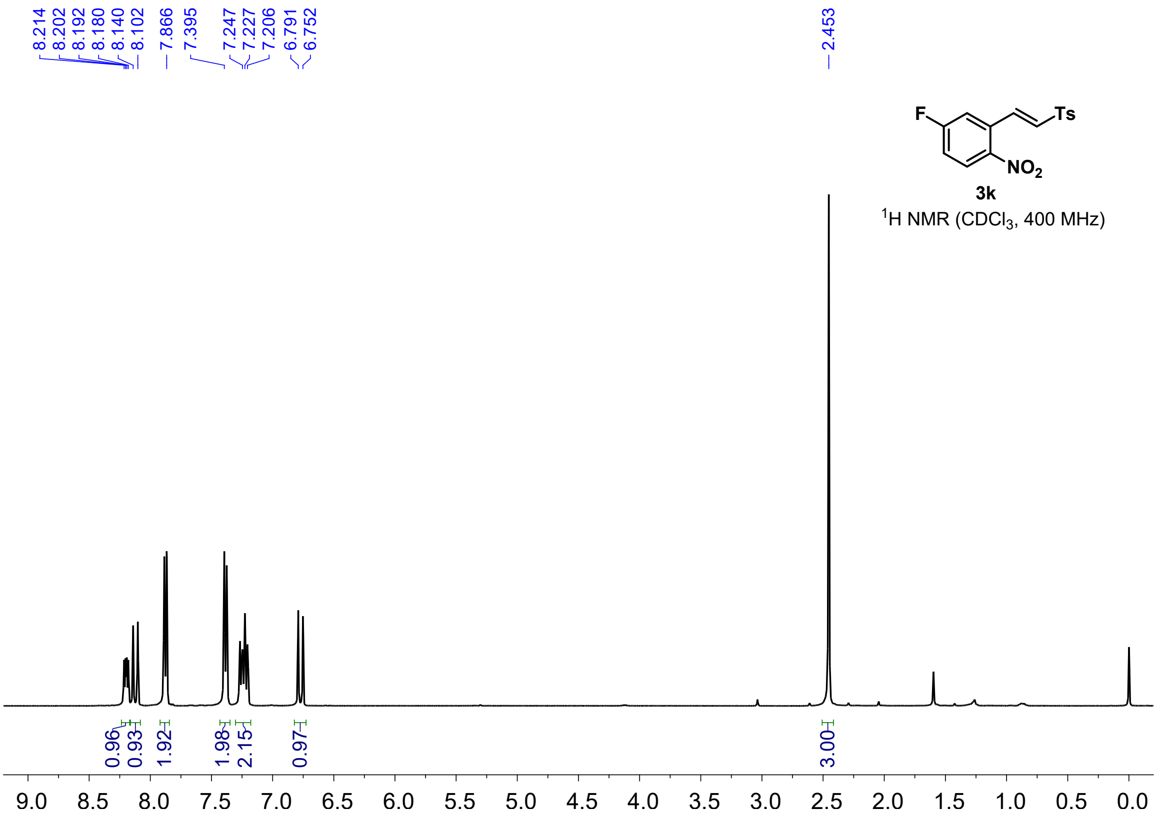
128.93
128.13
126.65
77.32
77.00
76.68
21.68
Br
Ts
NO2
3j
13C NMR (CDCl3, 101 MHz)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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8.180
8.140
8.102
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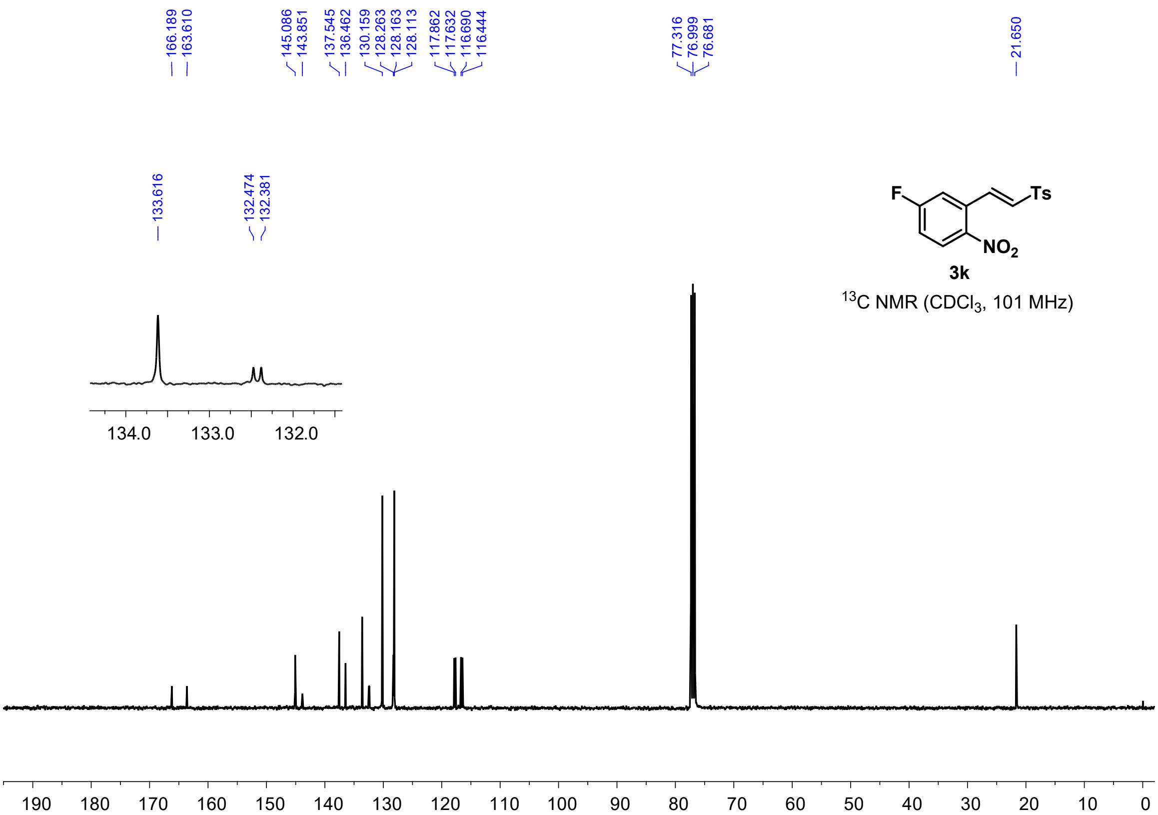
7.395
7.247
7.227
7.206
6.791
6.752
2.453
F
Ts
NO2
3k
1H NMR (CDCl3, 400 MHz)
0.96
0.93
1.92
1.98
2.15
0.97
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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136.462
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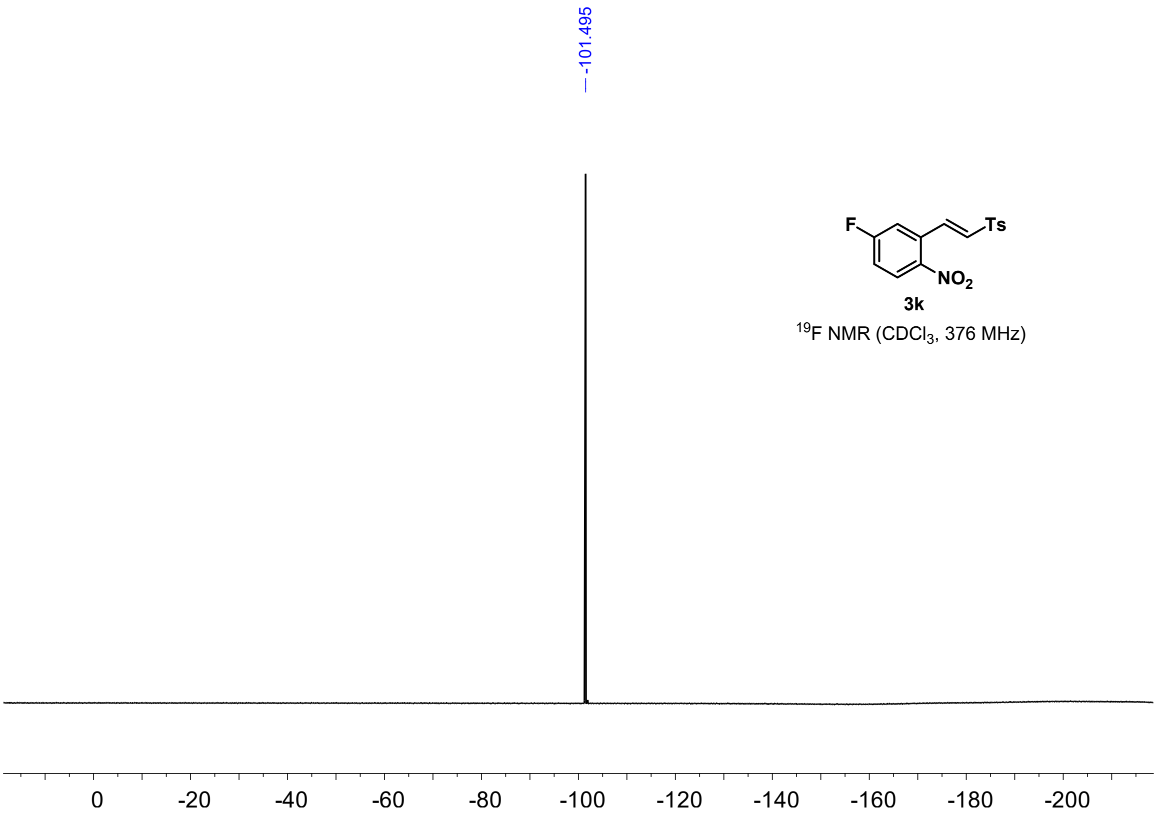
128.113
117.862
117.632
116.690
116.444
77.316
76.999
76.681
21.650
133.616
132.474
132.381
134.0 133.0 132.0
F
Ts
NO2
3k
13C NMR (CDCl3, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


-101.495
F
Ts
NO2
3k
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0
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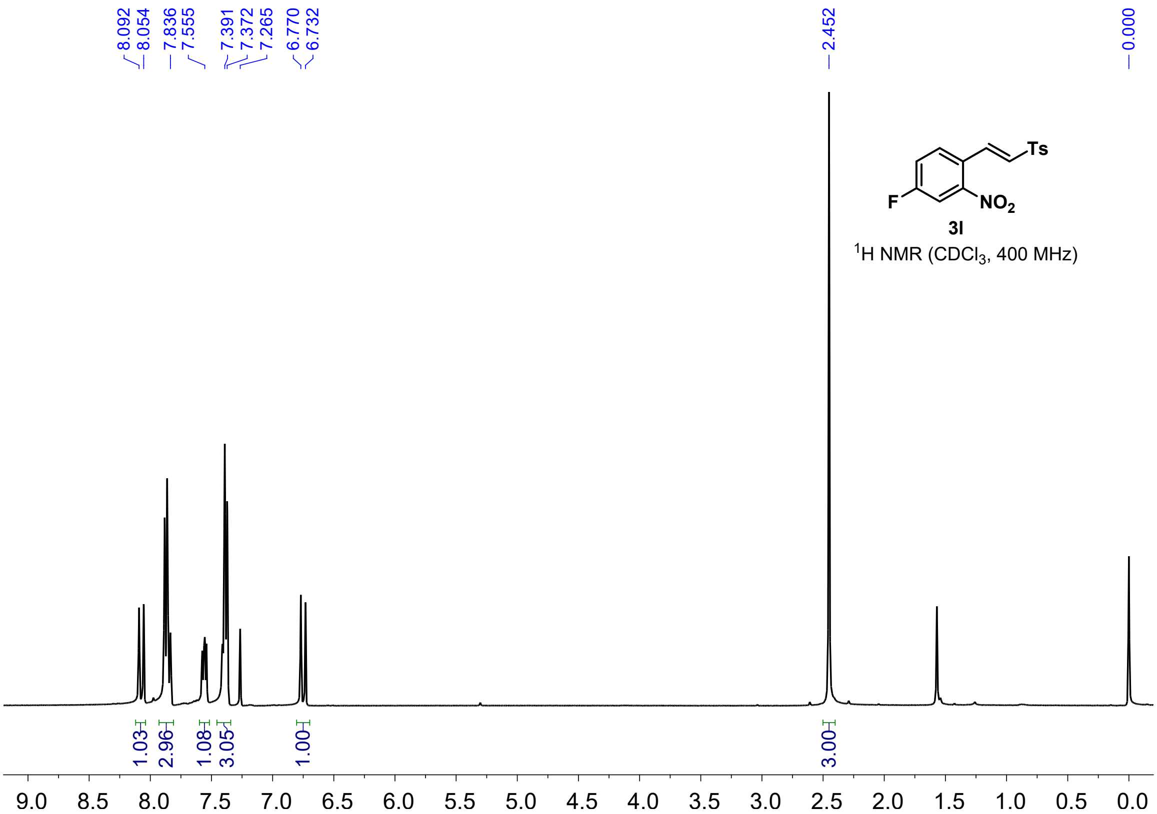
-40
-60
-80
-100
-120
-140
-160
-180
-200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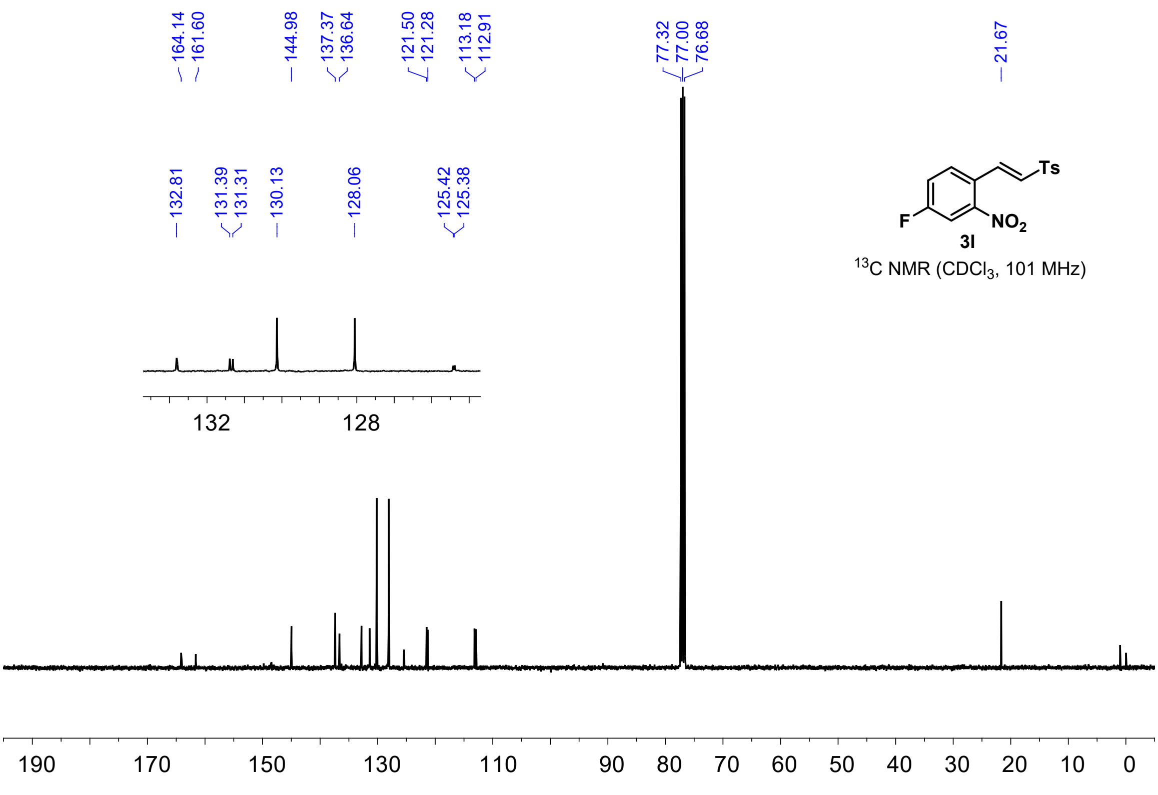
7.391
7.372
7.265
6.770
6.732
2.452
0.000
Ts
F
NO2
3l
1H NMR (CDCl3, 400 MHz)
1.03
2.96
1.08
3.05
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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136.64
121.50
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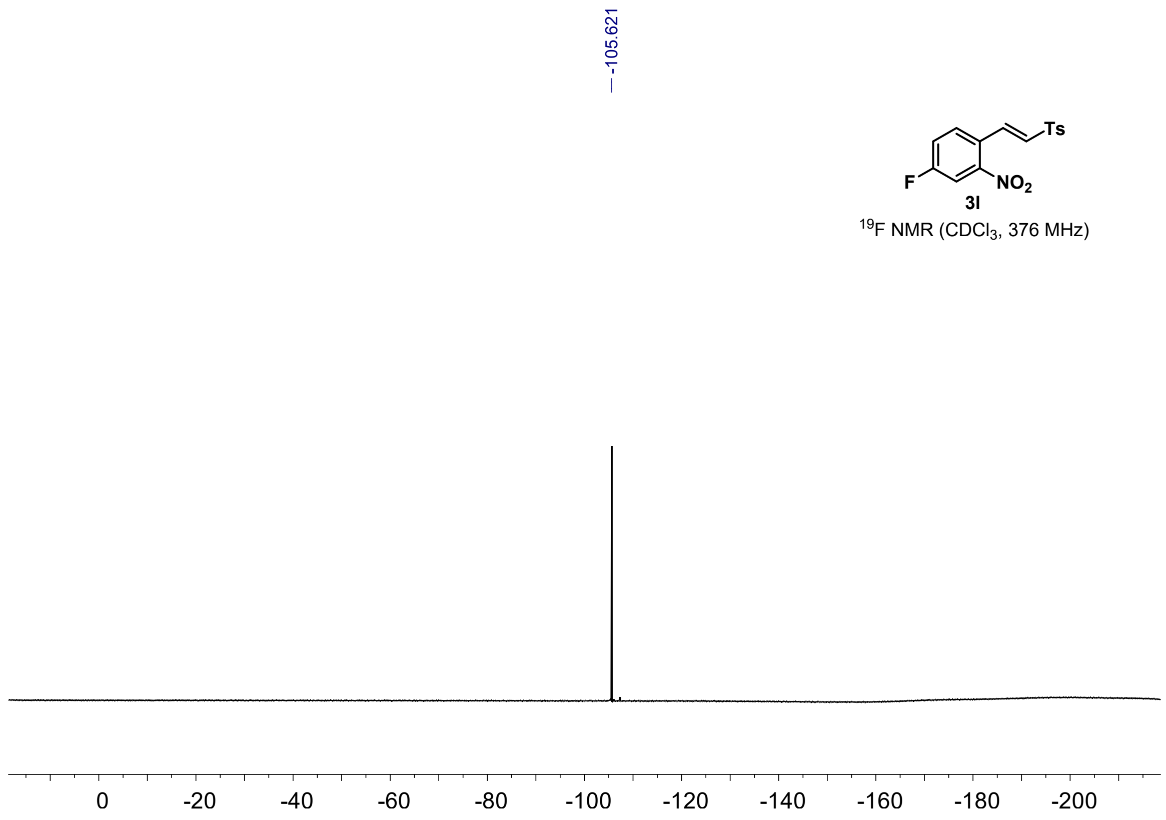
113.18
112.91
77.32
77.00
76.68
21.67
132.81
131.39
131.31
130.13
128.06
125.42
125.38
132
128
Ts
F
NO2
3l
13C NMR (CDCl3, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0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Ts
F
NO2
3l
19F NMR (CDCl3, 376 MHz)
0
-20
-40
-60
-80
-100
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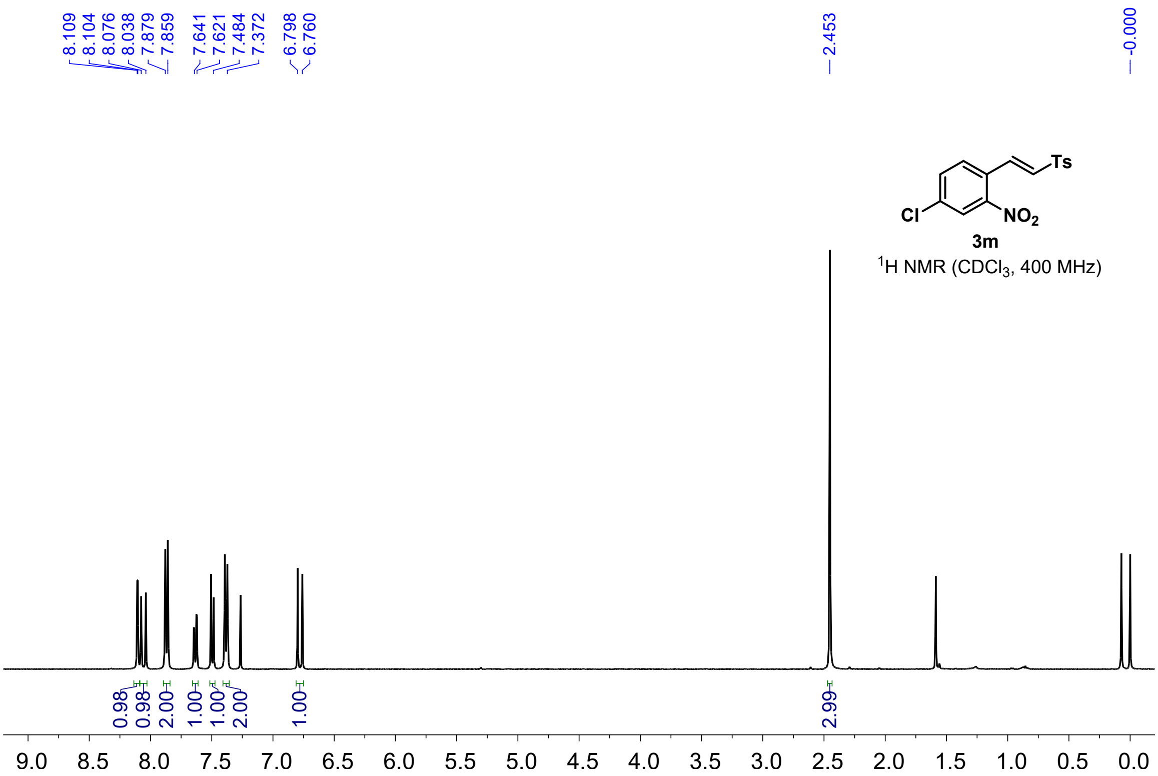
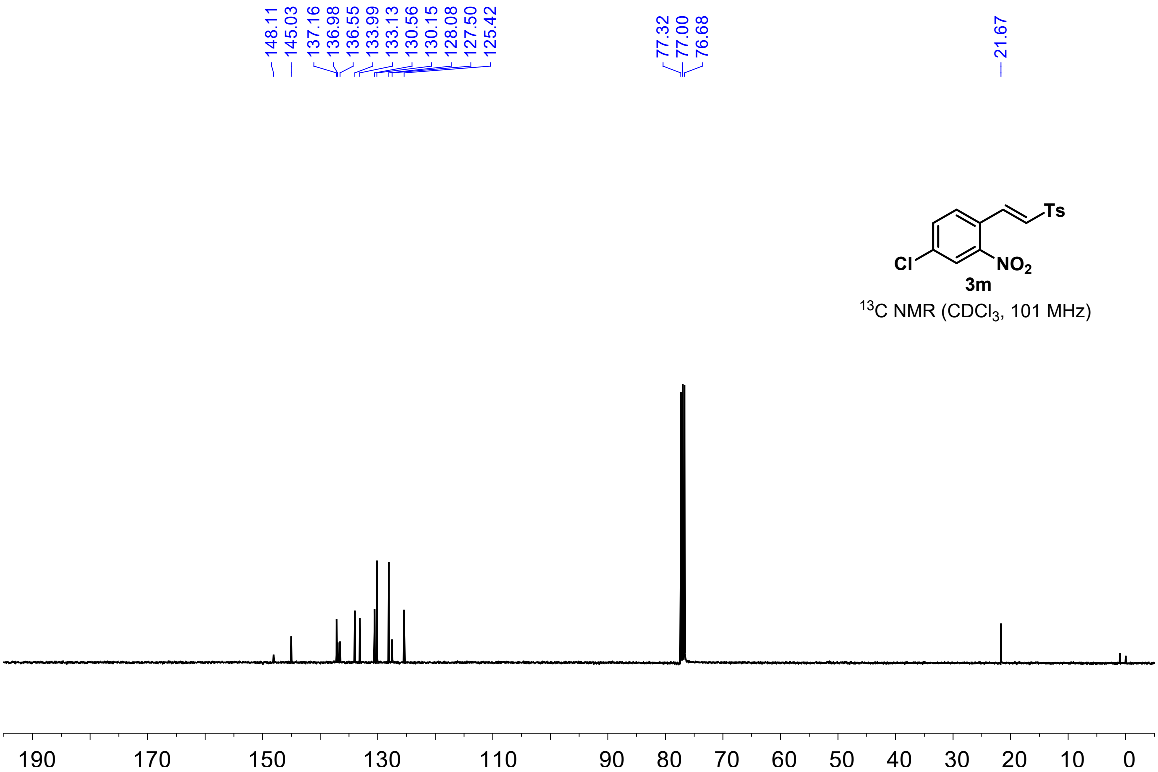
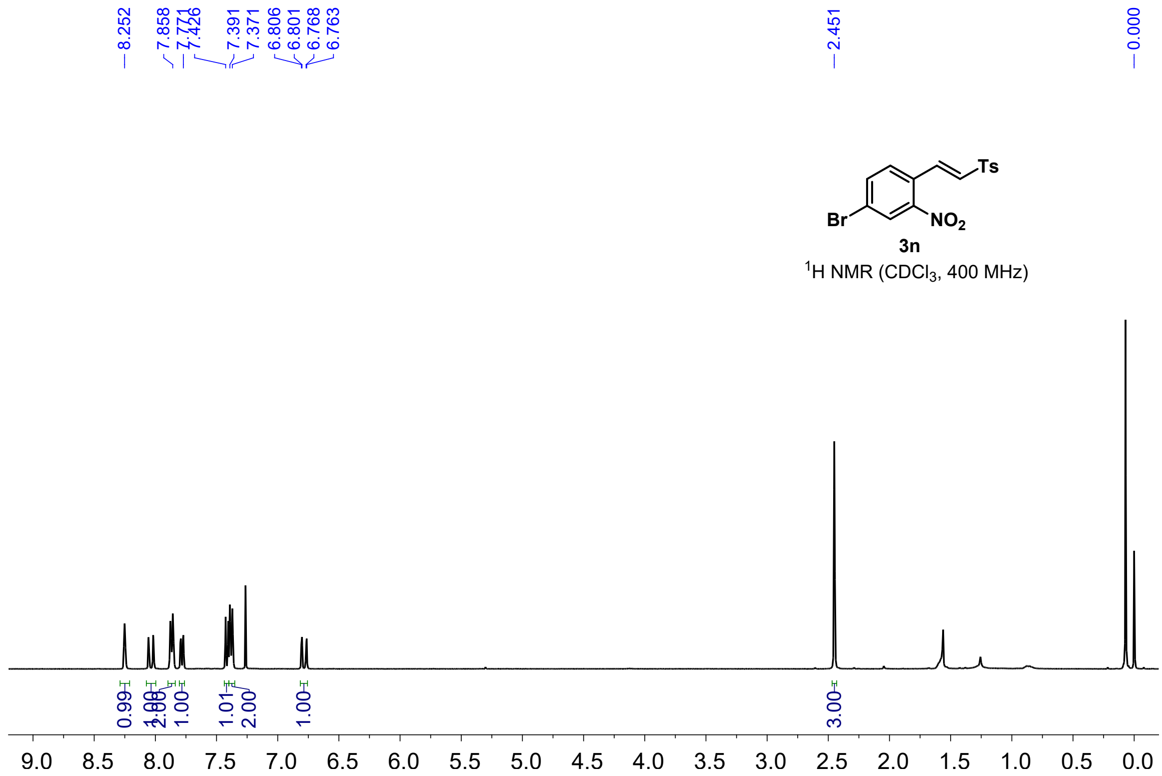
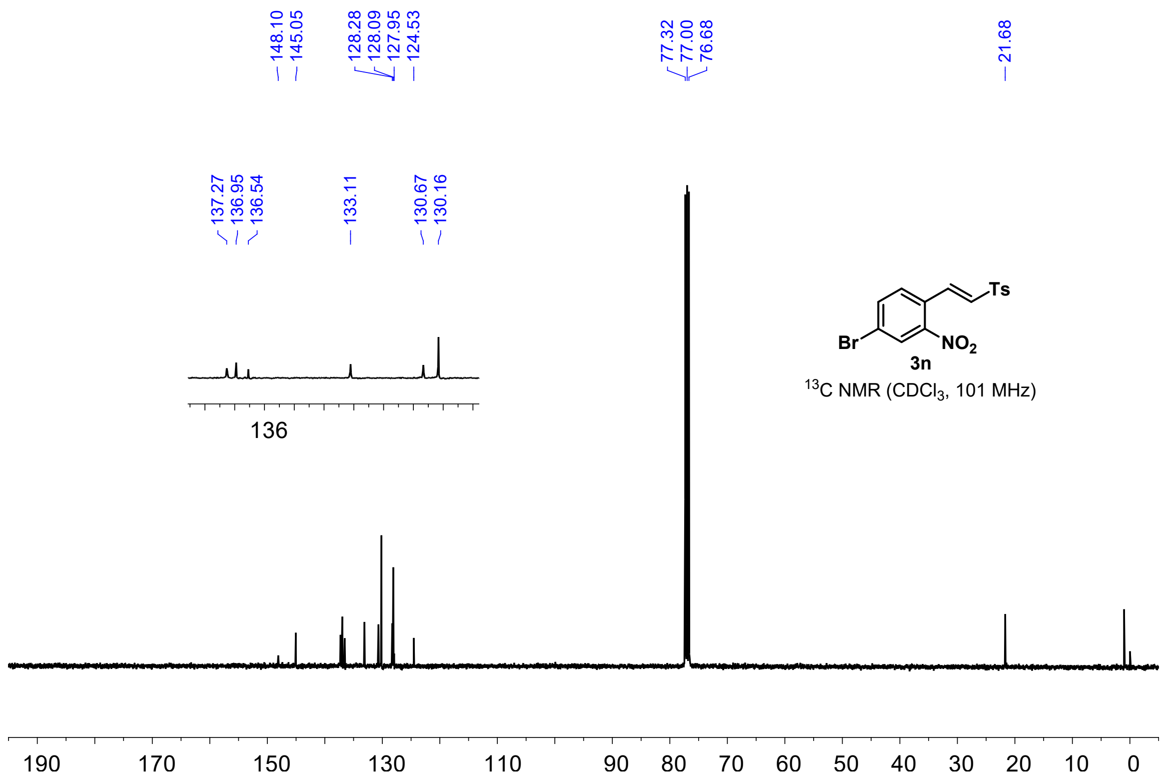
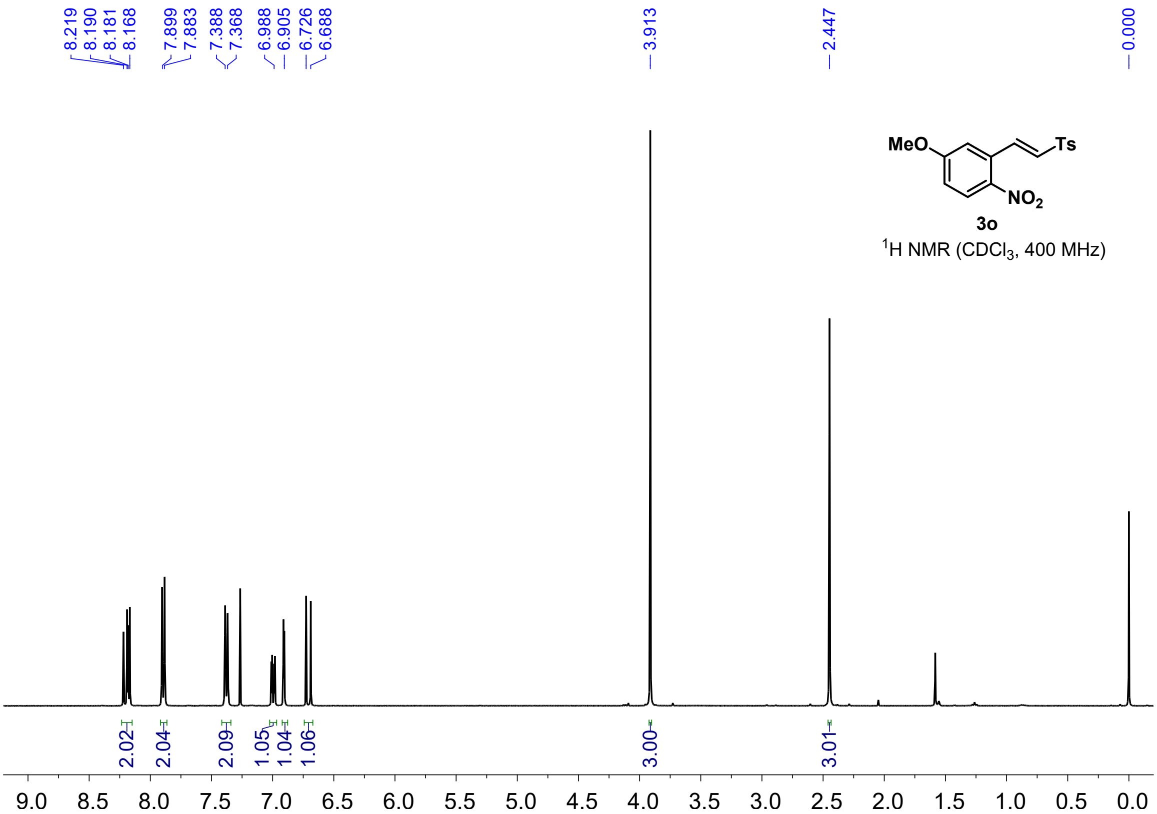
-140
-160
-180
-200

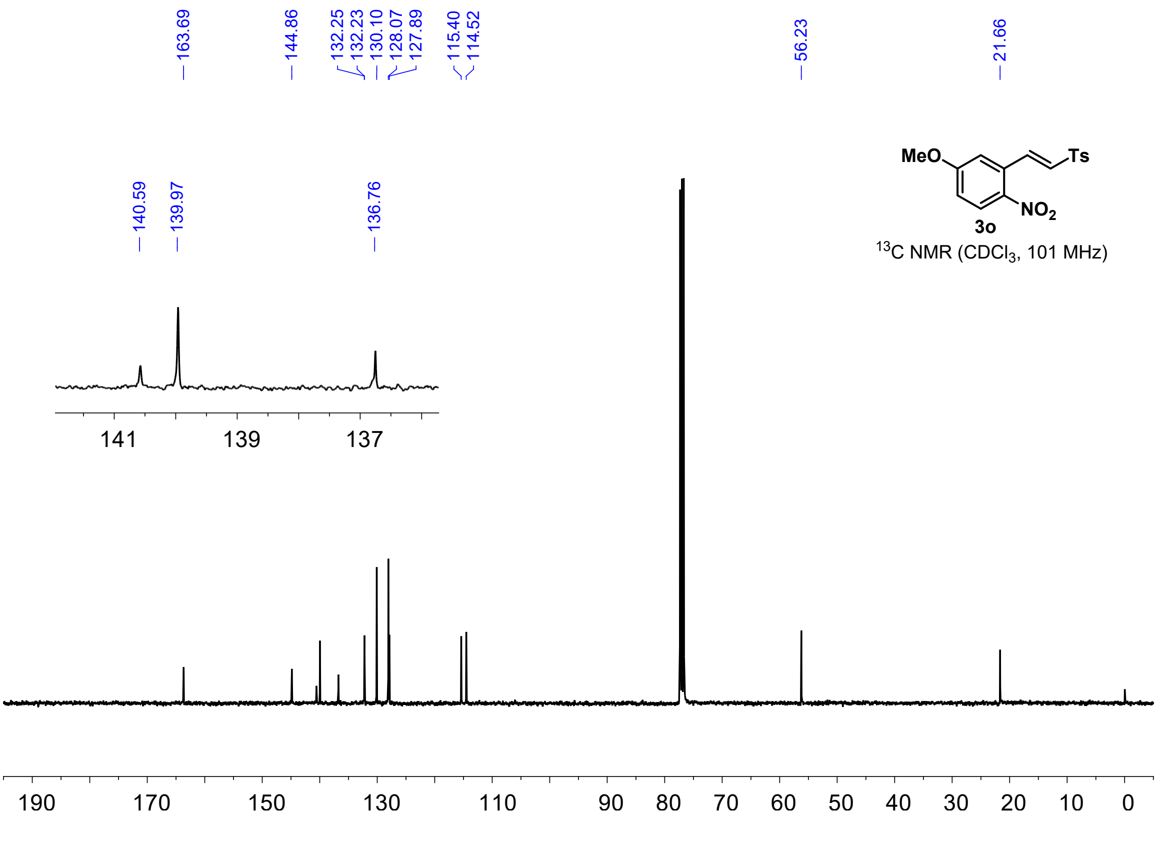

8.109
8.104
8.076
8.038
7.879
7.859
7.641
7.621
7.484
7.372
6.798
6.760
2.453
-0.000
Ts
Cl
NO2
3m
1H NMR (CDCl3, 400 MHz)
0.98
0.98
2.00
1.00
1.00
2.00
1.00
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

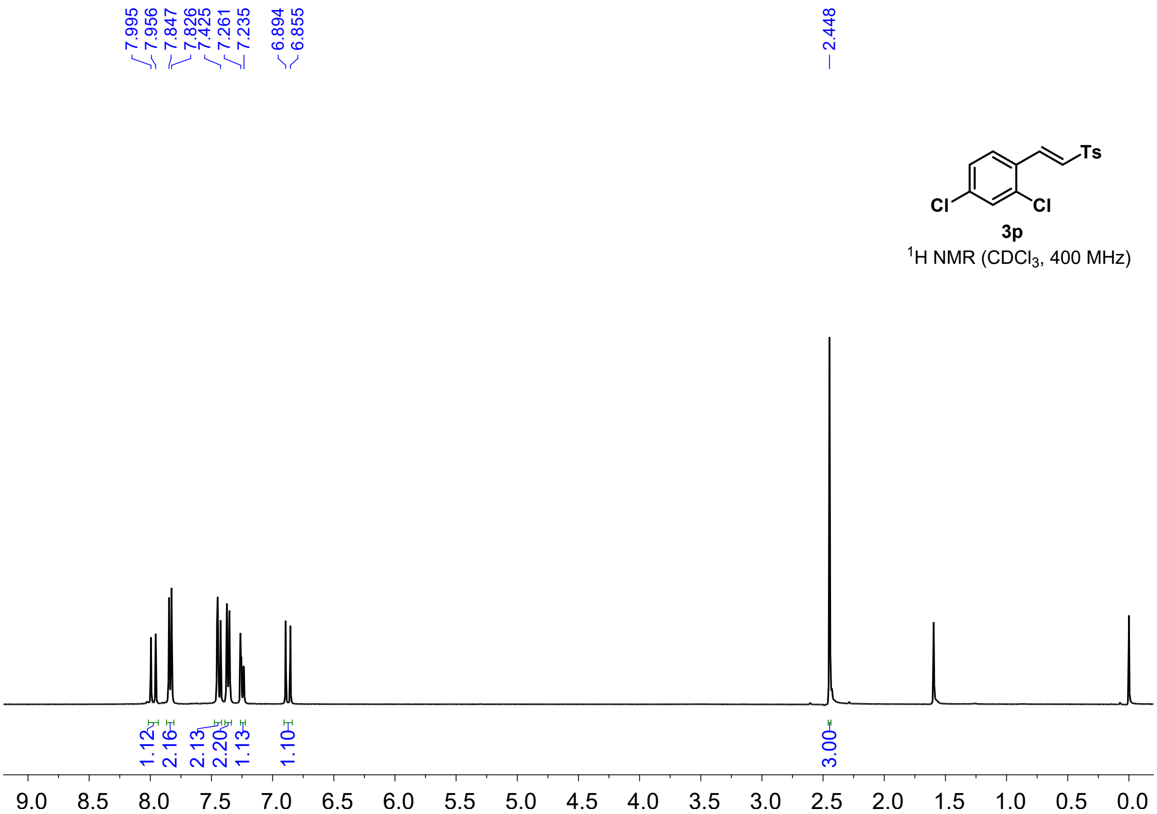

148.11
145.03
137.16
136.98
136.55
133.99
133.13
130.56
130.15
128.08
127.50
125.42
77.32
77.00
76.68
21.67
Ts
Cl
NO2
3m
13C NMR (CDCl3, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

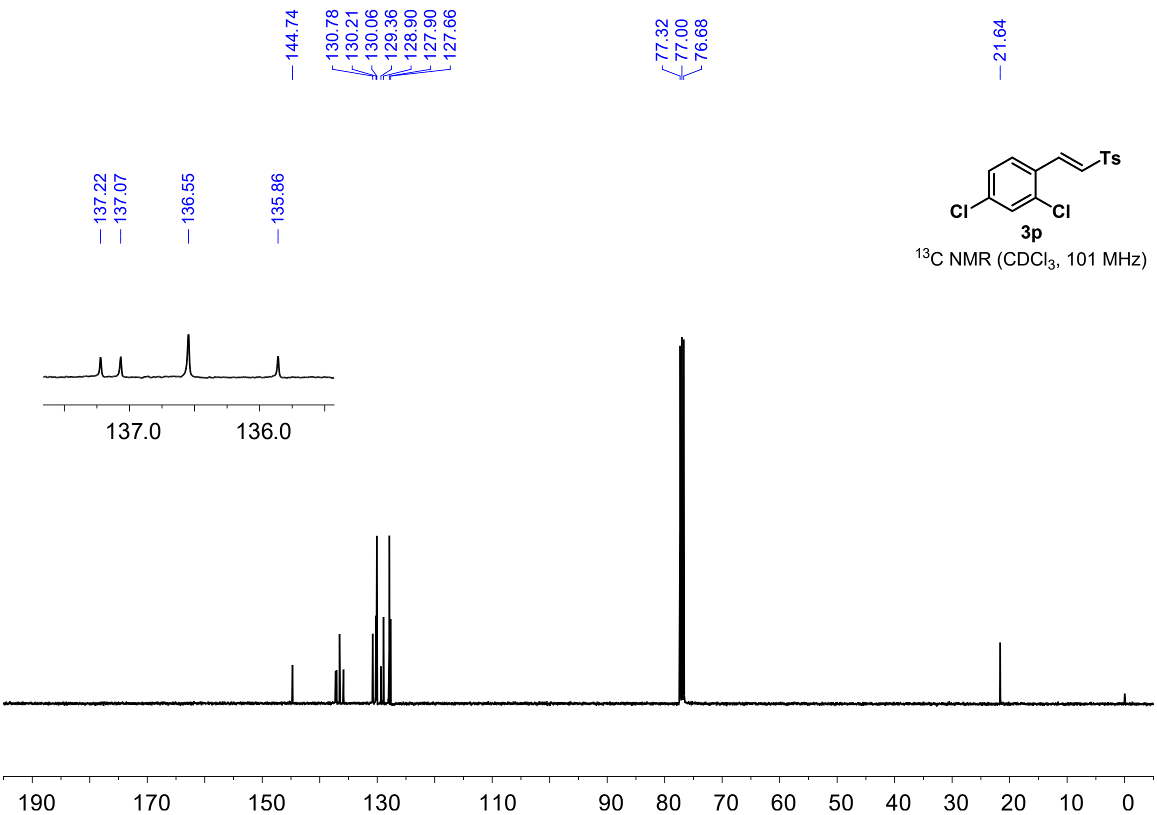

8.252
7.858
7.771
7.426
7.391
7.371
6.806
6.801
6.768
6.763
2.451
0.000
Br
NO2
Ts
3n
1H NMR (CDCl3, 400 MHz)
0.99
1.00
2.00
1.00
1.01
2.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

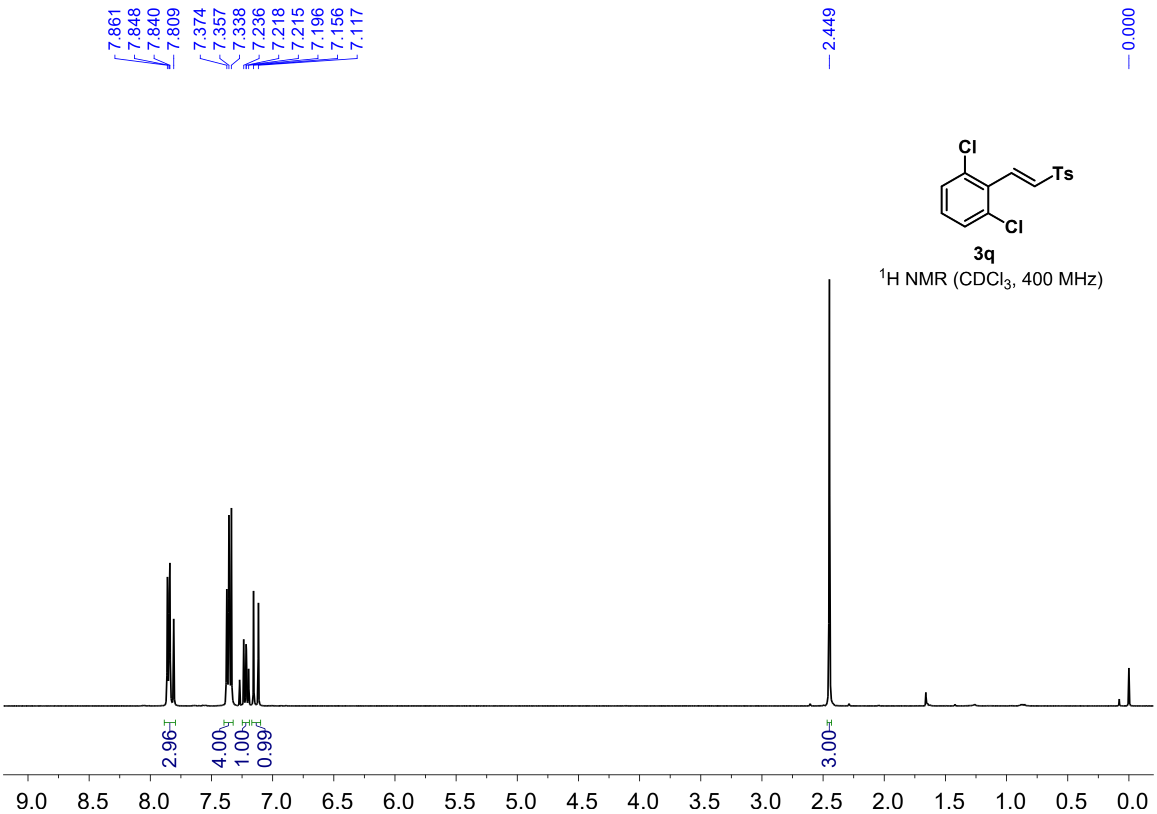

148.10
145.05
128.28
128.09
127.95
124.53
77.32
77.00
76.68
21.68
137.27
136.95
136.54
133.11
130.67
130.16
136
Br
NO2
Ts
3n
13C NMR (CDCl3, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

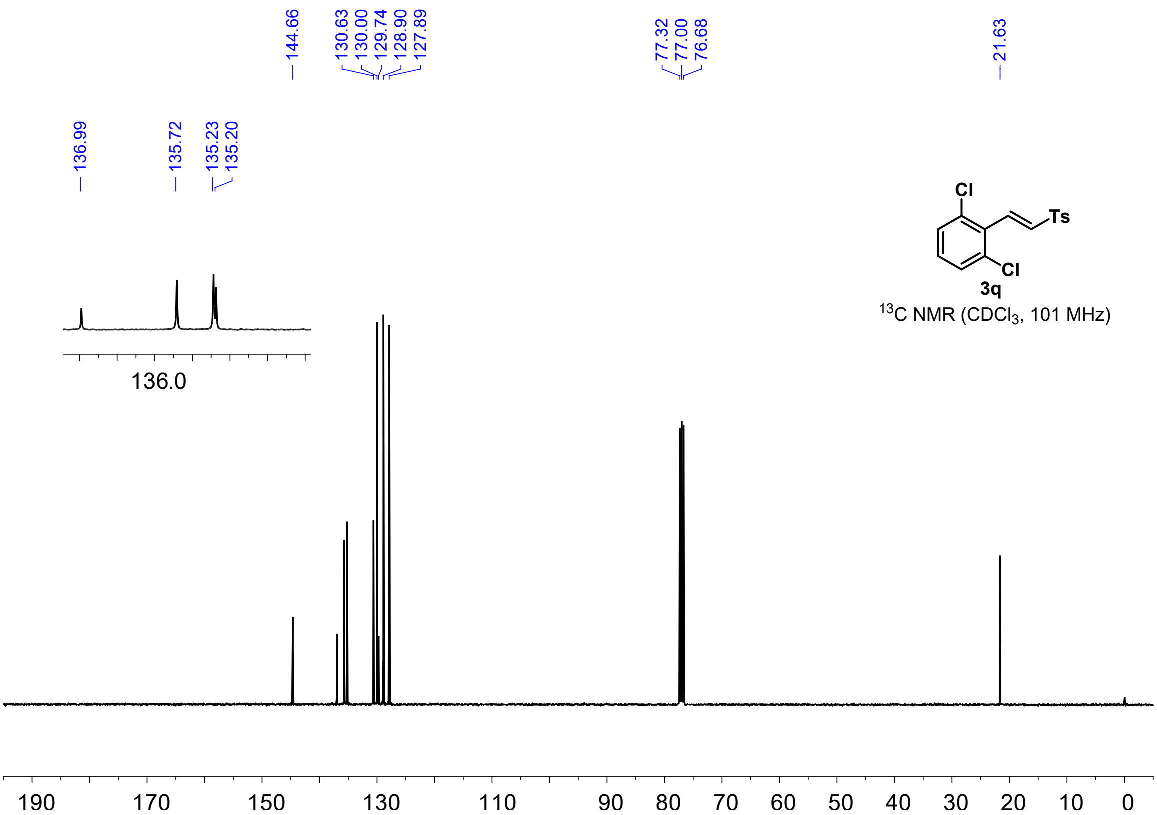

8.219
8.190
8.181
8.168
7.899
7.883
7.388
7.368
6.988
6.905
6.726
6.688
3.913
2.447
0.000
MeO
Ts
NO2
3o
1H NMR (CDCl3, 400 MHz)
2.02
2.04
2.09
1.05
1.04
1.06
3.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

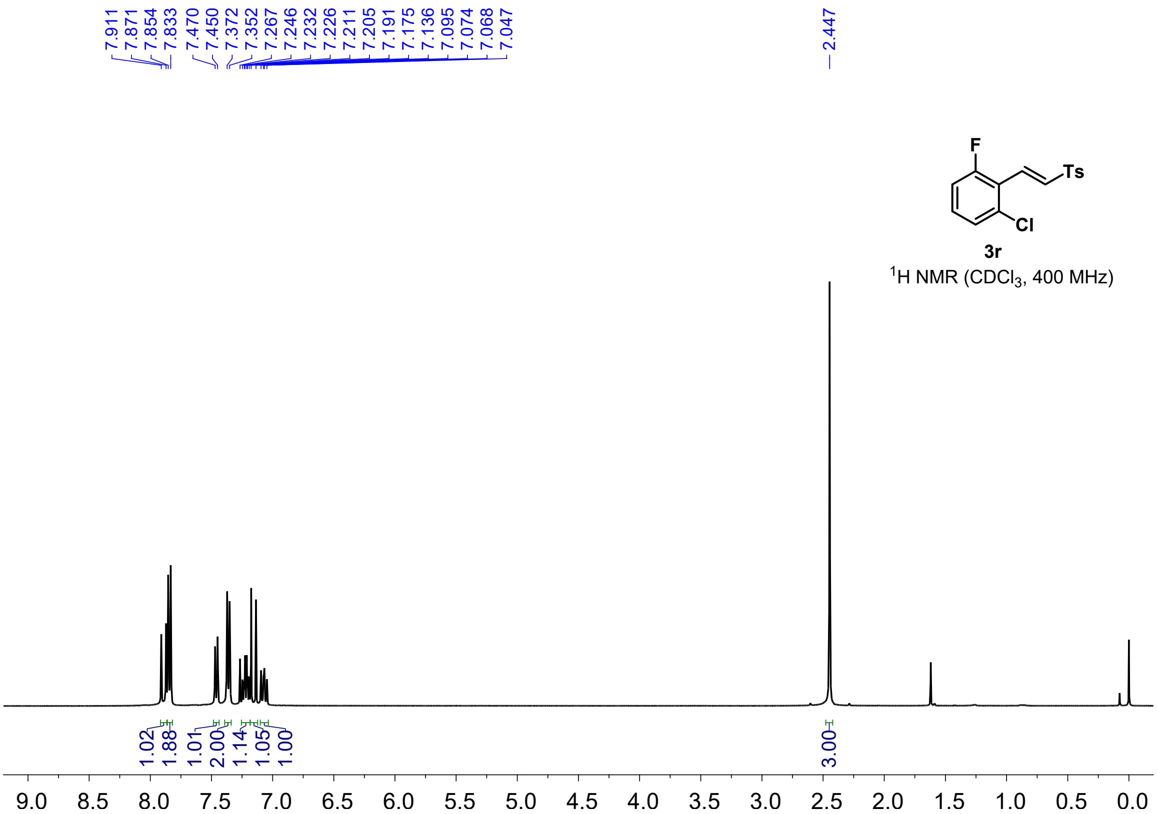

163.69
144.86
132.25
132.23
130.10
128.07
127.89
115.40
114.52
56.23
21.66
MeO
Ts
NO2
3o
13C NMR (CDCl3, 101 MHz)
140.59
139.97
136.76
141 139 137
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

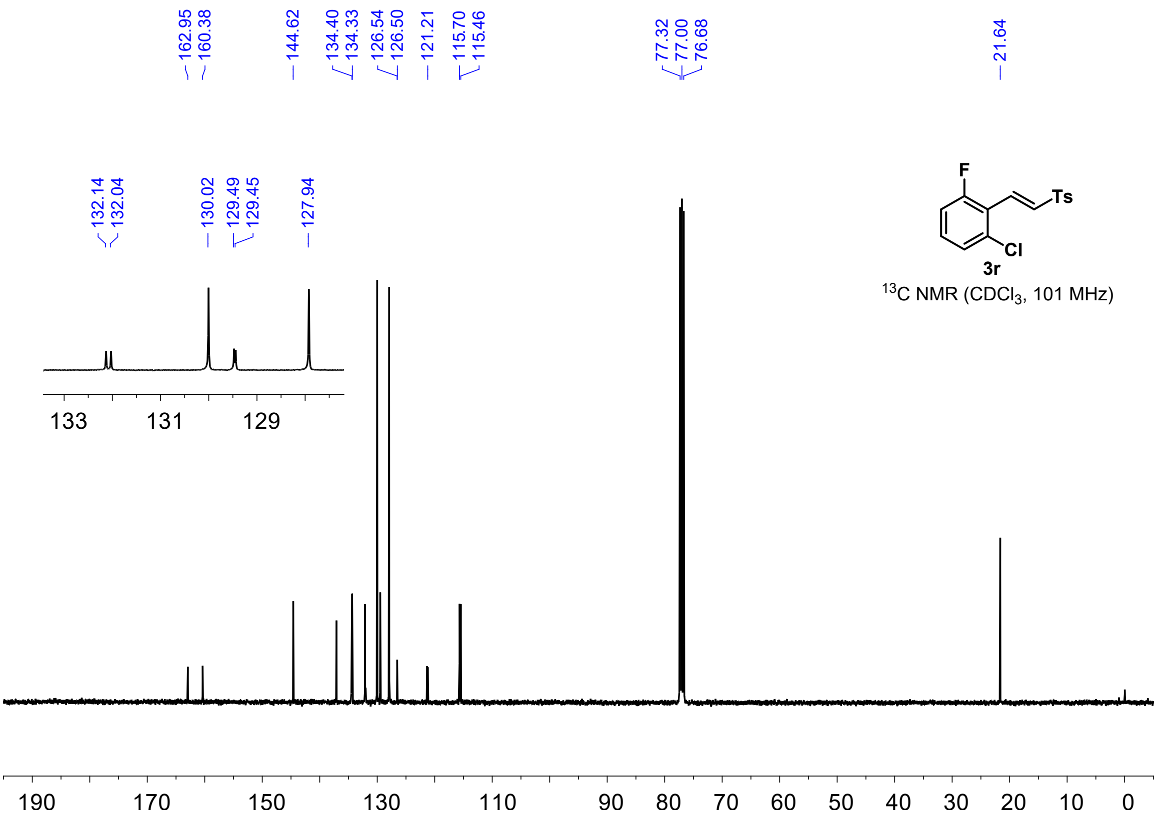

7.995
7.956
7.847
7.826
7.425
7.261
7.235
6.894
6.855
2.448
Ts
Cl
Cl
3p
1H NMR (CDCl3, 400 MHz)
1.12
2.16
2.13
2.20
1.13
1.10
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

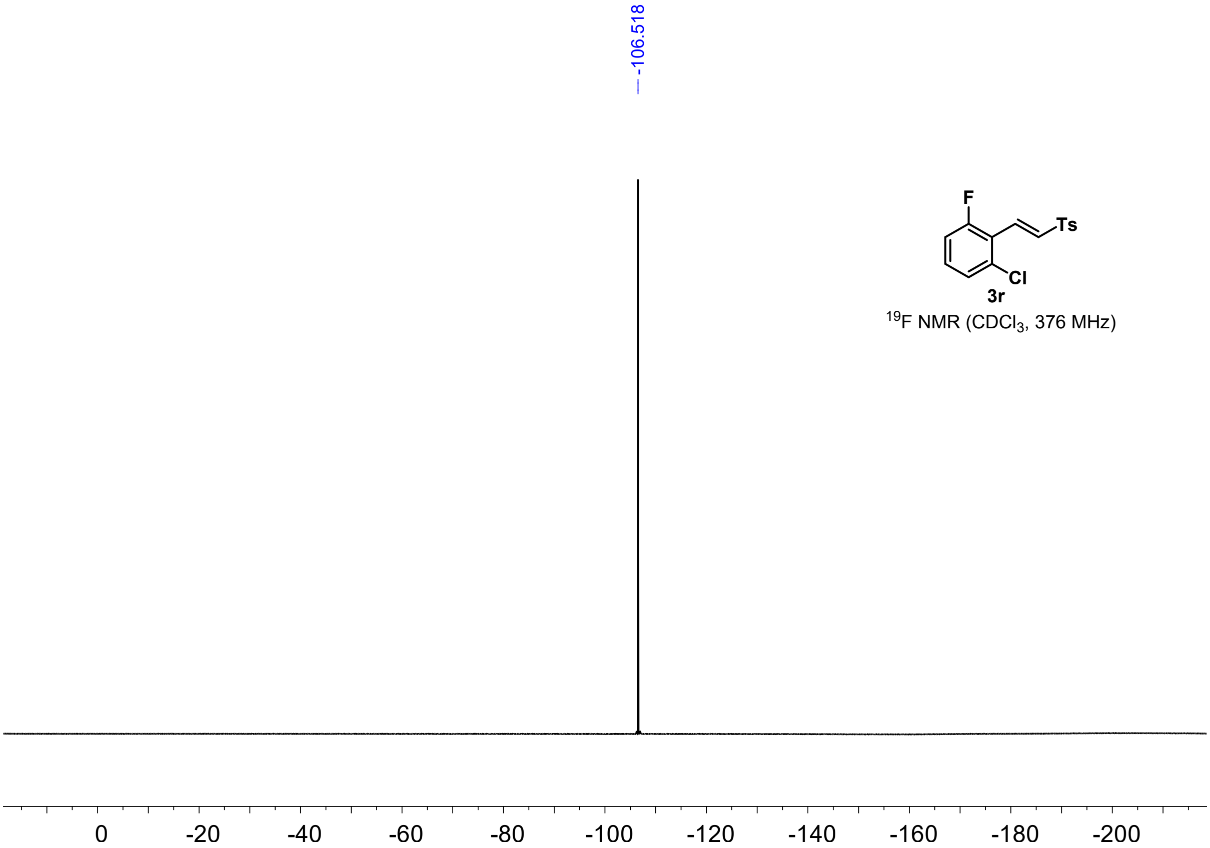

144.74
130.78
130.21
130.06
129.36
128.90
127.90
127.66
77.32
77.00
76.68
21.64
137.22
137.07
136.55
135.86
Ts
Cl
Cl
3p
13C NMR (CDCl3, 101 MHz)
137.0
136.0
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

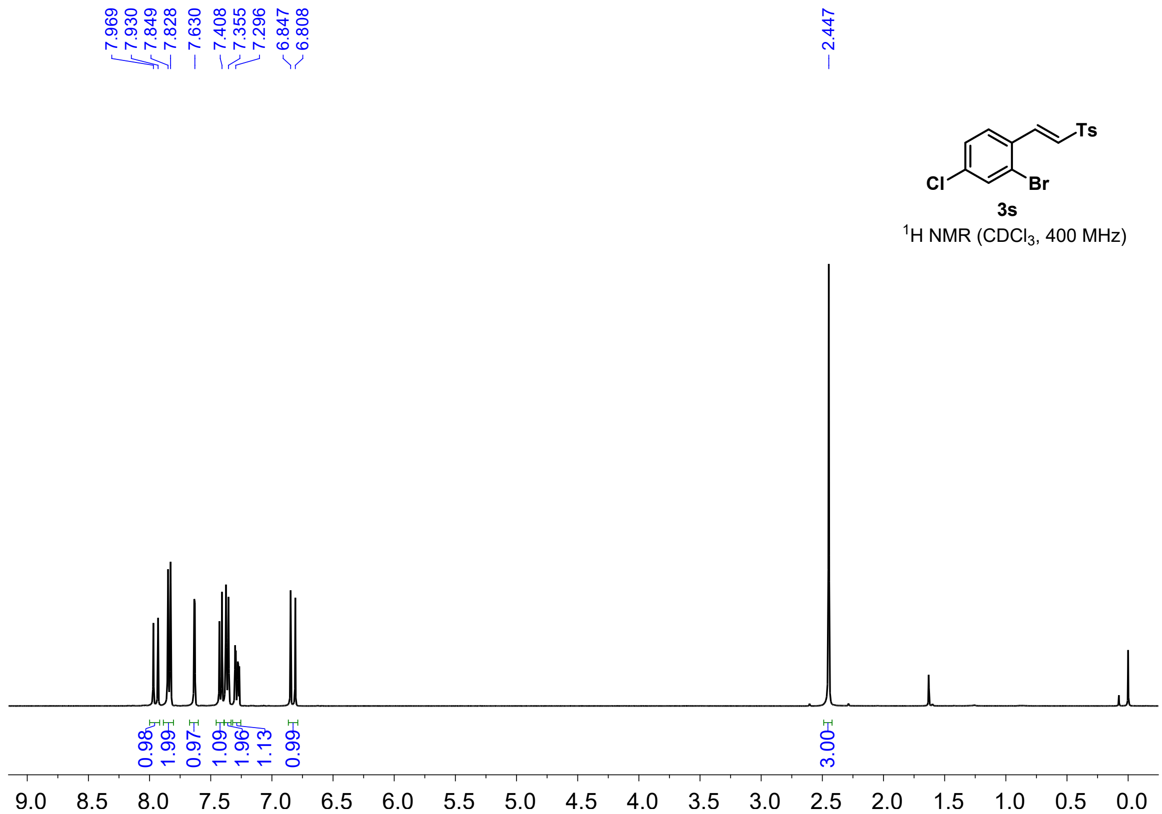

7.861
7.848
7.840
7.809
7.374
7.357
7.338
7.236
7.218
7.215
7.196
7.156
7.117
2.449
0.000
Cl
Ts
Cl
3q
1H NMR (CDCl3, 400 MHz)
2.96
4.00
1.00
0.99
3.00

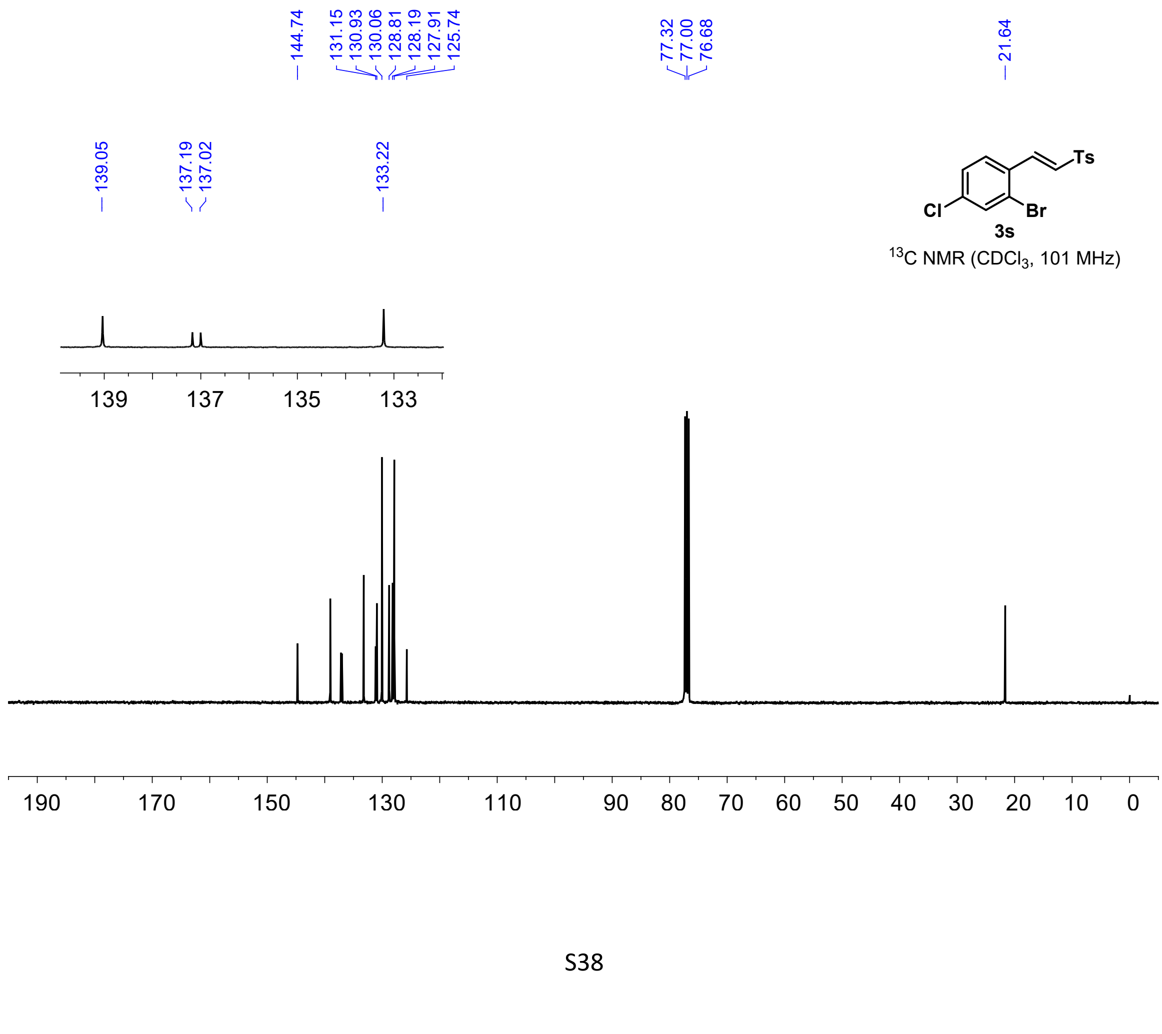

144.66
130.63
130.00
129.74
128.90
127.89
77.32
77.00
76.68
21.63
136.99
135.72
135.23
135.20
136.0
Cl
Ts
Cl
3q
13C NMR (CDCl3, 101 MHz)

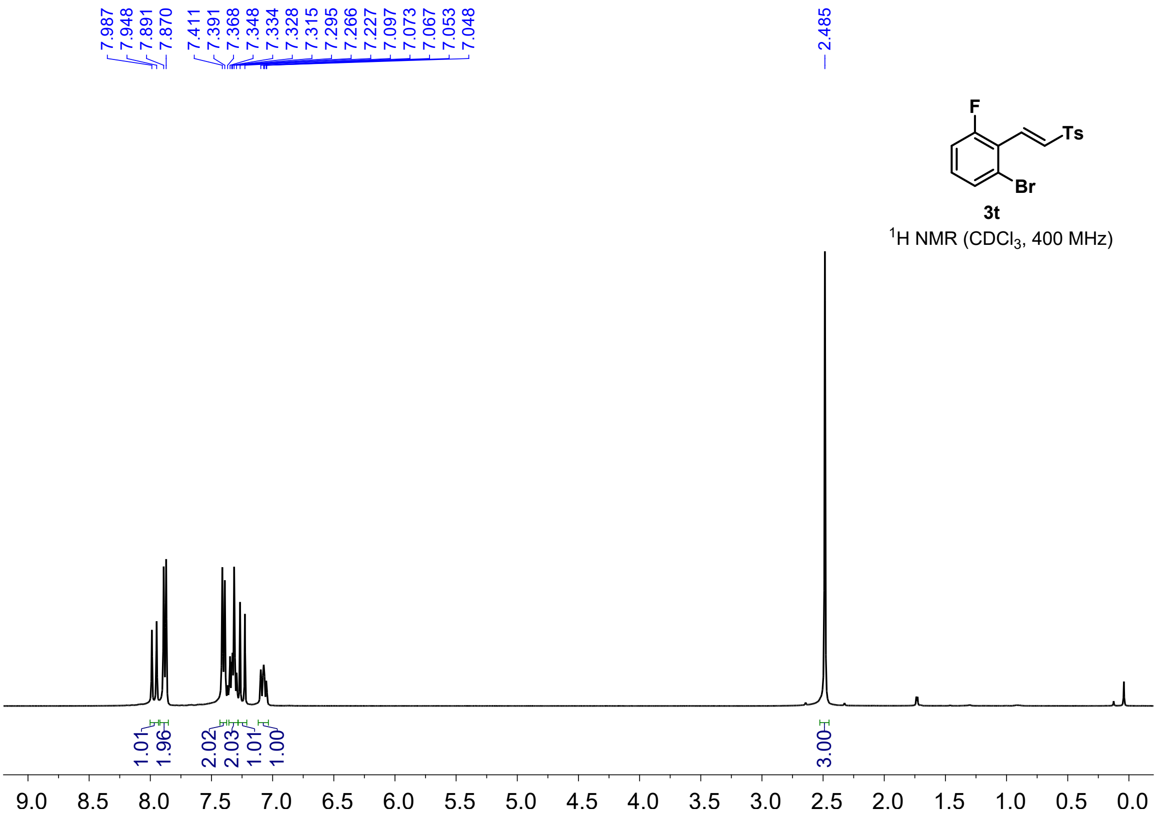

7.911
7.871
7.854
7.833
7.470
7.450
7.372
7.352
7.267
7.246
7.232
7.226
7.211
7.205
7.191
7.175
7.136
7.095
7.074
7.068
7.047
2.447
F
Ts
Cl
3r
1H NMR (CDCl3, 400 MHz)
1.02
1.88
1.01
2.00
1.14
1.05
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

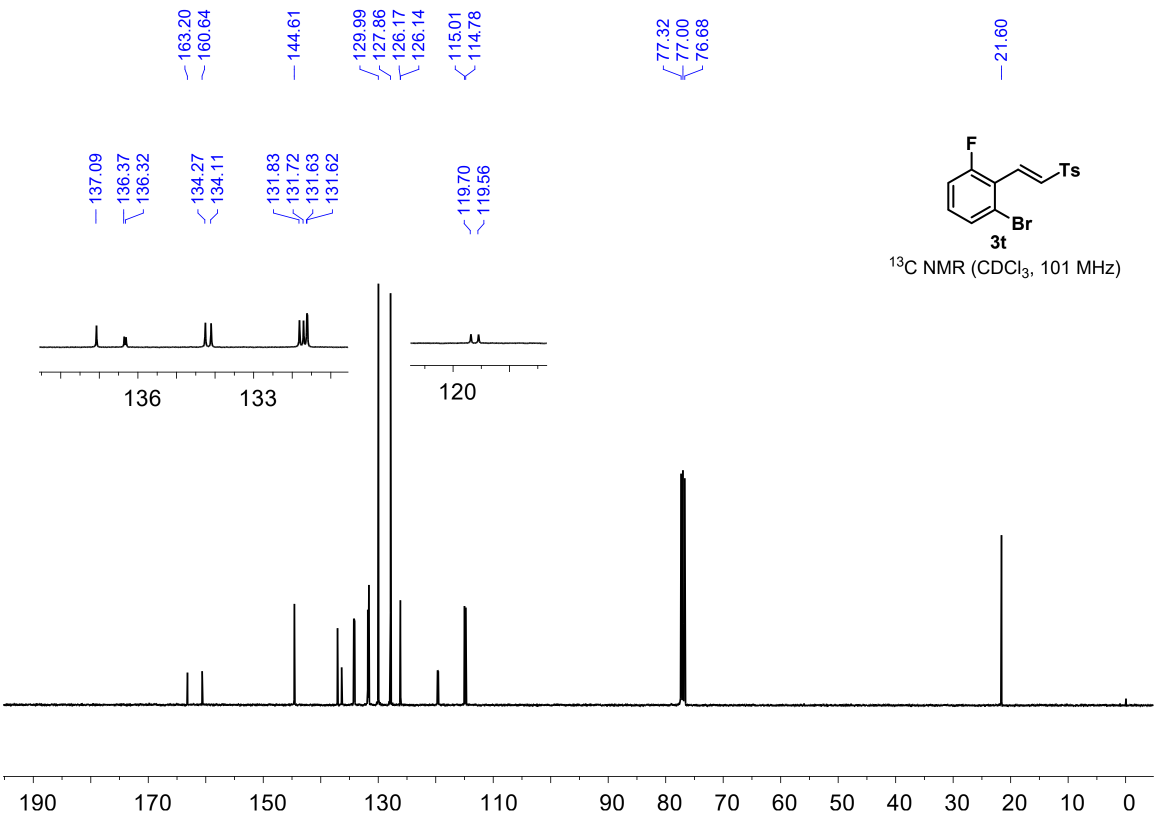

162.95
160.38
144.62
134.40
134.33
126.54
126.50
121.21
115.70
115.46
77.32
77.00
76.68
21.64
132.14
132.04
130.02
129.49
129.45
127.94
133 131 129
F
Ts
Cl
3r
13C NMR (CDCl3, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

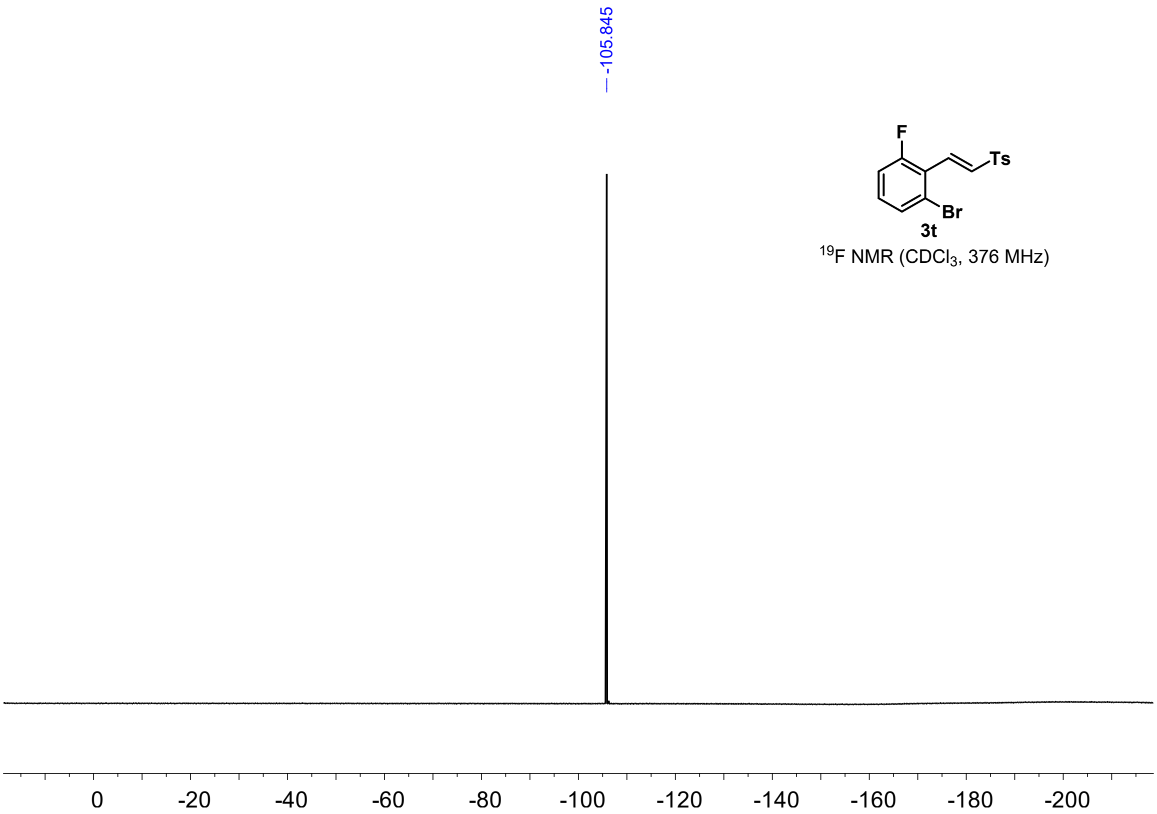

-106.518
F
Ts
Cl
3r
^{19}F NMR (CDCl$_3$, 376 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200


7.969
7.930
7.849
7.828
7.630
7.408
7.355
7.296
6.847
6.808
2.447
Ts
Cl
Br
3s
^{1}H NMR ($CDCl_3$, 400 MHz)
0.98
1.99
0.97
1.09
1.96
1.13
0.99
3.00
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


144.74
131.15
130.93
130.06
128.81
128.19
127.91
125.74
77.32
77.00
76.68
21.64
139.05
137.19
137.02
133.22
Ts
Cl
Br
3s
^{13}C NMR ($CDCl_3$, 101 MHz)
139 137 135 133
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

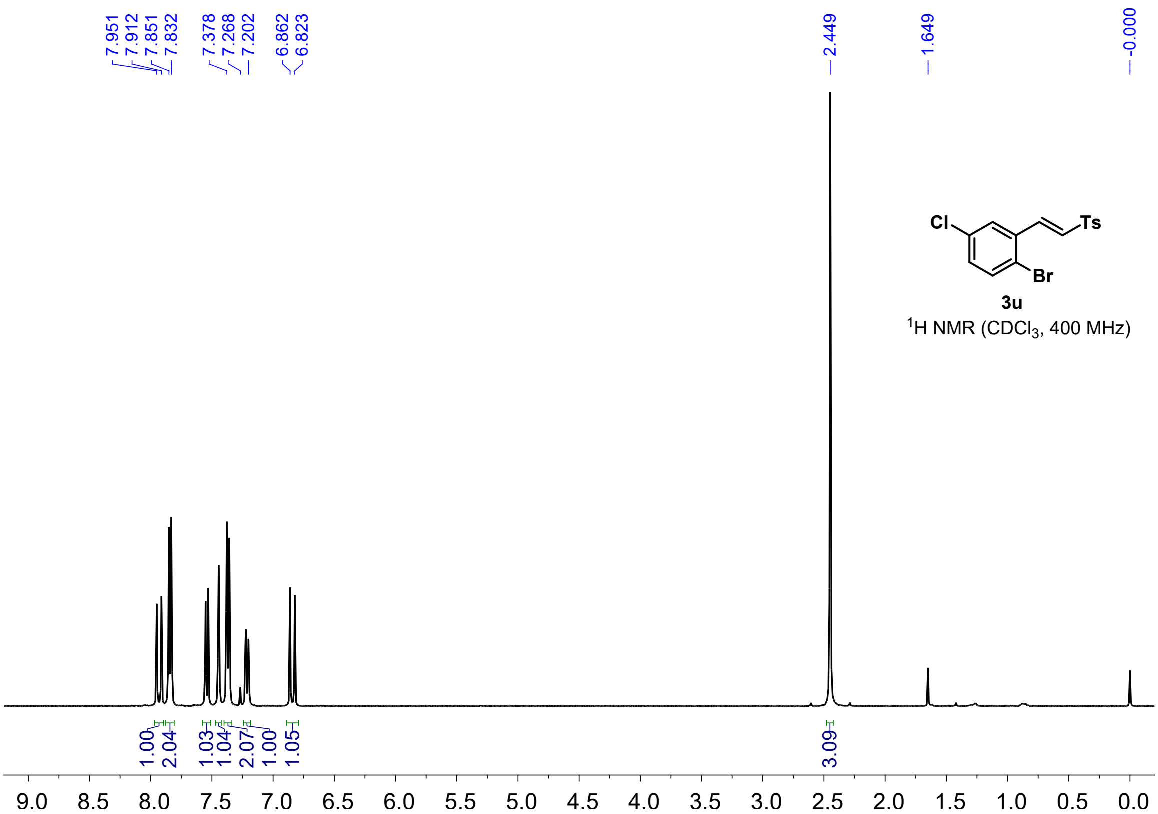

7.987 7.948 7.891 7.870 7.411 7.391 7.368 7.348 7.334 7.328 7.315 7.295 7.266 7.227 7.097 7.073 7.067 7.053 7.048
2.485
F
Ts
Br
3t
^{1}H NMR (CDCl$_3$, 400 MHz)
1.01 1.96 2.02 2.03 1.01 1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

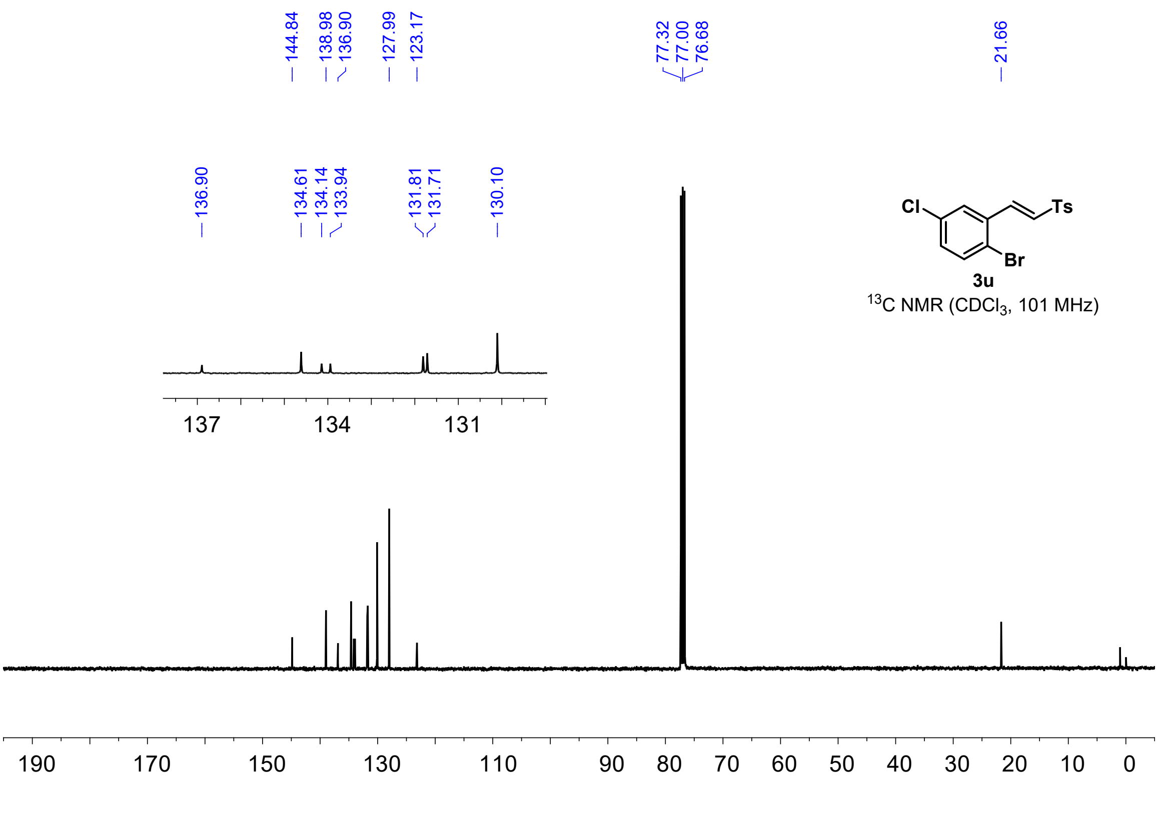

163.20 160.64
144.61
129.99 127.86 126.17 126.14
115.01 114.78
77.32 77.00 76.68
21.60
137.09 136.37 136.32
134.27 134.11
131.83 131.72 131.63 131.62
119.70 119.56
F
Ts
Br
3t
^{13}C NMR (CDCl$_3$, 101 MHz)
136 133
120
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

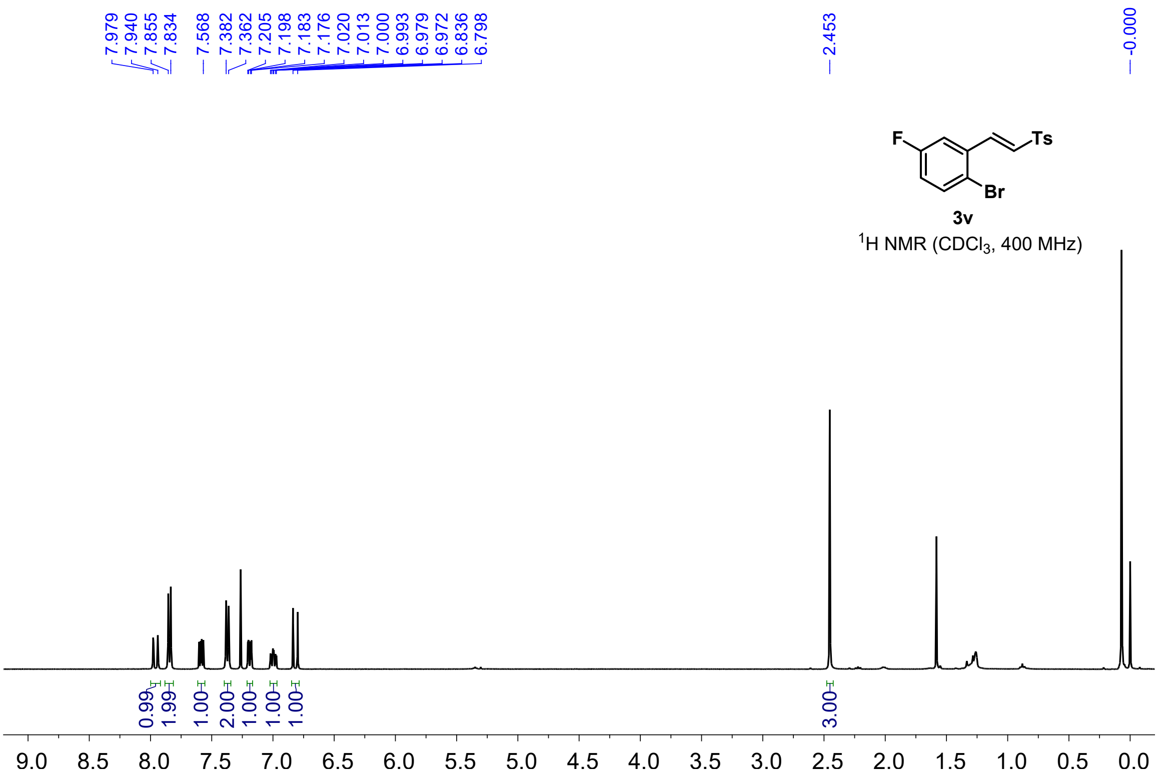


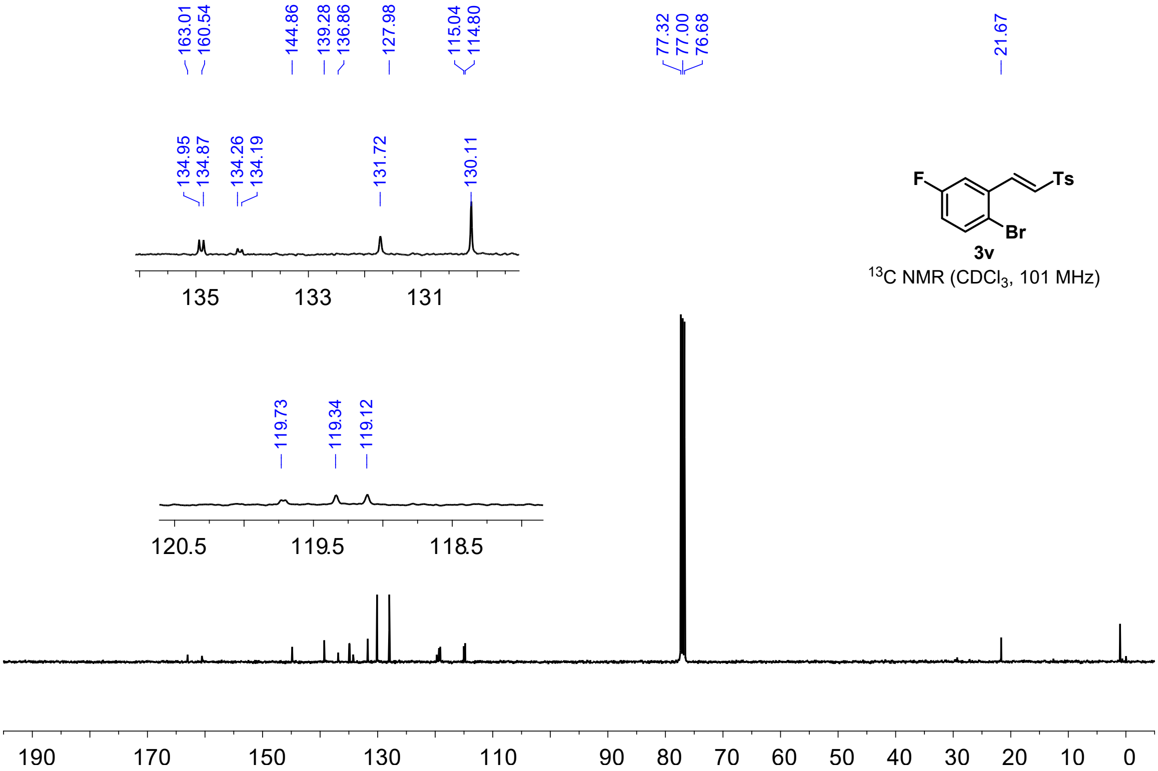
3t

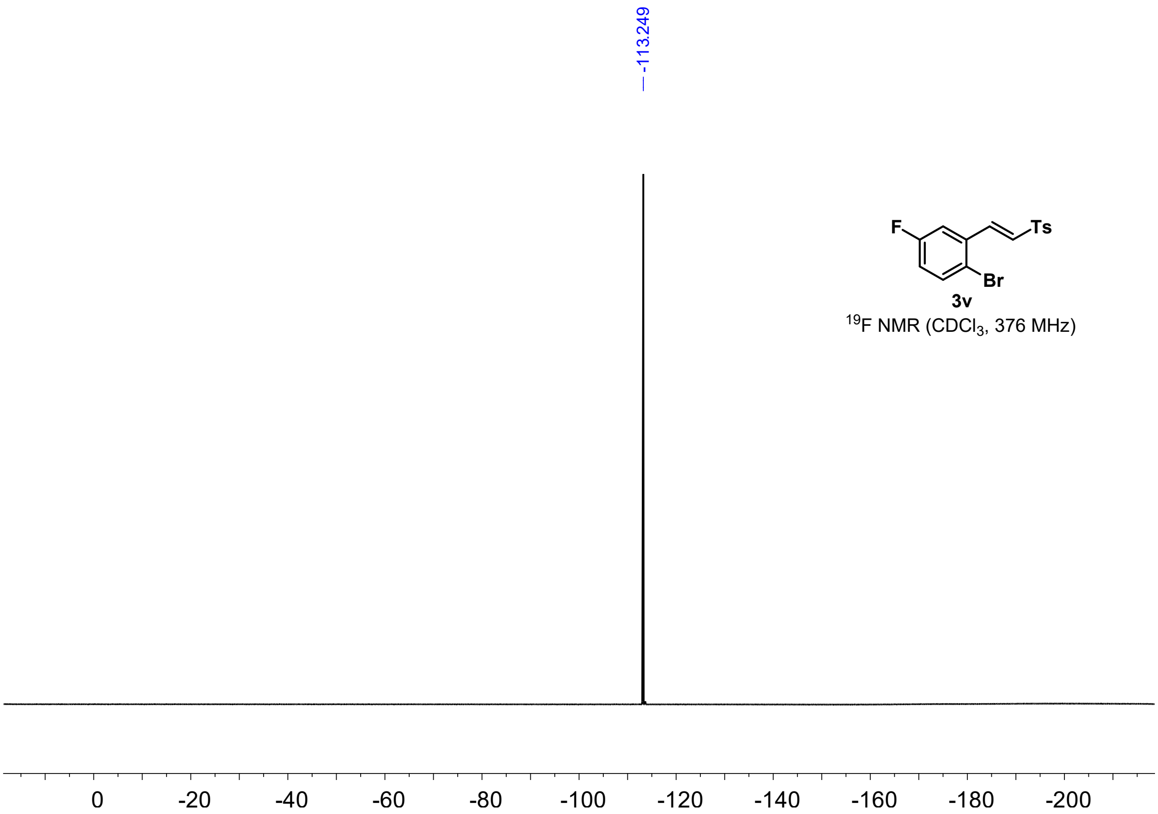
^{19}F NMR (CDCl$_3$, 376 MHz)

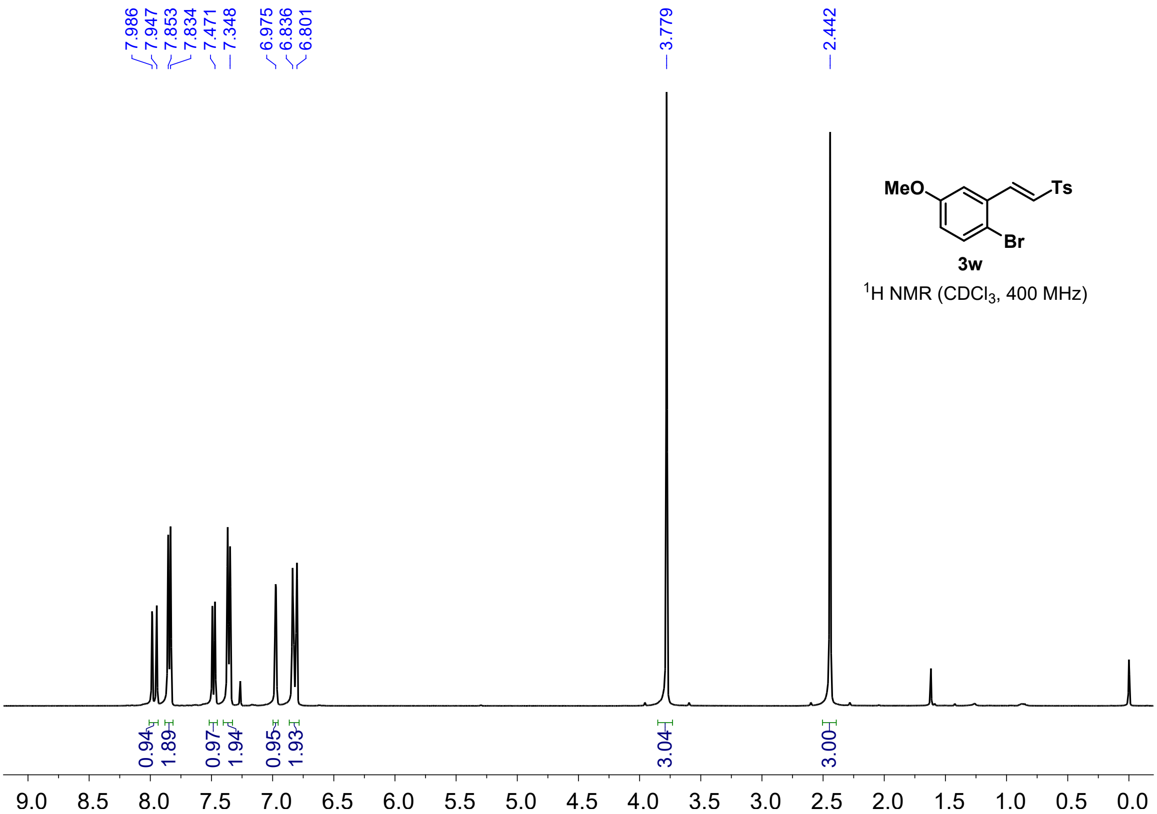

7.951
7.912
7.851
7.832
7.378
7.268
7.202
6.862
6.823
2.449
1.649
-0.000
Cl
Ts
Br
3u
^{1}H NMR (CDCl$_3$, 400 MHz)
1.00
2.04
1.03
1.04
2.07
1.00
1.05
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

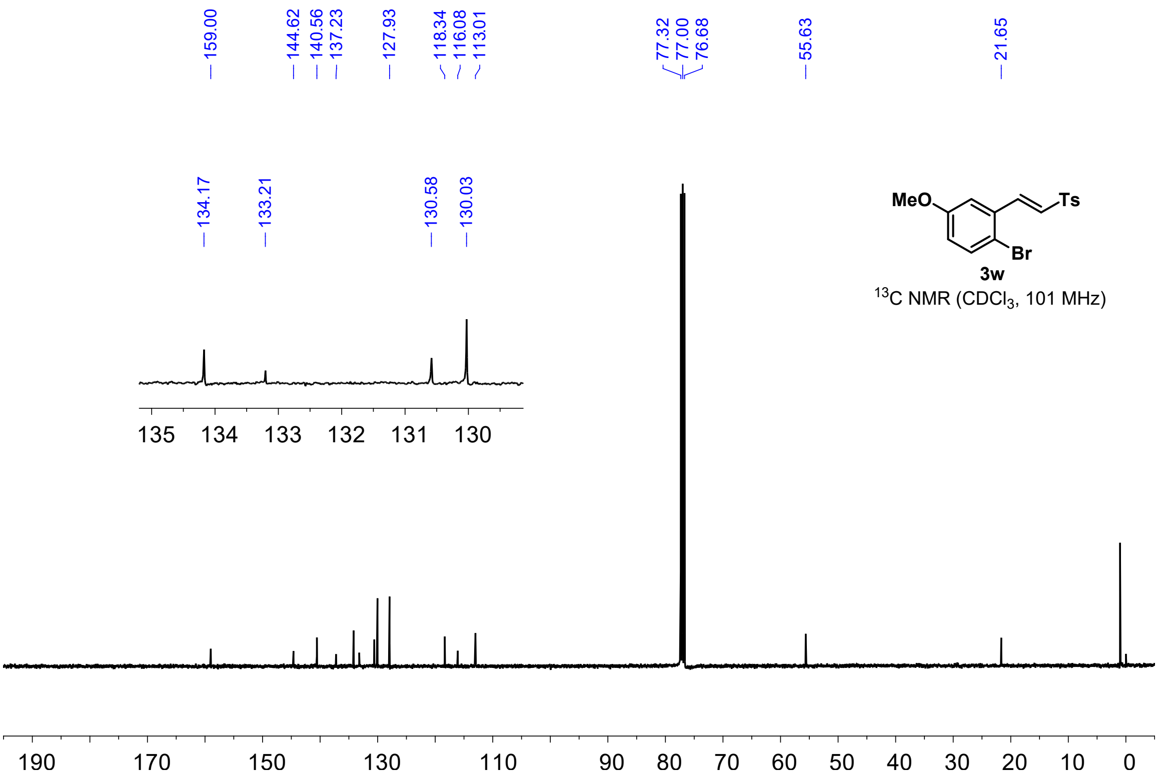

144.84
138.98
136.90
127.99
123.17
77.32
77.00
76.68
21.66
136.90
134.61
134.14
133.94
131.81
131.71
130.10
137 134 131
Cl
Ts
Br
3u
^{13}C NMR (CDCl$_3$, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

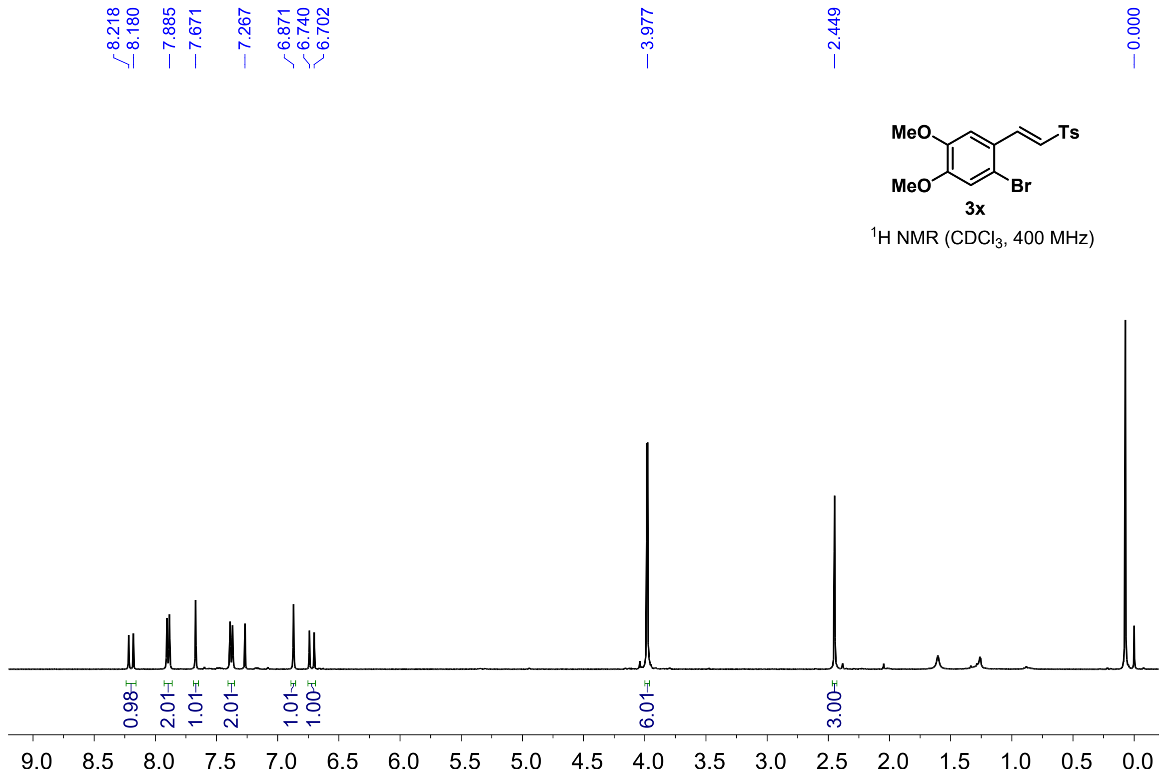

7.979
7.940
7.855
7.834
7.568
7.382
7.362
7.205
7.198
7.183
7.176
7.020
7.013
7.000
6.993
6.979
6.972
6.836
6.798
2.453
-0.000
F
Ts
Br
3v
1H NMR (CDCl3, 400 MHz)
0.99
1.99
1.00
2.00
1.00
1.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

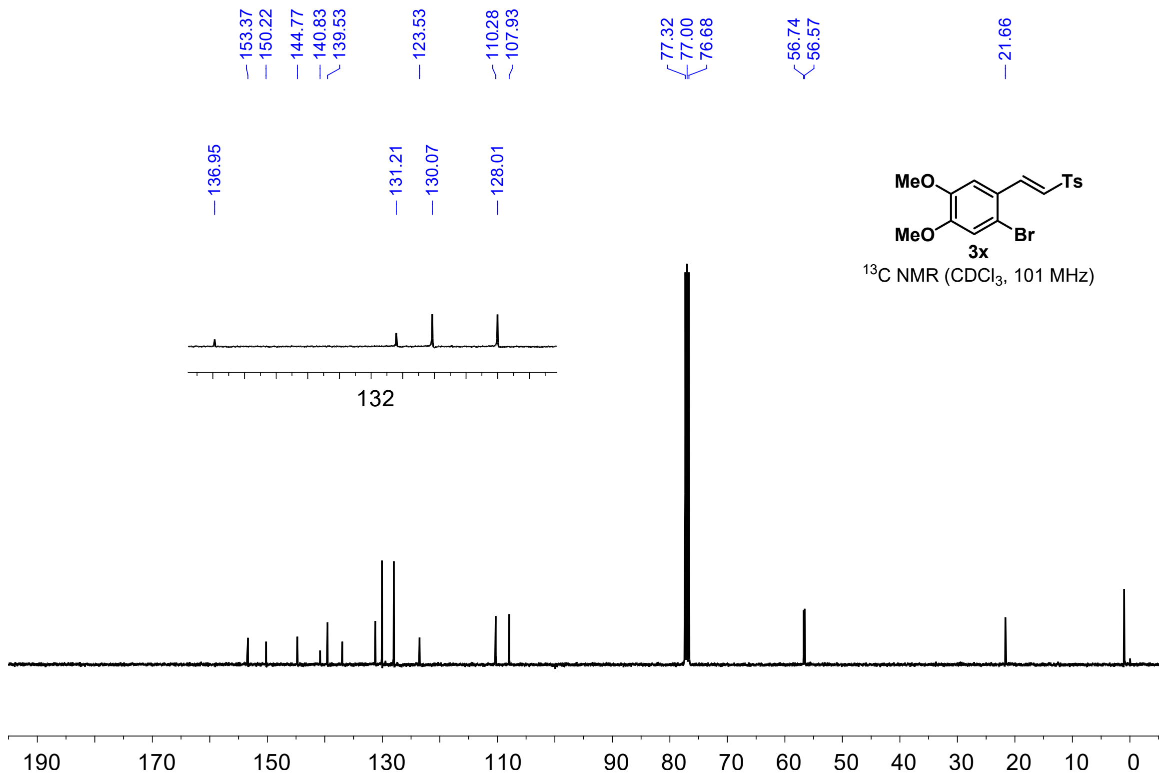

163.01
160.54
144.86
139.28
136.86
127.98
115.04
114.80
77.32
77.00
76.68
21.67
134.95
134.87
134.26
134.19
131.72
130.11
135 133 131
F
Ts
Br
3v
13C NMR (CDCl3, 101 MHz)
119.73
119.34
119.12
120.5 119.5 118.5
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

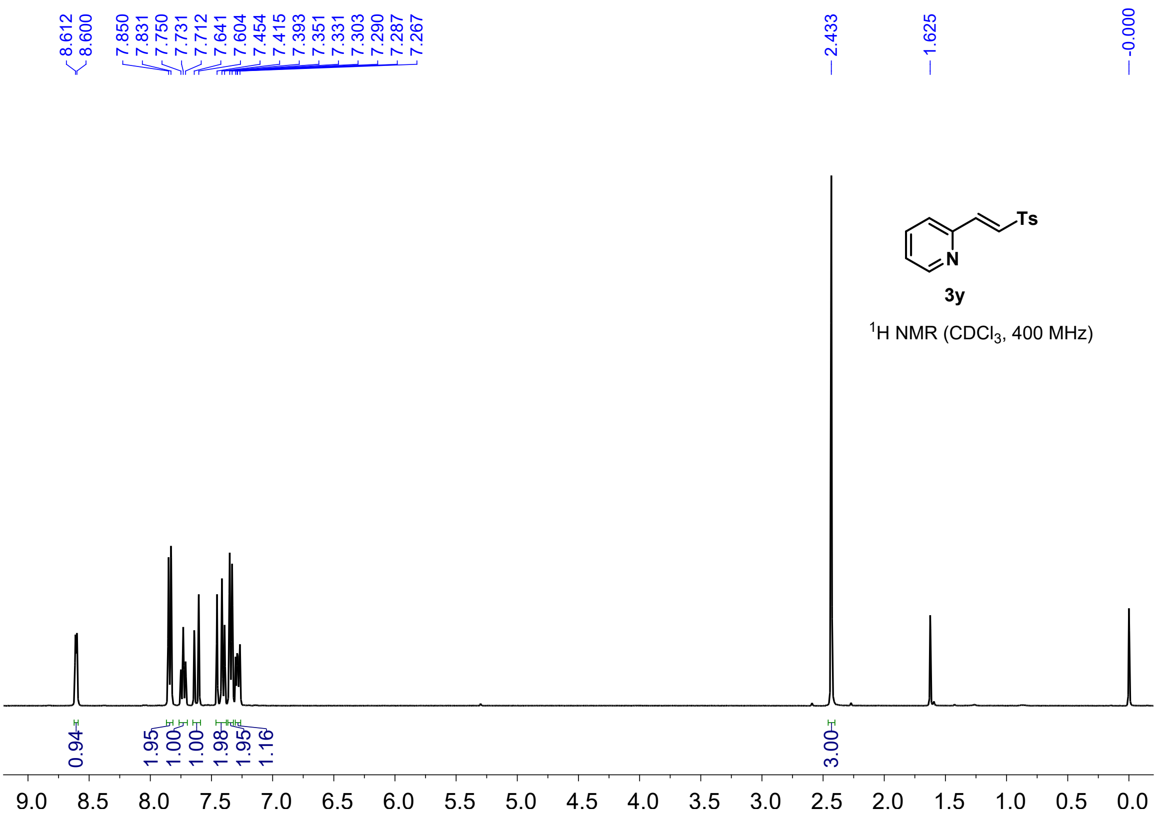

-113.249
F
Ts
Br
3v
19F NMR (CDCl3, 376 MHz)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

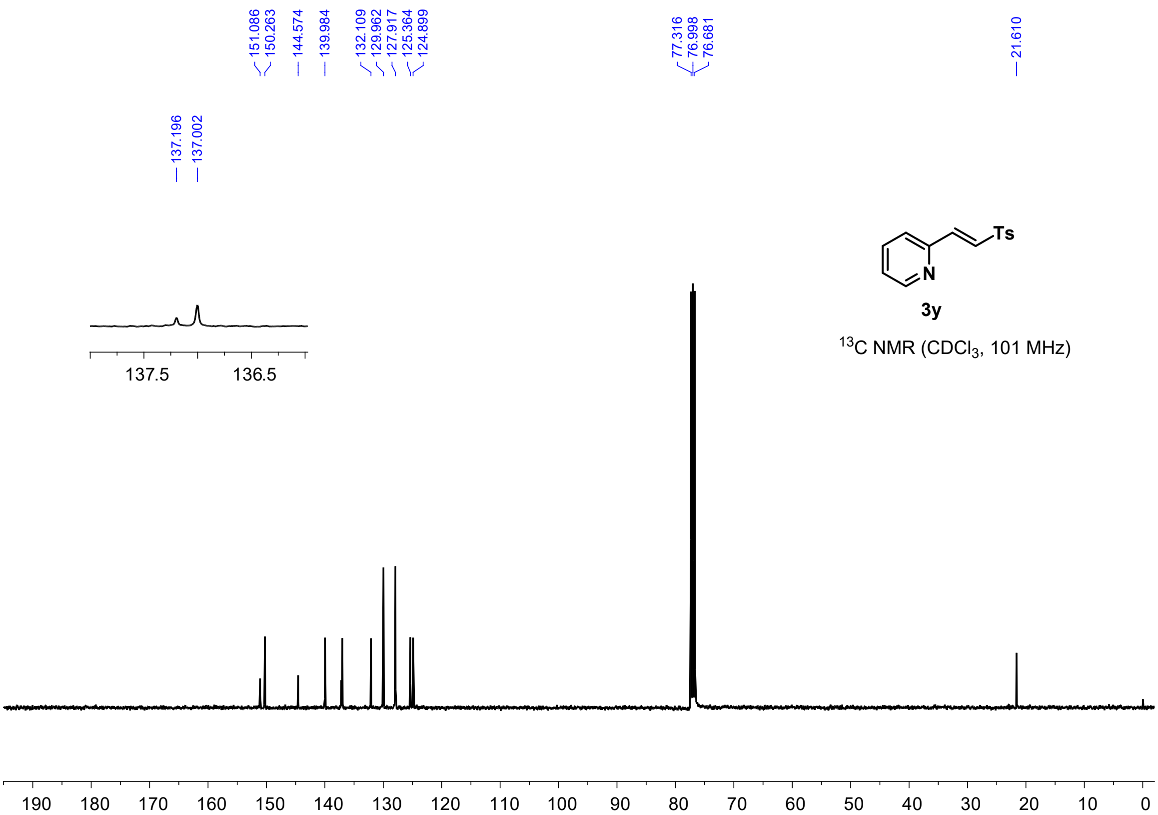

7.986
7.947
7.853
7.834
7.471
7.348
6.975
6.836
6.801
3.779
2.442
MeO
Ts
Br
3w
^{1}H NMR ($CDCl_3$, 400 MHz)
0.94
1.89
0.97
1.94
0.95
1.93
3.04
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

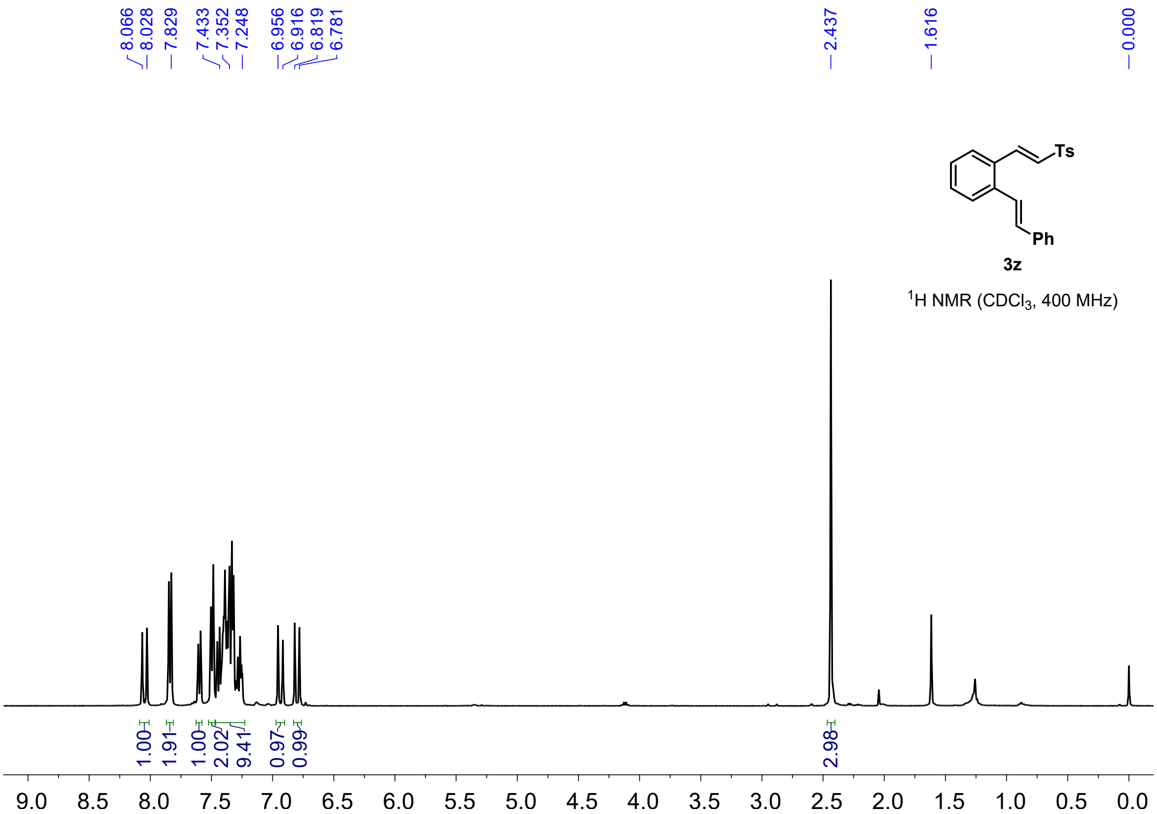

159.00
144.62
140.56
137.23
127.93
118.34
116.08
113.01
77.32
77.00
76.68
55.63
21.65
134.17
133.21
130.58
130.03
135 134 133 132 131 130
MeO
Ts
Br
3w
^{13}C NMR ($CDCl_3$, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

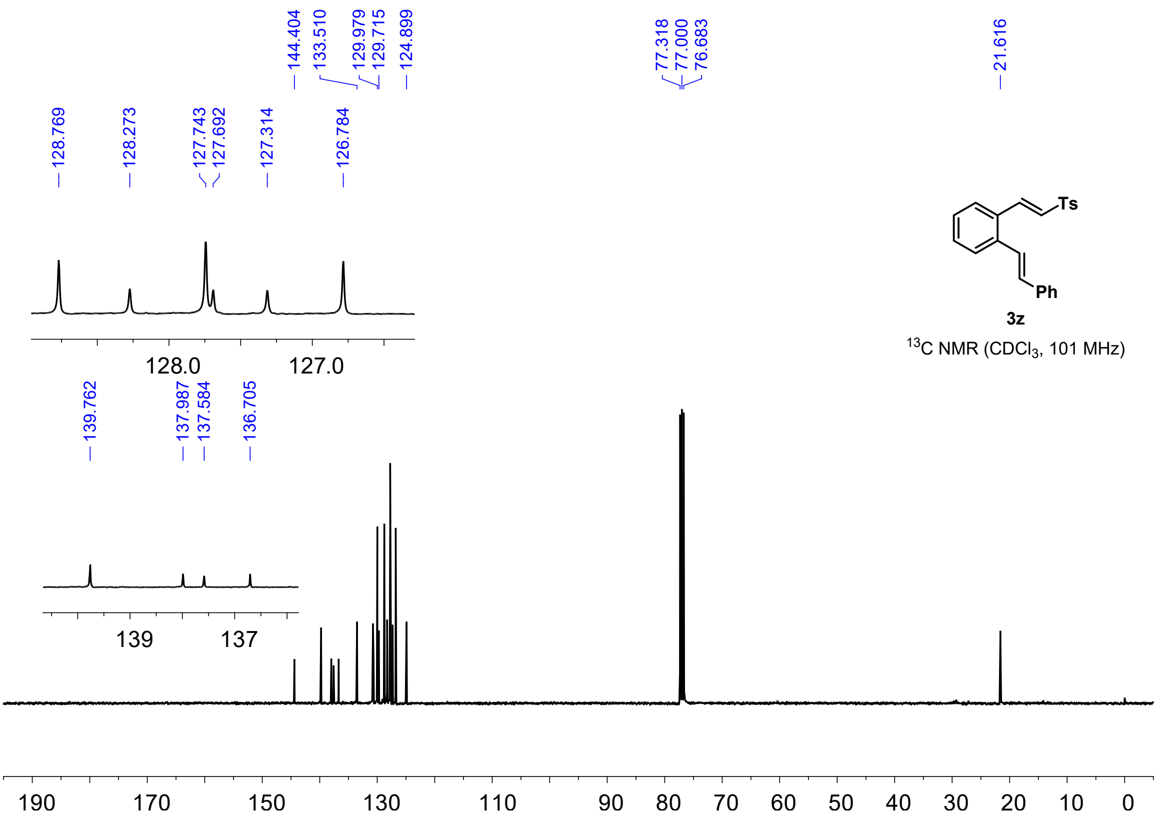

8.218
8.180
7.885
7.671
7.267
6.871
6.740
6.702
3.977
2.449
0.000
MeO
MeO
Ts
Br
3x
^{1}H NMR (CDCl$_3$, 400 MHz)
0.98
2.01
1.01
2.01
1.01
1.00
6.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

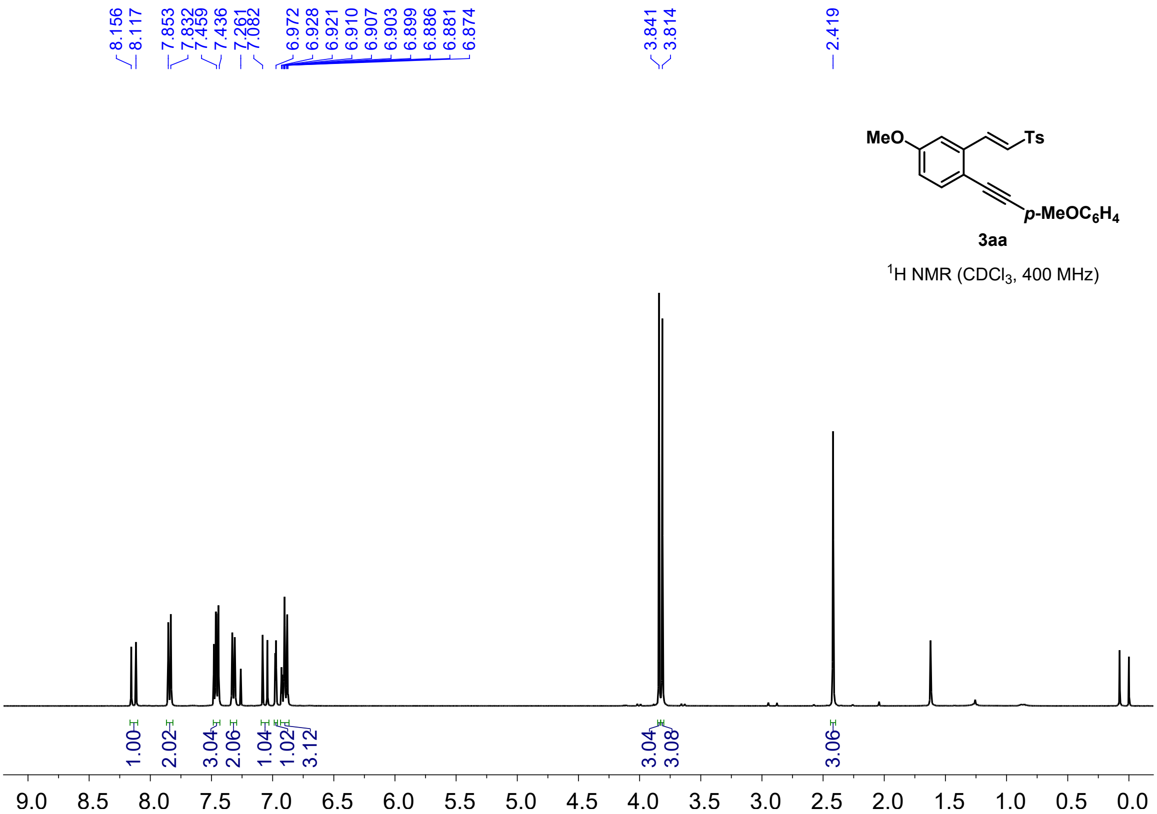

153.37
150.22
144.77
140.83
139.53
123.53
110.28
107.93
77.32
77.00
76.68
56.74
56.57
21.66
136.95
131.21
130.07
128.01
132
MeO
MeO
Ts
Br
3x
^{13}C NMR (CDCl$_3$, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

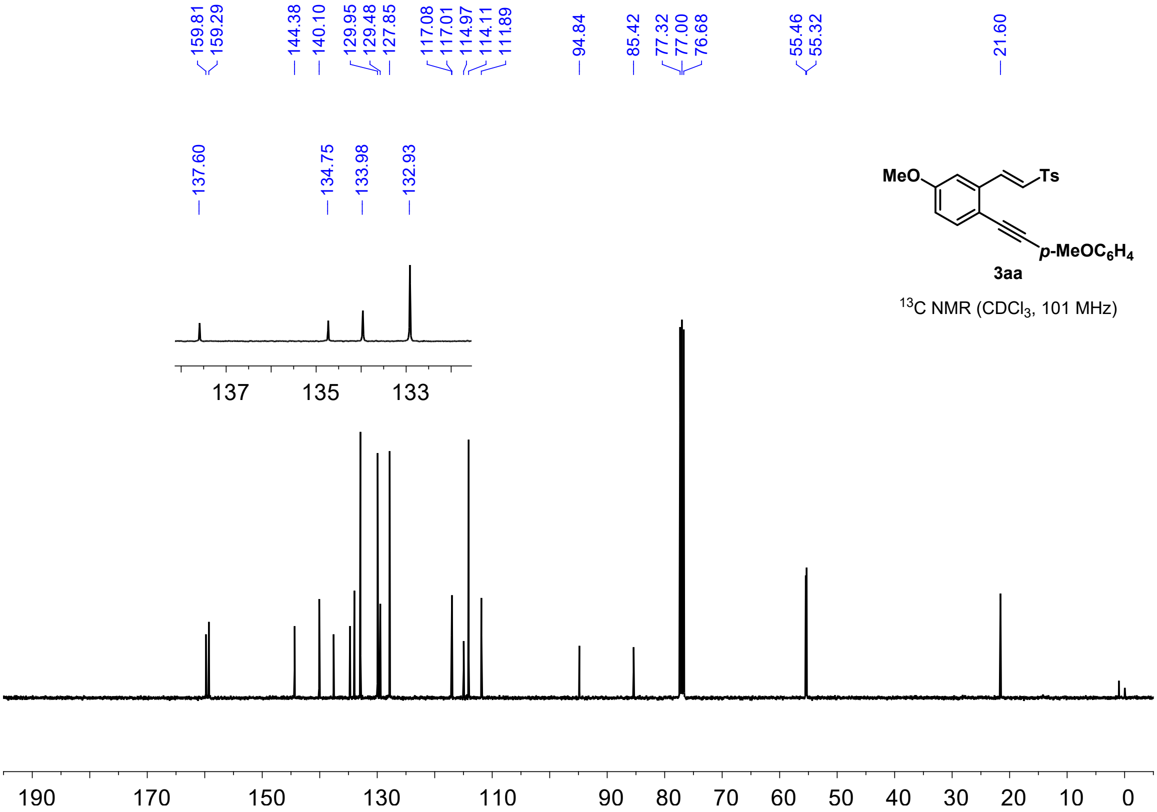

8.612
8.600
7.850
7.831
7.750
7.731
7.712
7.641
7.604
7.454
7.415
7.393
7.351
7.331
7.303
7.290
7.287
7.267
2.433
1.625
-0.000
Ts
N
3y
^{1}H NMR ($CDCl_3$, 400 MHz)
0.94
1.95
1.00
1.00
1.98
1.95
1.16
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

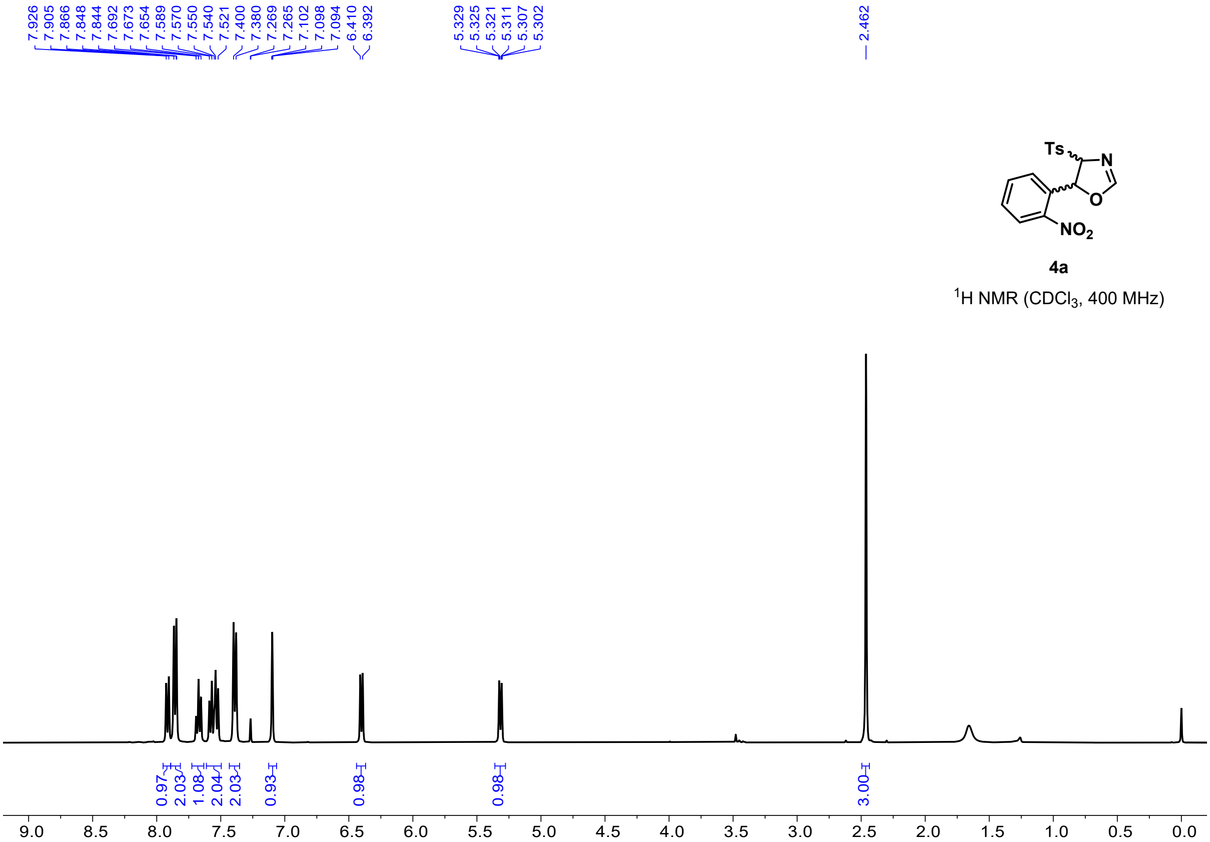

151.086
150.263
144.574
139.984
132.109
129.962
127.917
125.364
124.899
77.316
76.998
76.681
21.610
137.196
137.002
137.5
136.5
Ts
N
3y
^{13}C NMR ($CDCl_3$, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.066
8.028
7.829
7.433
7.352
7.248
6.956
6.916
6.819
6.781
2.437
1.616
0.000
Ts
Ph
3z
^{1}H NMR ($CDCl_3$, 400 MHz)
1.00
1.91
1.00
2.02
9.41
0.97
0.99
2.98
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


144.404
133.510
129.979
129.715
124.899
77.318
77.000
76.683
21.616
128.769
128.273
127.743
127.692
127.314
126.784
128.0
127.0
139.762
137.987
137.584
136.705
139
137
Ts
Ph
3z
^{13}C NMR ($CDCl_3$, 101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

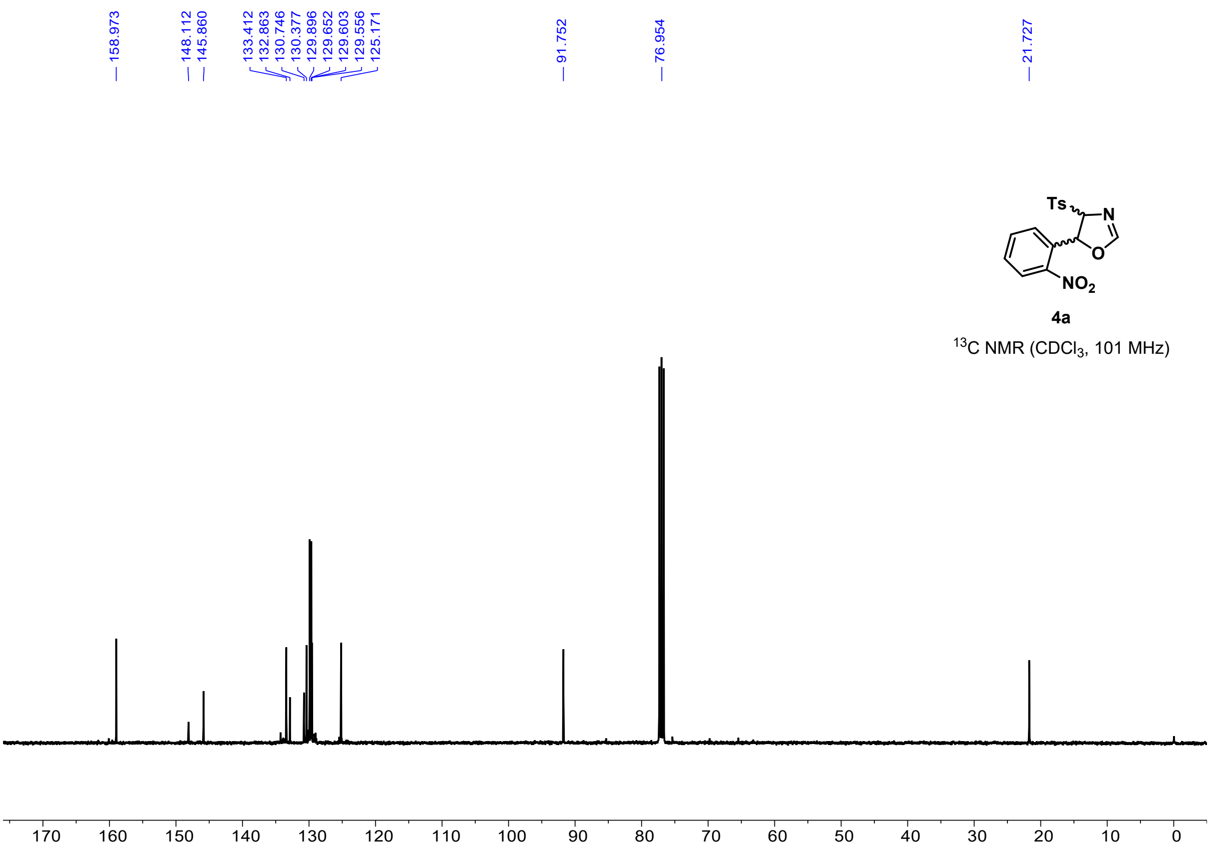

8.156
8.117
7.853
7.832
7.459
7.436
7.261
7.082
6.972
6.928
6.921
6.910
6.907
6.903
6.899
6.886
6.881
6.874
3.841
3.814
2.419
MeO
Ts
p-MeOC6H4
3aa
1H NMR (CDCl3, 400 MHz)
1.00
2.02
3.04
2.06
1.04
1.02
3.12
3.04
3.08
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


159.81
159.29
144.38
140.10
129.95
129.48
127.85
117.08
117.01
114.97
114.11
111.89
94.84
85.42
77.32
77.00
76.68
55.46
55.32
21.60
137.60
134.75
133.98
132.93
MeO
Ts
p-MeOC6H4
3aa
13C NMR (CDCl3, 101 MHz)
137
135
133
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0



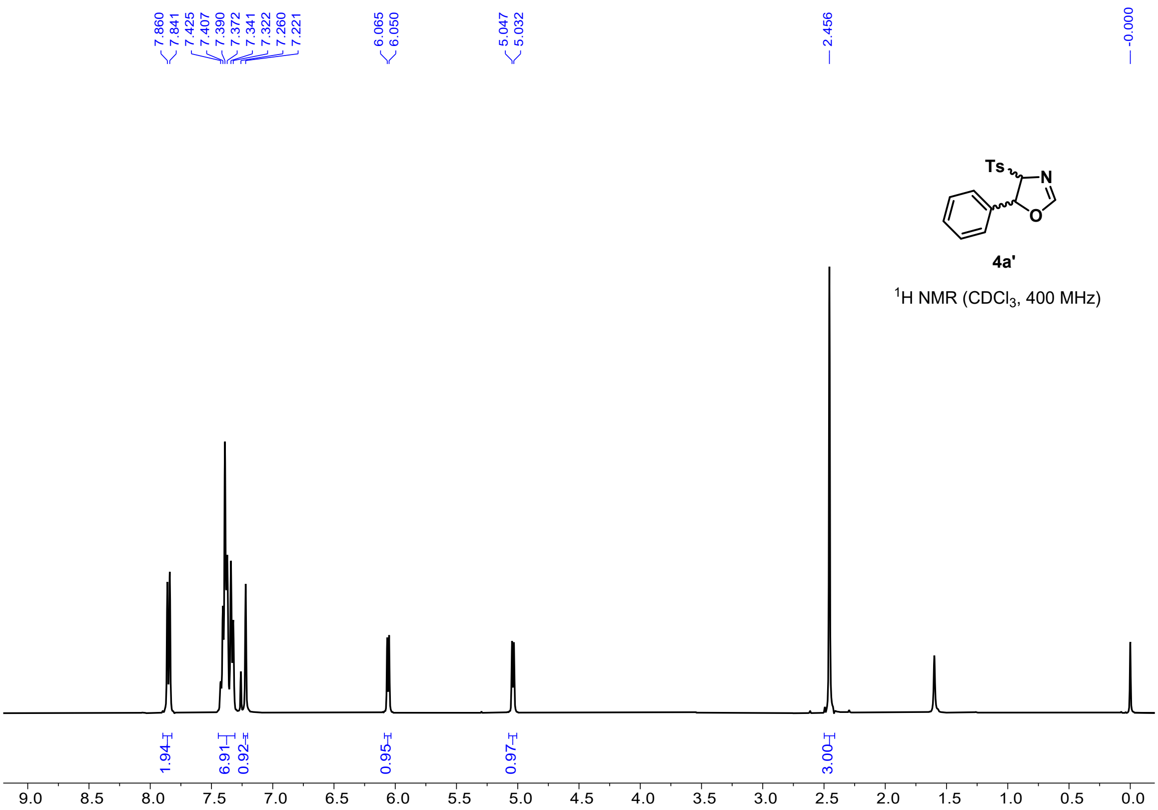
4a

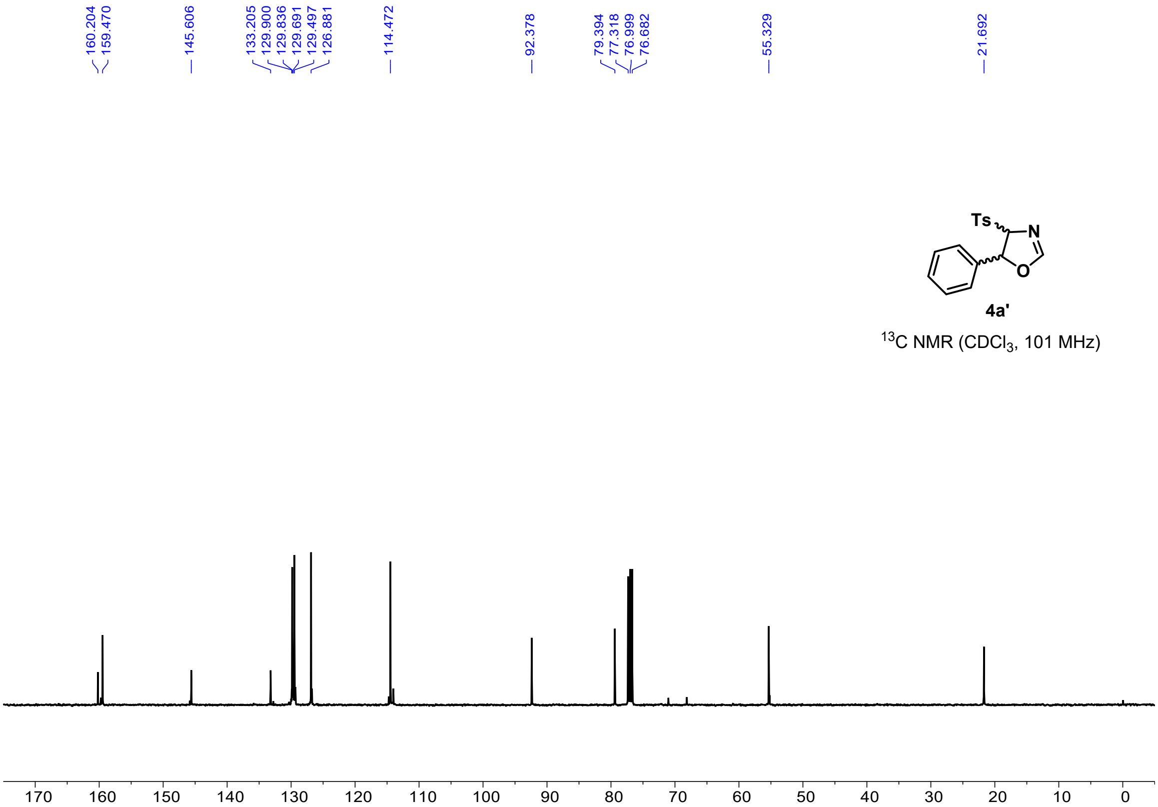
^{1}H NMR ($CDCl_3$, 400 MHz)

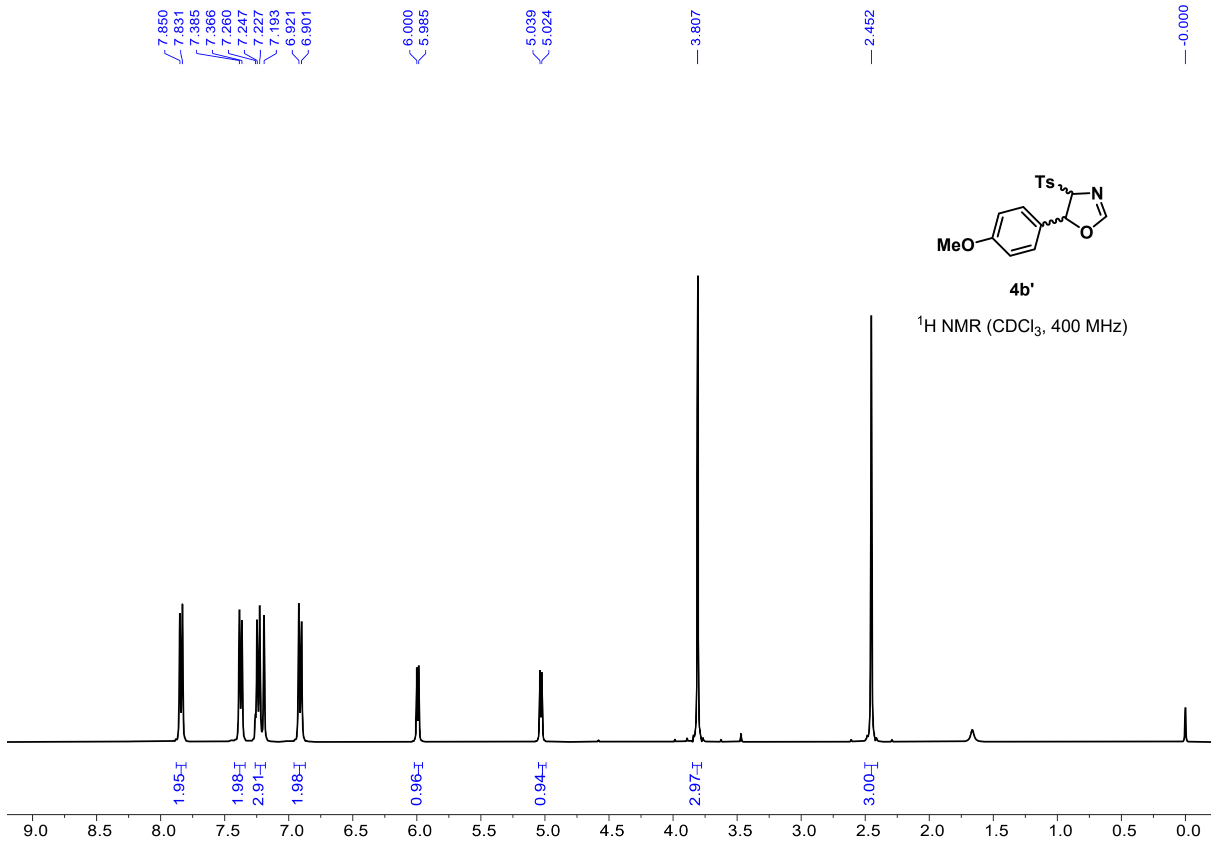


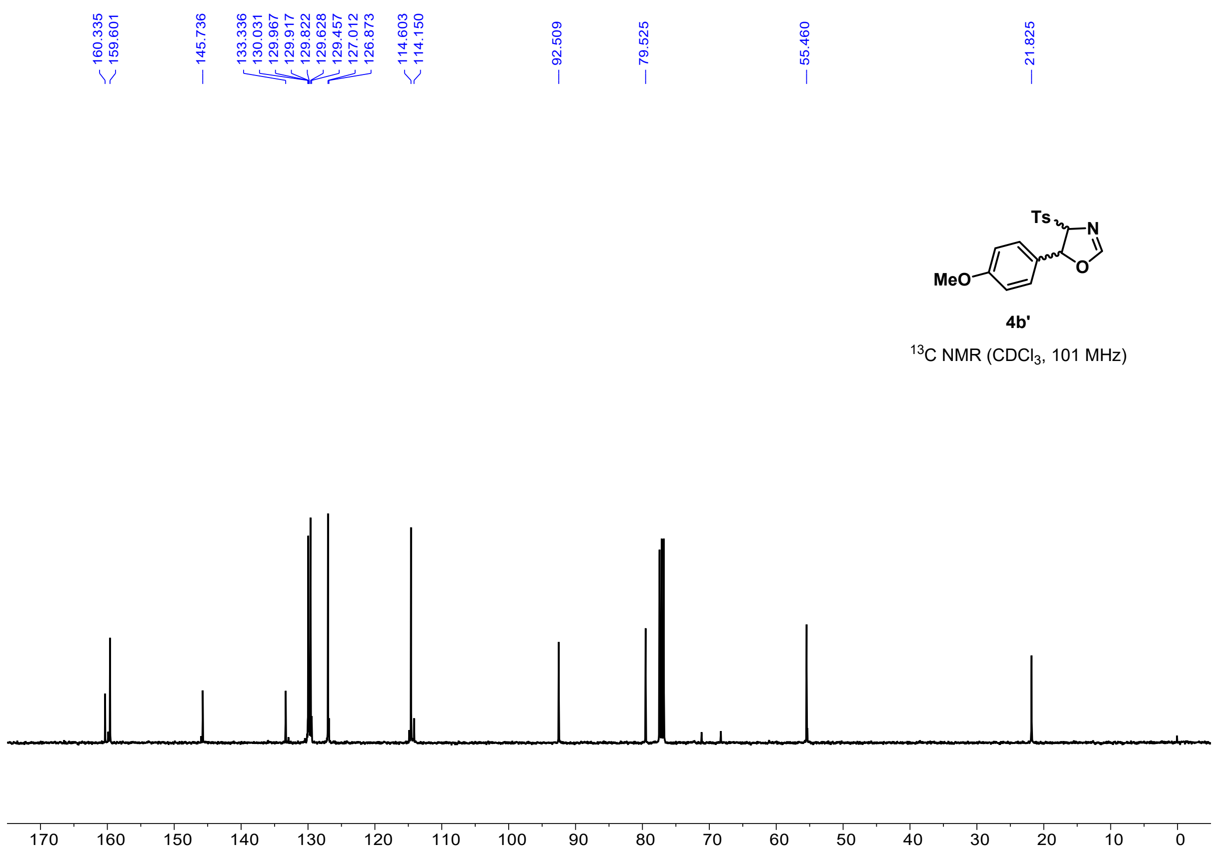
4a

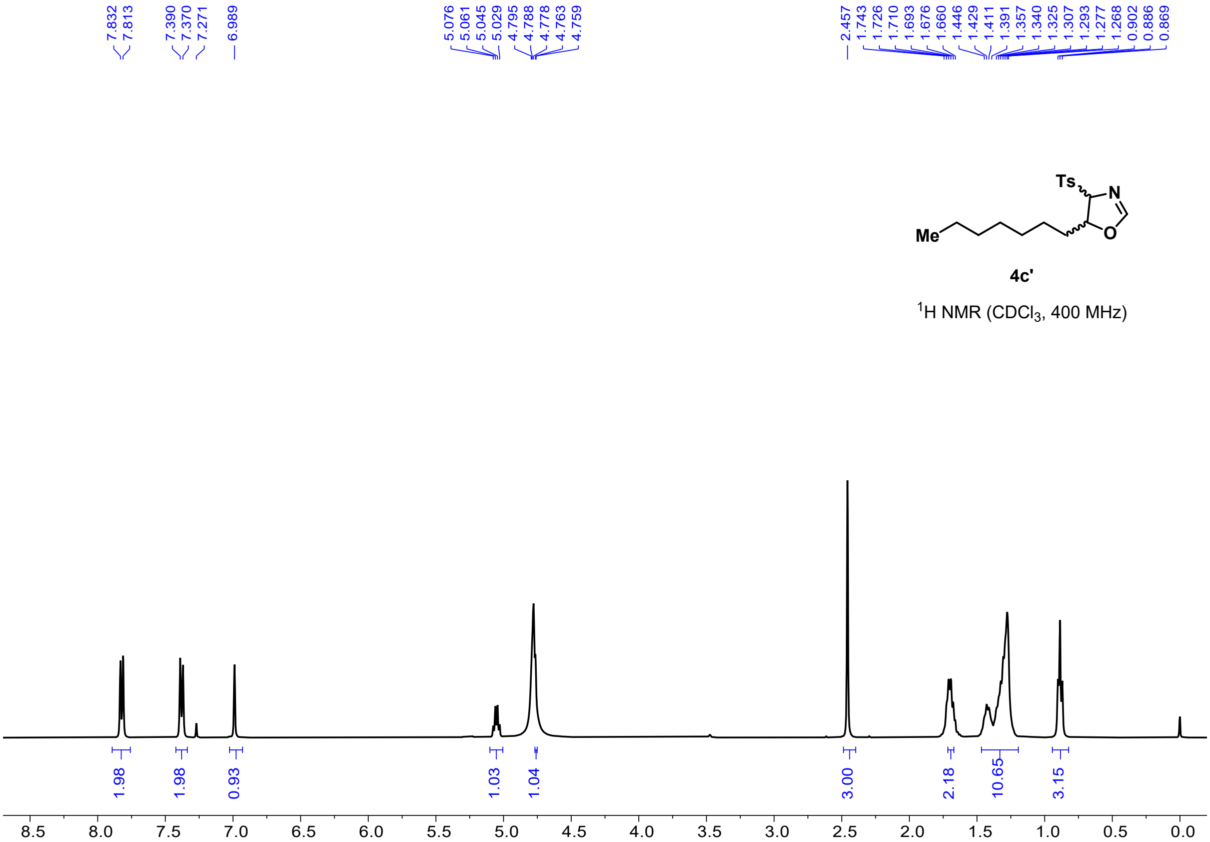
^{13}C NMR ($CDCl_3$, 101 MHz)

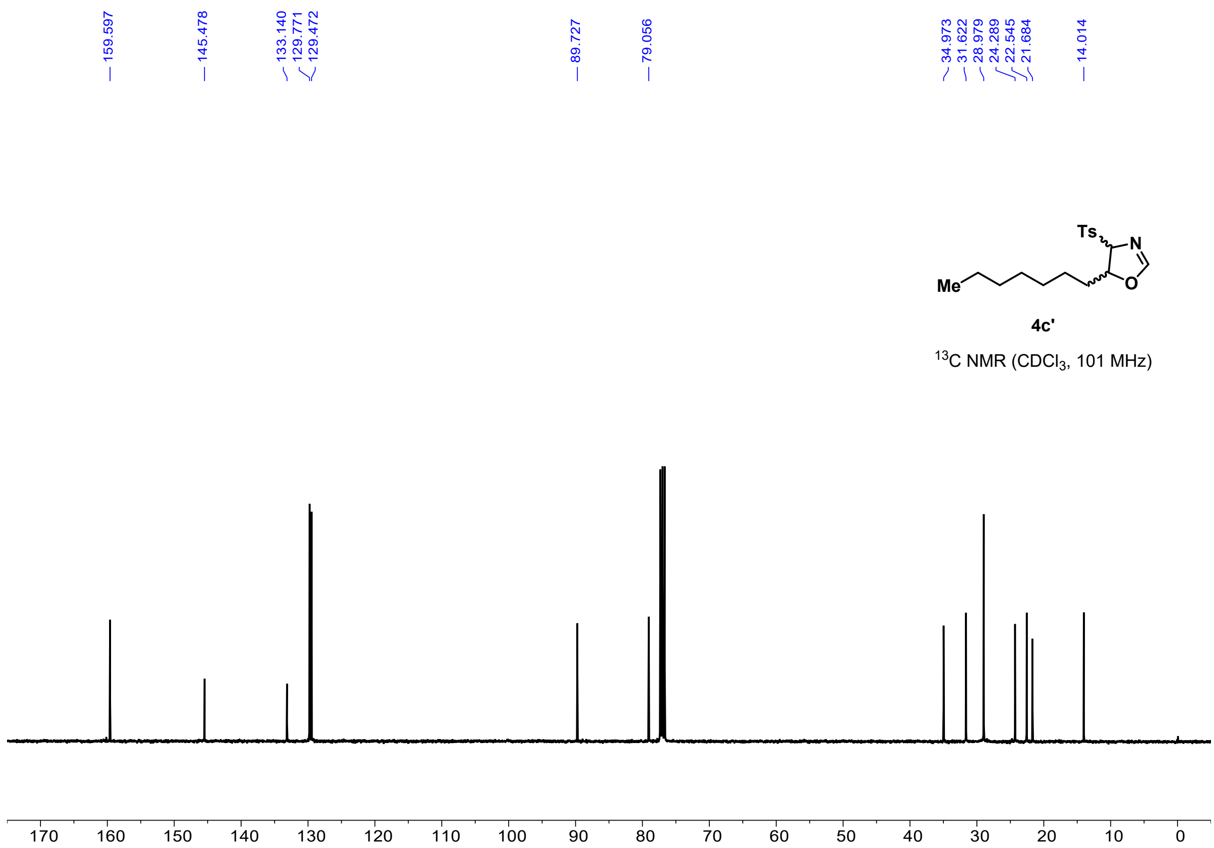

7.860
7.841
7.425
7.407
7.390
7.372
7.341
7.322
7.260
7.221
6.065
6.050
5.047
5.032
2.456
-0.000
Ts
N
O
4a'
1H NMR (CDCl3, 400 MHz)
1.94
6.91
0.92
0.95
0.97
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

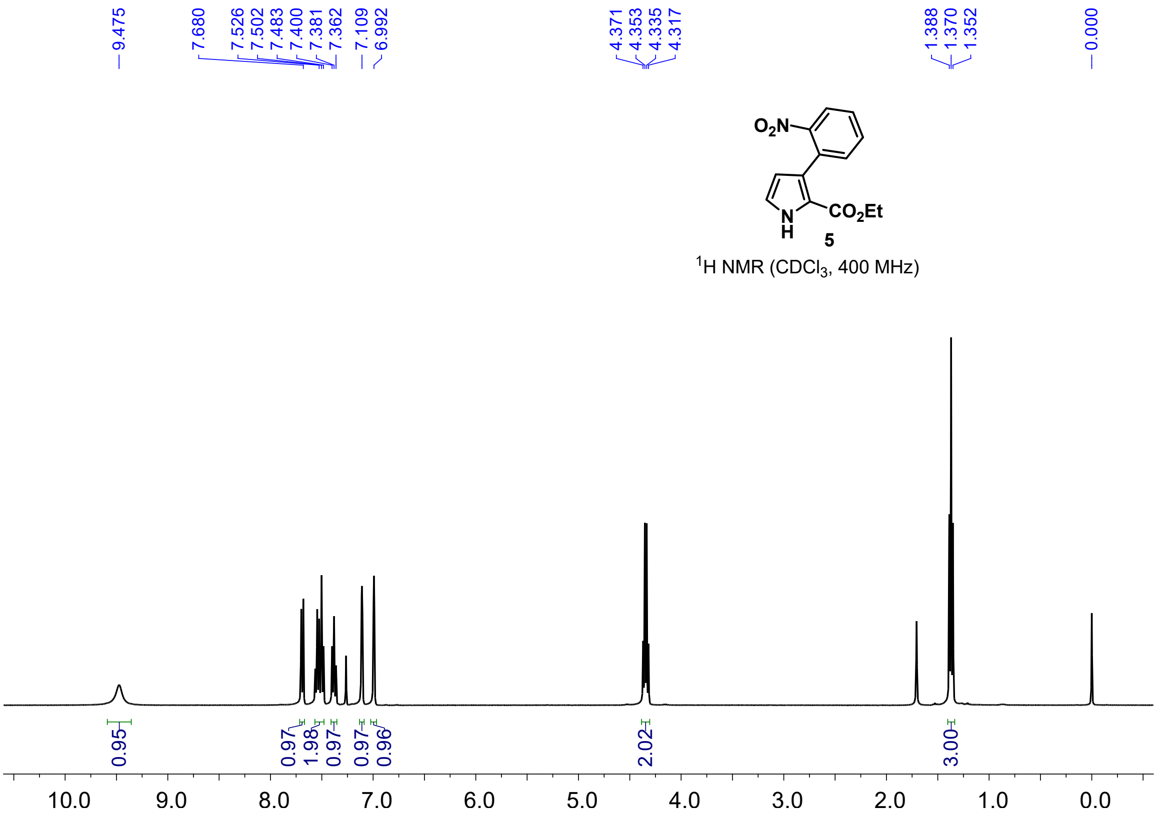

160.204
159.470
145.606
133.205
129.900
129.836
129.691
129.497
126.881
114.472
92.378
79.394
77.318
76.999
76.682
55.329
21.692
Ts
N
O
4a'
13C NMR (CDCl3, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.850
7.831
7.385
7.366
7.260
7.247
7.227
7.193
6.921
6.901
6.000
5.985
5.039
5.024
3.807
2.452
-0.000
Ts
N
O
MeO
4b'
1H NMR (CDCl3, 400 MHz)
1.95
1.98
2.91
1.98
0.96
0.94
2.97
3.00
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

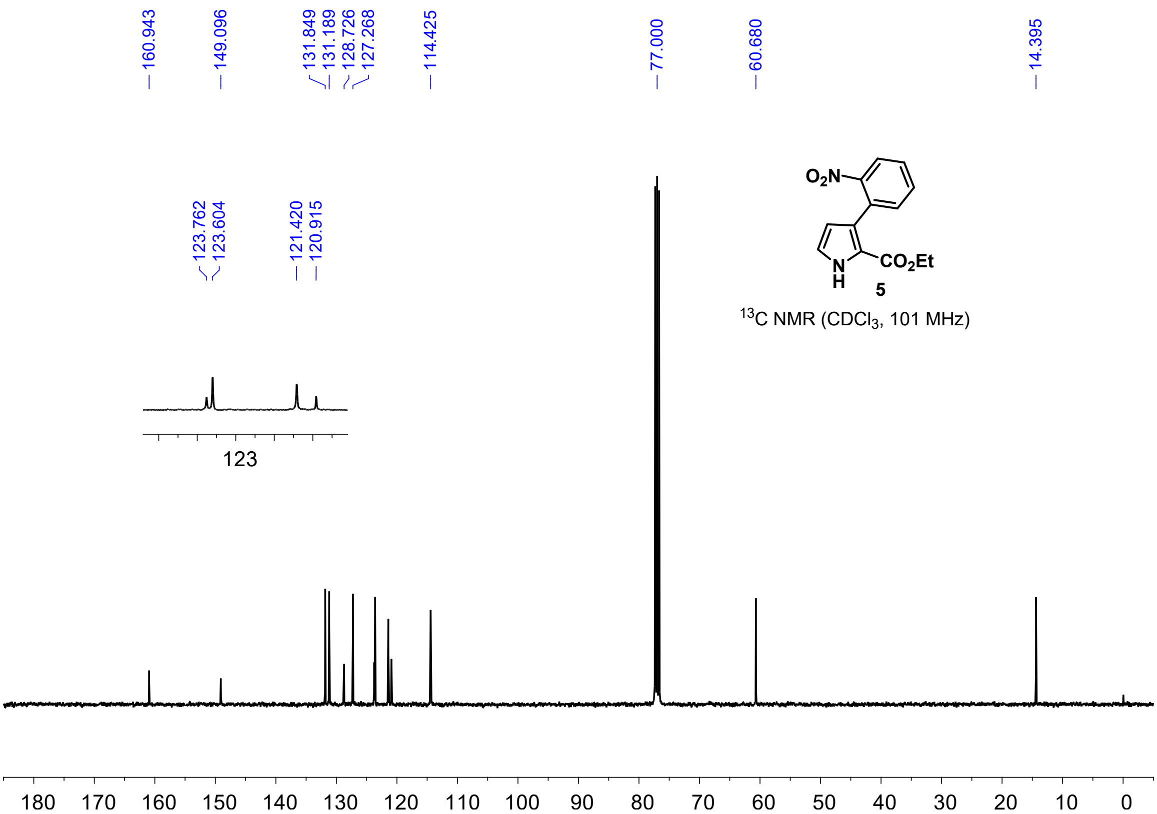

160.335
159.601
145.736
133.336
130.031
129.967
129.917
129.822
129.628
129.457
127.012
126.873
114.603
114.150
92.509
79.525
55.460
21.825
Ts
N
O
MeO
4b'
13C NMR (CDCl3, 101 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.832
7.813
7.390
7.370
7.271
6.989
5.076
5.061
5.045
5.029
4.795
4.788
4.778
4.763
4.759
2.457
1.743
1.726
1.710
1.693
1.676
1.660
1.446
1.429
1.411
1.391
1.357
1.340
1.325
1.307
1.293
1.277
1.268
0.902
0.886
0.869
Ts
N
O
Me
4c'
^{1}H NMR ($CDCl_3$, 400 MHz)
1.98
1.98
0.93
1.03
1.04
3.00
2.18
10.65
3.15
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


159.597
145.478
133.140
129.771
129.472
89.727
79.056
34.973
31.622
28.979
24.289
22.545
21.684
14.014
Ts
N
O
Me
4c'
^{13}C NMR (CDCl$_3$, 101 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 101 MHz)

VIII. Optimized geometries, cartesian coordinates and energies for calculated species

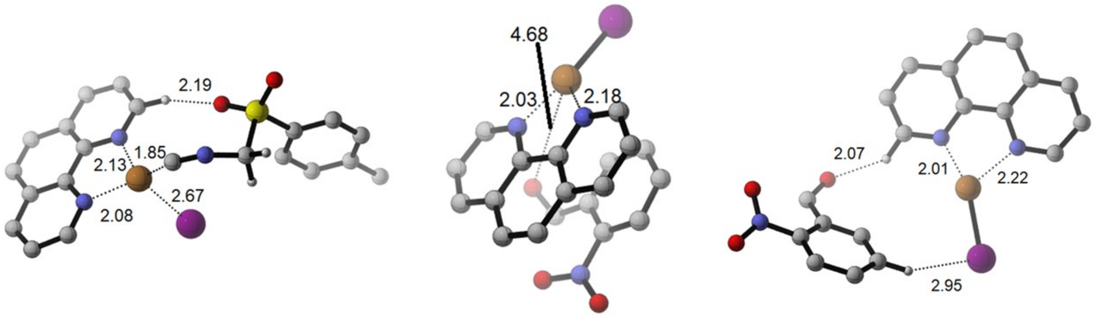


Figure S1. Optimized geometries of potential complexes generated between the copper catalyst, TosMIC and substrate **1a**.

Three stable complexes (**ComI**, **ComII-1** and **ComII-2**) can be formed by the copper catalyst, TosMIC and substrate **1a**. In **ComI**, a strong coordination interaction (1.85 Å) was found between TosMIC and the copper center. However, in complexes **ComII-1** (4.68 Å) and **ComII-2** there is no coordination interaction between **1a** and the copper center. Furthermore, the interaction energies were calculated to be 13.6, 7.6 and 1.5 kcal·mol^{-1} in **ComI**, **ComII-1** and **ComII-2**, respectively. Thus, the copper catalyst preferentially coordinates and activates TosMIC to produce complex **ComI**.

Int1-H

[B3LYP-D3/6-31+G(d,p)-SDD (Cu)] G: -2065.525813 hartree

C	0.26106500	1.03634000	0.07250200
C	-1.62085700	-0.00352300	0.64586900
C	-1.98555300	1.06528000	-0.41610200
O	-0.69351300	1.63874900	-0.72444100
H	-2.23312100	0.04214000	1.55168300
N	-0.21181900	0.14771200	0.89680700
H	-2.37112700	0.62119700	-1.33728800
S	-1.90089200	-1.73416300	0.01974000
C	-3.67151700	-1.74052300	-0.27785000
C	-4.14892200	-1.60848800	-1.58154800
C	-4.54740400	-1.78711800	0.80881700
C	-5.52524800	-1.51711200	-1.79437600
H	-3.44504300	-1.58055200	-2.40642300
C	-5.91815300	-1.68714400	0.57987500
H	-4.15827300	-1.90477200	1.81474500

C	-6.42744900	-1.55005000	-0.72130300
H	-5.90312800	-1.41323100	-2.80790100
H	-6.60403600	-1.71490000	1.42225100
C	-7.91528700	-1.47052900	-0.95871200
H	-8.35598200	-2.47431700	-1.00003000
H	-8.41854600	-0.92580200	-0.15402200
H	-8.14234200	-0.97182500	-1.90527900
O	-1.22803700	-1.88924700	-1.28642200
O	-1.60755800	-2.67086500	1.12496900
C	-2.95385400	2.09419900	0.11019500
C	-4.33031500	1.89939100	-0.06329800
C	-2.50347800	3.20681600	0.82935300
C	-5.24562200	2.80248000	0.48112100
H	-4.68642400	1.03817400	-0.62097300
C	-3.41950900	4.11156000	1.37080000
H	-1.43629800	3.36137600	0.94867600
C	-4.79274200	3.91186600	1.20089100
H	-6.31057900	2.64201800	0.33863100
H	-3.06034500	4.97440900	1.92448900
H	-5.50342700	4.61733000	1.62152800
Cu	2.13695600	1.20187700	-0.11656100
C	2.96380300	-3.17976400	1.12479400
C	4.32929100	-3.23370500	0.91866900
C	5.01711000	-2.07787100	0.47714500
C	4.23875700	-0.91302600	0.26697300
C	2.27861000	-1.96509300	0.89418400
C	6.43144400	-2.03229100	0.23836100
C	4.87334400	0.30194200	-0.19576800
C	6.27394600	0.31242900	-0.41816000
C	7.03436700	-0.88478200	-0.18835400
C	6.85703200	1.51820400	-0.86585300
H	7.92758500	1.56103300	-1.04529100
C	6.05802500	2.62677000	-1.07132500
C	4.67614000	2.52598300	-0.83271200
H	7.01702700	-2.93207000	0.40463600
H	2.40899900	-4.04973800	1.45908100
H	4.88392700	-4.15234500	1.08973800
H	1.20735400	-1.86011700	1.05029400
H	8.10533300	-0.85667200	-0.36607400
H	6.47373700	3.56732700	-1.41515600
H	4.01950600	3.37457500	-0.99101900
N	4.09496800	1.40344100	-0.40905200
N	2.90805900	-0.87595600	0.47941200

TS1-H

[B3LYP-D3/6-31+G(d,p)-SDD (Cu)] G: -2065.492465 hartree

C	0.45323200	2.42166500	1.49438100
C	1.47171000	0.76998800	0.18127200
C	2.58535400	1.05263800	1.07003900
O	1.53107700	2.49798800	2.08922400
H	1.68957900	0.90150600	-0.87987600
N	0.18876300	1.64235300	0.49750000
H	2.68624800	0.42027800	1.94494400
S	0.89014400	-0.96185800	0.31007800
C	2.27672400	-1.89902900	-0.32419900
C	3.25225200	-2.36311600	0.56037900
C	2.39263900	-2.10175800	-1.69878400
C	4.36161400	-3.03292100	0.05104700
H	3.12967900	-2.20691900	1.62616000
C	3.51309400	-2.77189200	-2.19175800
H	1.60961500	-1.75275600	-2.36325100
C	4.51431000	-3.23959100	-1.32954700
H	5.12291900	-3.40031600	0.73397600
H	3.60870700	-2.93663300	-3.26145900
C	5.74128000	-3.93254500	-1.86813800
H	5.58242400	-4.29081500	-2.88902900
H	6.59687500	-3.24633700	-1.88575400
H	6.02181600	-4.78747500	-1.24469300
O	0.70370400	-1.32263700	1.73259800
O	-0.23548200	-1.12680500	-0.64324900
C	3.79650200	1.70479100	0.59920400
C	5.01343200	1.49608100	1.28084600
C	3.80942500	2.56338400	-0.52110900
C	6.19368200	2.10072500	0.85271100
H	5.02216500	0.84765200	2.15300900
C	4.98999000	3.16464100	-0.94898400
H	2.88080800	2.78018000	-1.04109700
C	6.19228300	2.93600500	-0.26890700
H	7.11761800	1.91993900	1.39520200
H	4.97234200	3.82544700	-1.81136800
H	7.11058500	3.40928300	-0.60321400
Cu	-1.52657600	1.19866000	-0.18027600
C	-3.34906500	-1.74448700	2.90836800
C	-4.60032400	-1.92011100	2.35010300
C	-4.93668000	-1.22957400	1.16253400
C	-3.94697100	-0.37706600	0.61190700
C	-2.43528200	-0.86719300	2.28417000

C	-6.20602800	-1.35695300	0.50539800
C	-4.22284300	0.33662700	-0.61586700
C	-5.48732300	0.18617200	-1.24010500
C	-6.47116800	-0.67537400	-0.64591000
C	-5.71656600	0.89738000	-2.43815600
H	-6.67485300	0.80452300	-2.94116900
C	-4.71777200	1.70049200	-2.95441700
C	-3.49228000	1.78924600	-2.27189000
H	-6.95473800	-2.01108800	0.94308800
H	-3.05697300	-2.26941400	3.81149900
H	-5.32807500	-2.58559800	2.80622800
H	-1.43217700	-0.72140300	2.67373200
H	-7.43336200	-0.77619700	-1.13919100
H	-4.85996000	2.26059000	-3.87190900
H	-2.68804900	2.41080500	-2.64994200
N	-3.24496800	1.13047100	-1.13909300
N	-2.73529700	-0.20202300	1.17941300

3-H + CuNCO-L
[B3LYP-D3/6-31+G(d,p)-SDD (Cu)] G: -2065.580500 hartree

C	1.88619400	-1.17639000	2.91459200
C	0.36795500	-0.87670000	-1.02452900
C	-0.48813500	-1.67688700	-1.67091300
O	3.02105700	-1.34453700	3.27932900
H	0.57115000	-0.91426500	0.04198000
N	0.76080000	-1.02636700	2.53748200
H	-0.62209200	-1.53162200	-2.74155600
S	1.24446300	0.41840900	-1.85991600
C	2.91890600	0.10110600	-1.32673500
C	3.86400300	-0.36072200	-2.23972800
C	3.22595100	0.25092200	0.02994100
C	5.14684700	-0.66544700	-1.77947500
H	3.59105600	-0.47878800	-3.28273000
C	4.50089900	-0.08202600	0.47457200
H	2.47395500	0.59746000	0.73020100
C	5.47998200	-0.54009100	-0.42364300
H	5.89467400	-1.02097300	-2.48295900
H	4.72379100	-0.01479500	1.53483100
C	6.85906900	-0.89112000	0.07632400
H	6.80248900	-1.58060800	0.92529400
H	7.46224400	-1.35880500	-0.70659100
H	7.38976200	0.00417900	0.42123100
O	1.14718200	0.21809800	-3.31925000
O	0.80461100	1.70011600	-1.26944100
C	-1.29704500	-2.71670800	-1.02772900
C	-2.41124100	-3.23199700	-1.71217800
C	-1.01947000	-3.19047600	0.26968200
C	-3.24979100	-4.17014500	-1.10912800
H	-2.62623800	-2.87836200	-2.71700700
C	-1.85564900	-4.13018100	0.86826000
H	-0.16036100	-2.82005200	0.81871700
C	-2.97721500	-4.61847400	0.18656100
H	-4.10971600	-4.55414000	-1.65010400
H	-1.62892200	-4.48244100	1.86991800
H	-3.62468100	-5.35221600	0.65746000
Cu	-0.76499100	-0.17701900	1.94184900
C	0.57515900	4.13150400	1.16169500
C	-0.37122100	4.49128200	0.22244500
C	-1.41832300	3.59643100	-0.08879000
C	-1.43462100	2.35775600	0.59682800
C	0.46220600	2.87828800	1.79566400

C	-2.42989500	3.87627700	-1.06574800
C	-2.45271200	1.38263400	0.28379300
C	-3.44150700	1.69238400	-0.68209600
C	-3.40428700	2.96451900	-1.34693400
C	-4.41986400	0.71068300	-0.95569400
H	-5.19101200	0.91534900	-1.69292000
C	-4.37785600	-0.49733800	-0.28777000
C	-3.34765300	-0.73131200	0.63883600
H	-2.39931900	4.82865600	-1.58675900
H	1.40013700	4.78991000	1.41115200
H	-0.31277300	5.44619200	-0.29181400
H	1.18816200	2.55927900	2.53944200
H	-4.16527000	3.17971200	-2.09111100
H	-5.10572800	-1.27747900	-0.47772800
H	-3.26779800	-1.68395100	1.14859100
N	-2.40863400	0.17382900	0.91591700
N	-0.51460800	2.02549700	1.52857000

Int1-NO_2

[B3LYP-D3/6-31+G(d,p)-SDD (Cu)] G: -2270.031134 hartree

C	0.45534100	0.90384300	0.39234800
C	-1.43486600	0.04800100	1.19799800
C	-1.80143600	0.85571500	-0.06961800
O	-0.49124800	1.24444100	-0.56503300
H	-2.07924000	0.24428700	2.05873300
N	-0.03730900	0.31233500	1.43907000
H	-2.29128600	0.26525700	-0.83772000
S	-1.56745400	-1.81302000	0.98310300
C	-3.21625700	-2.10256600	0.35124800
C	-3.38821800	-2.46233900	-0.98513300
C	-4.30832800	-1.95497800	1.20755000
C	-4.67816900	-2.67208500	-1.46726500
H	-2.51849100	-2.57792100	-1.62229300
C	-5.59217100	-2.15415300	0.70385800
H	-4.15282600	-1.70983600	2.25305400
C	-5.79628500	-2.50663400	-0.63865000
H	-4.82056400	-2.94994100	-2.50792100
H	-6.44870300	-2.03907100	1.36258600
C	-7.19002100	-2.66740800	-1.19087900
H	-7.90781600	-2.91530200	-0.40351700
H	-7.52180000	-1.73414600	-1.66268700
H	-7.23021800	-3.45187100	-1.95278300
O	-0.61747700	-2.22400900	-0.07795400
O	-1.47733100	-2.40945600	2.33051200
C	-2.57723500	2.11747500	0.26476600
C	-2.00398700	3.00000400	1.19741200
C	-3.78056600	2.53632600	-0.32564700
C	-2.60579300	4.20747200	1.53651300
H	-1.05892400	2.72435700	1.65288600
C	-4.38404200	3.76213700	-0.02115900
C	-3.80354300	4.59529200	0.92592200
H	-2.13532900	4.85139500	2.27319400
H	-5.30142900	4.03286100	-0.52893700
H	-4.27689800	5.53745700	1.18205200
Cu	2.30750300	1.00980100	0.03354900
N	-4.49370100	1.71255900	-1.31241100
O	-5.12100000	2.29823400	-2.19850700
O	-4.45092300	0.48678400	-1.18988500
C	6.13686800	2.86715500	-0.56427600
C	7.00320200	1.79089000	-0.59587400
C	6.49205500	0.48123500	-0.46036700

C	5.09094600	0.33845300	-0.29895700
C	4.76081100	2.63243800	-0.39171400
C	7.32237000	-0.69111000	-0.47574400
C	4.52205700	-0.98310100	-0.16273800
C	5.36923900	-2.11749100	-0.17419700
C	6.78415900	-1.93742900	-0.33523400
C	4.74747800	-3.38000300	-0.02296600
H	5.35678600	-4.27967800	-0.02329400
C	3.37557700	-3.45099300	0.12385100
C	2.61431000	-2.25968300	0.11518200
H	8.39364500	-0.56292500	-0.59915300
H	6.49677200	3.88493900	-0.66579900
H	8.07192400	1.93858400	-0.72276000
H	4.05433600	3.45469300	-0.35573700
H	7.42265700	-2.81621700	-0.34420500
H	2.87055800	-4.40333100	0.24377900
H	1.53105600	-2.27248600	0.21569700
N	3.18187900	-1.06947600	-0.02658800
N	4.24774900	1.40976000	-0.26124400

TS1-NO_2

[B3LYP-D3/6-31+G(d,p)-SDD (Cu)] G: -2270.007527 hartree

C	-0.70859100	-0.66570200	1.51658700
C	-1.46510700	-0.58982600	-0.69406000
C	-2.75843000	-0.57930400	-0.01062500
O	-1.89282500	-0.62760700	1.85429900
H	-1.33996600	-1.38904600	-1.42750500
N	-0.26750700	-0.68219800	0.29690000
H	-3.23905500	0.36891400	0.15042500
S	-1.21796000	0.92829700	-1.72241800
C	-1.44061800	2.28491300	-0.58459800
C	-0.36453000	2.71705300	0.19236100
C	-2.70885400	2.85455900	-0.45122300
C	-0.57153500	3.73396100	1.12204500
H	0.61234000	2.26675000	0.06255900
C	-2.89584300	3.86858900	0.48535800
H	-3.52745200	2.50767800	-1.07154300
C	-1.83675600	4.31699300	1.28871000
H	0.26039200	4.07826500	1.73025900
H	-3.88128700	4.31141600	0.59774600
C	-2.06346800	5.38614900	2.32818800
H	-1.13099600	5.89471100	2.58938300
H	-2.77887200	6.13663000	1.97848800
H	-2.47188000	4.94814200	3.24728400
O	0.19551700	0.93070300	-2.17798800
O	-2.29559300	0.96060400	-2.72822800
C	-3.60253300	-1.75513500	-0.00736600
C	-2.99850300	-3.03527200	-0.11591800
C	-5.02102000	-1.75725700	0.10848400
C	-3.72923200	-4.21038500	-0.11240400
H	-1.91612700	-3.08671300	-0.16642600
C	-5.76368000	-2.94721200	0.10168700
C	-5.12812000	-4.17415200	-0.00148400
H	-3.21205500	-5.16267200	-0.18434900
H	-6.84065200	-2.87835900	0.18028400
H	-5.70891900	-5.09029500	0.00883600
Cu	1.53740700	-0.49039400	-0.20361200
N	-5.81375700	-0.53000000	0.20556100
O	-7.03020300	-0.61082300	-0.00765800
O	-5.25447000	0.53398300	0.50137100
C	4.17743700	-1.30273400	3.48101200
C	5.42877900	-1.19165500	2.90326900
C	5.53873300	-0.86691000	1.53115200

C	4.32942800	-0.67644000	0.81762200
C	3.03326100	-1.08581900	2.68375100
C	6.79124100	-0.71874000	0.84467700
C	4.37232200	-0.34227900	-0.58774300
C	5.62332600	-0.18897900	-1.23204000
C	6.83070500	-0.39036200	-0.47940800
C	5.61041400	0.16098700	-2.60147100
H	6.55030000	0.28690700	-3.13134400
C	4.40153200	0.34499200	-3.24539900
C	3.20266400	0.16742600	-2.52921700
H	7.71099700	-0.86938200	1.40233800
H	4.06345200	-1.54875500	4.53129000
H	6.32940500	-1.34852600	3.49027700
H	2.02875700	-1.15483900	3.09543700
H	7.78221200	-0.27474700	-0.98994400
H	4.35757100	0.62300800	-4.29253200
H	2.23092800	0.31601000	-2.98835500
N	3.18985900	-0.17731500	-1.24109900
N	3.11225300	-0.78278000	1.39646400

3a-NO$_2$ + CuNCO-L

[B3LYP-D3/6-31+G(d,p)-SDD (Cu)] G: -2270.086622 hartree

C	-4.79751600	0.02858100	-1.21122700
C	-0.23262600	0.21430500	-1.75184800
C	0.02389300	1.38956300	-1.16130300
O	-5.62427200	0.82125000	-1.58962500
H	-1.21591700	-0.21073100	-1.93755600
N	-3.95608400	-0.73204900	-0.84446800
H	1.05163600	1.68382700	-1.00853400
S	1.07137800	-0.85032600	-2.34567400
C	2.56240000	-0.12431800	-1.68112200
C	2.93851000	-0.43748900	-0.37470000
C	3.27625100	0.80305200	-2.43987900
C	4.04301100	0.20146000	0.18152000
H	2.37592000	-1.17003800	0.18889000
C	4.38239200	1.43035100	-1.86768700
H	2.96467300	1.02150200	-3.45554300
C	4.77280300	1.15215900	-0.54923800
H	4.33961000	-0.03666800	1.19932100
H	4.94458700	2.15513900	-2.44951900
C	5.92995700	1.88441000	0.08092600
H	5.57910600	2.80512300	0.56313300
H	6.41973000	1.27581600	0.84667800
H	6.67824900	2.16750000	-0.66483900
O	0.87558900	-2.16788400	-1.70892000
O	1.10546100	-0.74890400	-3.81529300
C	-0.99830700	2.32459600	-0.67484900
C	-2.33531400	2.19544500	-1.09131300
C	-0.73426100	3.34425200	0.27116700
C	-3.35124400	3.00687200	-0.59471900
H	-2.58693300	1.43096100	-1.81384500
C	-1.74522300	4.15760300	0.78880200
C	-3.05603400	3.99313100	0.35173100
H	-4.36694000	2.84638500	-0.94203200
H	-1.48611000	4.91039300	1.52272000
H	-3.83975700	4.63300400	0.74351700
Cu	-2.59061500	-1.66507000	-0.06703900
N	0.61174100	3.59675400	0.80892600
O	0.68874900	4.02649100	1.96432900
O	1.59513500	3.38906100	0.09297300
C	0.06801600	-4.94317700	-0.01414600
C	1.07595300	-4.53330300	0.83401900
C	0.97442500	-3.28080600	1.47725900

C	-0.17427900	-2.49508700	1.21509000
C	-1.03551300	-4.09934800	-0.22052400
C	1.99028600	-2.77741000	2.35915000
C	-0.30487000	-1.19927400	1.84311400
C	0.72542400	-0.72597300	2.69585900
C	1.87467100	-1.54898200	2.94119200
C	0.55332400	0.55738100	3.26439200
H	1.32623400	0.96811100	3.90757200
C	-0.59364800	1.27671600	2.99149400
C	-1.56245800	0.71178500	2.13580300
H	2.86316400	-3.39643200	2.54412000
H	0.11737300	-5.89224400	-0.53538200
H	1.94987400	-5.15467700	1.00619400
H	-1.83424200	-4.38582000	-0.89516100
H	2.65220500	-1.17322800	3.60001300
H	-0.74414500	2.26834300	3.40123600
H	-2.47217900	1.25179900	1.88762100
N	-1.41890900	-0.48048700	1.57895800
N	-1.16186100	-2.91348400	0.37441900

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