# Synthesis of Multisubstituted Pyrroles by Nickel-Catalyzed Arylative Cyclizations of *N*-Tosyl Alkynamides

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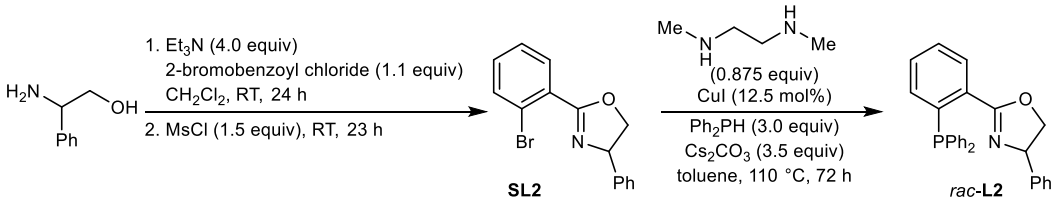
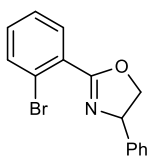
**Contents**

## 1. General Information

All air-sensitive reactions were carried out under an inert atmosphere using oven-dried apparatus. 2,2,2-Trifluoroethanol (TFE) was purchased from Alfa Aesar and degassed before use using a stream of argon gas (20 min). All commercially available reagents were used as received unless otherwise stated. Petroleum ether refers to Sigma-Aldrich product 24587 (petroleum ether boiling point 40-60 °C). Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F254 0.2 mm precoated plates. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of potassium permanganate or vanillin followed by gentle heating. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35-70 micron or Fluorochem 60 Å particle size 40-63 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The solvent of recrystallization is reported in parentheses. Infrared (IR) spectra were recorded on Bruker platinum alpha FTIR spectrometer on the neat compound using the attenuated total refraction technique. NMR spectra were acquired on Bruker Ascend 400 spectrometers. $^{1}$H and $^{13}$C NMR spectra were referenced to external tetramethylsilane via the residual protonated solvent ($^{1}$H) or the solvent itself ($^{13}$C). All chemical shifts are reported in parts per million (ppm). For $CDCl_3$, the shifts are referenced to 7.26 ppm for $^{1}$H NMR spectroscopy and 77.16 ppm for $^{13}$C NMR spectroscopy. For DMSO-$d_6$, the shifts are referenced to 2.50 ppm for $^{1}$H NMR spectroscopy and 39.52 ppm for $^{13}$C NMR spectroscopy. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. High-resolution mass spectra were recorded using the electrospray ionization (ESI) technique. X-ray diffraction data were collected at 120 K on an Agilent SuperNova diffractometer using CuKα radiation. Ligand **L6** was prepared according to a literature procedure.[1]

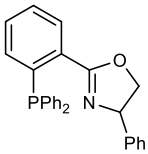
## 2. Preparation of *rac*-L2



**2-(2-Bromophenyl)-4-phenyl-4,5-dihydrooxazole (SL2). SL2** was prepared by modification of a previously reported procedure.[2] $Et_3N$ (20.3 mL, 145.6 mmol) was added to a flask containing DL-2-phenylglycinol (5.00 g, 36.4 mmol) in $CH_2Cl_2$ (150 mL) and the solution was cooled to 0 °C before 2-bromobenzoyl chloride (5.2 mL, 40.0 mmol) was added dropwise. The mixture was gradually warmed to room temperature and stirred for 24 h. The reaction was recooled to 0 °C and MsCl (4.2 mL, 54.3 mmol) was added

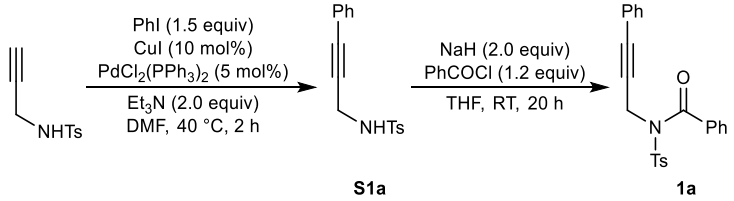
dropwise. The reaction was gradually warmed to room temperature, stirred for 23 h, quenched with saturated aqueous $NH_4Cl$ solution (100 mL) and extracted with $CH_2Cl_2$ (2 × 100 mL). The combined organic layers were washed with brine (50 mL), dried ($Na_2SO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (10% EtOAc/petroleum ether) to give the title compound as a yellow oil (7.34 g, 67%). The analytical data were consistent with those reported previously.[3]

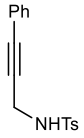



**2-[2-(Diphenylphosphanyl)phenyl]-4-phenyl-4,5-dihydrooxazole (*rac*-L2).** The Ligand **L2** was prepared by modification of a previously reported procedure.[2] *N*,*N*'-DMEDA (0.31 mL, 2.88 mmol), CuI (79.0 mg, 0.415 mmol) and $PPh_2H$ (1.7 mL, 9.77 mmol) were placed in a Schlenk flask and the contents were evacuated and refilled with $N_2$ gas (× 3 cycles). Toluene (25 mL) which had been freshly degassed (using a stream of argon for 15 min) was added and the mixture was stirred at room temperature for 20 min. A solution of oxazole **SL2**[2,3] (1.00 g, 3.31 mmol) in freshly degassed toluene (5 mL) was added, followed by $Cs_2CO_3$ (3.77 g, 11.6 mmol). The Schlenk flask was sealed and the contents were stirred at 110 °C for 72 h. The reaction was cooled to room temperature, filtered through celite and concentrated in *vacuo*. The residue was purified by column chromatography (10% EtOAc/petroleum ether) to give the title compound as a white solid (713 mg, 53%). The analytical data were consistent with those reported previously.[4]

## 3. Preparation of Substrates

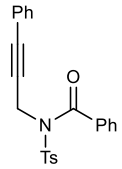
### Preparation of Substrate 1a



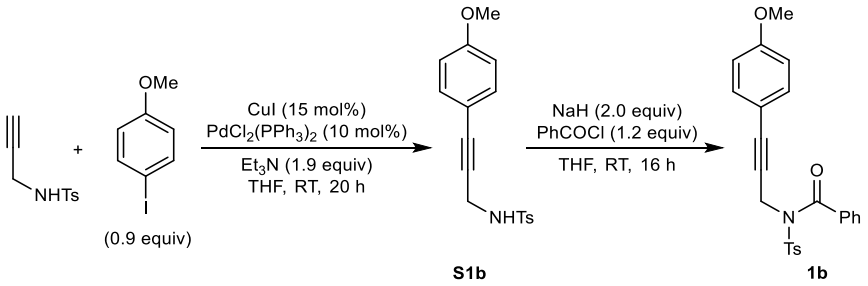

**4-Methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (S1a).**[5] To a stirred solution of $PdCl_2(PPh_3)_2$ (842 mg, 1.20 mmol) and CuI (457 mg, 2.40 mmol) in DMF (30 mL) was added freshly degassed $Et_3N$ (6.7 mL, 48.1 mmol) and iodobenzene (4.0 mL, 35.9 mmol) under a nitrogen atmosphere. A solution of 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide[6] (5.00 g, 23.9 mmol) in DMF (20 mL) was added and the resulting solution was stirred at 40 °C for 3 h. The reaction was quenched with 50% brine (500 mL) and extracted with EtOAc (3 × 250 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (2 × 500 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column

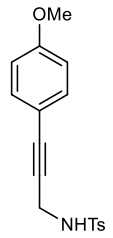
chromatography (10% to 20% EtOAc/petroleum ether) to give the title compound as a brown solid (5.54 g, 81%). The analytical data were consistent with those reported previously.[5]



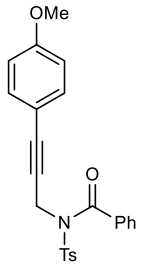

***N*-(3-Phenylprop-2-yn-1-yl)-*N*-tosylbenzamide (1a).**[7] A solution of *N*-tosyl propargyl amine **S1a**[5] (1.50 g, 5.26 mmol) in THF (20 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 250 mg, 10.4 mmol) in THF (25 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Benzoyl chloride (0.73 mL, 6.28 mmol) was added dropwise and the resulting solution was stirred at room temperature for 20 h. The reaction was quenched with brine (60 mL) and extracted with EtOAc (2 × 120 mL). The combined organic layers were washed with brine (60 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (5% to 20% EtOAc/petroleum ether) to give the title compound as a dark brown solid (1.34 g, 66%). The analytical data were consistent with those reported previously.[7]

**Preparation of Substrate 1b**



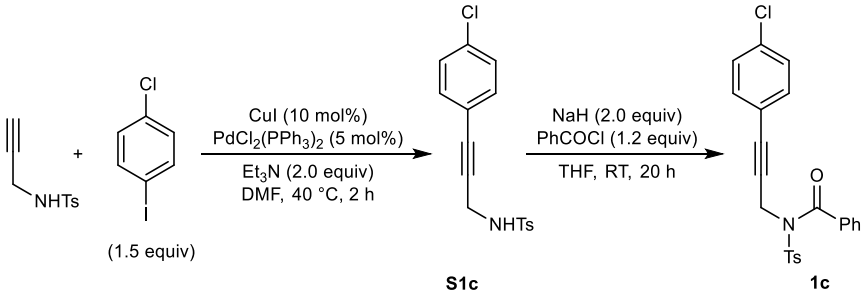



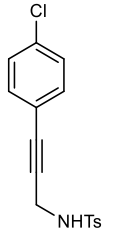

***N*-[3-(4-Chlorophenyl)prop-2-yn-1-yl]-4-methylbenzenesulfonamide (S1b).**[8] To a stirred solution of $PdCl_2(PPh_3)_2$ (562 mg, 0.801 mmol) and CuI (228 mg, 1.20 mmol) in THF (6 mL) was added freshly degassed $Et_3N$ (2.4 mL, 17.2 mmol) and iodobenzene (1.79 g, 7.65 mmol) under a nitrogen atmosphere. A solution of 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.85 g, 8.84 mmol) in THF (3.5 mL) was added and the resulting solution was stirred at room temperature for 20 h. The reaction was quenched with saturated aqueous $NH_4Cl$ solution (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (30 mL), dried ($Na_2SO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (5% to 20% EtOAc/petroleum ether) to give the title compound as a pale brown solid (1.67 g, 72%). The analytical data were consistent with those reported previously.[8]



***N*-[3-(4-Methoxyphenyl)prop-2-yn-1-yl]-*N*-tosylbenzamide (1b).** NaH (60% dispersion in mineral oil, 75.8 mg, 3.16 mmol) was added portionwise to a solution of the *N*-tosyl propargyl amine **S1b** (500 mg, 1.59 mmol) in THF (15 mL). The resulting solution was stirred for *ca.* 1 h. The mixture was cooled to 0 °C, and benzoyl chloride (0.22 mL, 1.89 mmol) was added dropwise. The resulting solution was gradually warmed to room temperature and stirred for 16 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (20% EtOAc/petroleum ether) to give the title compound as a pale yellow solid (345 mg, 52%). $R_f$ = 0.41 (40% EtOAc/petroleum ether); m.p. 122-123 °C ($Et_2O$); IR 2919, 2839, 2213 (C≡C), 1683 (C=O), 1604, 1509, 1363, 1295, 1183, 572 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.05-7.93 (2H, m, Ar**H**), 7.62-7.54 (2H, m, Ar**H**), 7.53-7.47 (1H, m, Ar**H**), 7.43-7.36 (2H, m, Ar**H**), 7.29-7.26 (2H, m, Ar**H**), 7.26-7.23 (2H, m, Ar**H**), 6.88-6.79 (2H, m, Ar**H**), 4.79 (2H, s, C**H**$_2$), 3.82 (3H, s, OC**H**$_3$), 2.40 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.9 (C), 160.1 (C), 145.0 (C), 135.9 (C), 134.3 (C), 133.3 (2 × CH), 131.8 (CH), 129.4 (2 × CH), 129.2 (2 × CH), 128.5 (2 × CH), 128.0 (2 × CH), 114.2 (C), 114.1 (2 × CH), 85.1 (C), 82.5 (C), 55.5 ($CH_3$), 39.1 ($CH_2$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{24}H_{21}NO_4SNa]^+$ $[M+Na]^+$: 442.1083, found 442.1083.

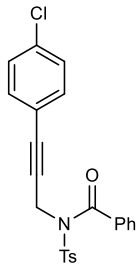
**Preparation of Substrate 1c**



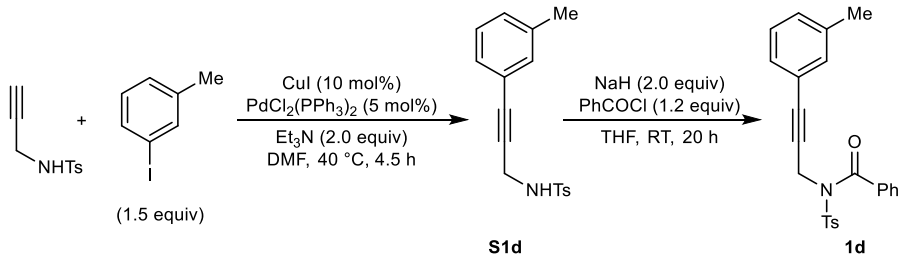
***N*-[3-(4-Chlorophenyl)prop-2-yn-1-yl]-4-methylbenzenesulfonamide (S1c).** [9] To a stirred solution of $PdCl_2(PPh_3)_2$ (168 mg, 0.240 mmol) and CuI (91.4 mg, 0.480 mmol) in DMF (6 mL) was added freshly degassed $Et_3N$ (1.3 mL, 9.33 mmol) and 1-chloro-4-iodobenzene (1.71 g, 7.17 mmol) under a nitrogen atmosphere. 4-Methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.00 g, 4.80 mmol) in DMF (4 mL) was added and the resulting solution was stirred at 40 °C for 2 h. The reaction was quenched with 50% brine (100 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (2 × 100 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (20% EtOAc/petroleum ether) to give the title

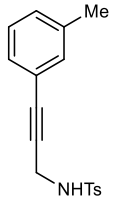
compound as a reddish-brown solid (1.01 g, 66%). The analytical data were consistent with those reported previously.[9]



***N*-[3-(4-Chlorophenyl)prop-2-yn-1-yl]-*N*-tosylbenzamide (1c).** A solution of the *N*-tosyl propargyl amine **S1c** (500 mg, 1.56 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 74.8 g, 3.12 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Benzoyl chloride (0.22 mL, 1.89 mmol) was added dropwise and the resulting solution was stirred at room temperature for 20 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (5% to 30% EtOAc/petroleum ether) to give the title compound as a white solid (425 mg, 64%). $R_f$ = 0.49 (40% EtOAc/petroleum ether); m.p. 145-147 °C ($Et_2O$); IR 1689 (C=O), 1489, 1352, 1309, 1244, 1165, 1071, 945, 714, 570 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.98-7.90 (2H, m, Ar**H**), 7.58-7.54 (2H, m, Ar**H**), 7.54-7.48 (1H, m, Ar**H**), 7.43-7.37 (2H, m, Ar**H**), 7.31-7.22 (6H, m, Ar**H**), 4.80 (2H, s, C**H**$_2$), 2.41 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.8 (C), 145.2 (C), 135.9 (C), 135.0 (C), 134.2 (C), 133.1 (2 × CH), 132.0 (CH), 129.5 (2 × CH), 129.1 (2 × CH), 128.8 (2 × CH), 128.5 (2 × CH), 128.1 (2 × CH), 120.7 (C), 84.9 (C), 84.0 (C), 38.8 ($CH_2$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{23}H_{18}ClNO_3SNa]^+$ $[M+Na]^+$: 446.0588, found 446.0597.

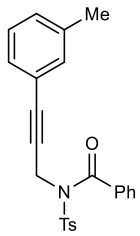
**Preparation of Substrate 1d**



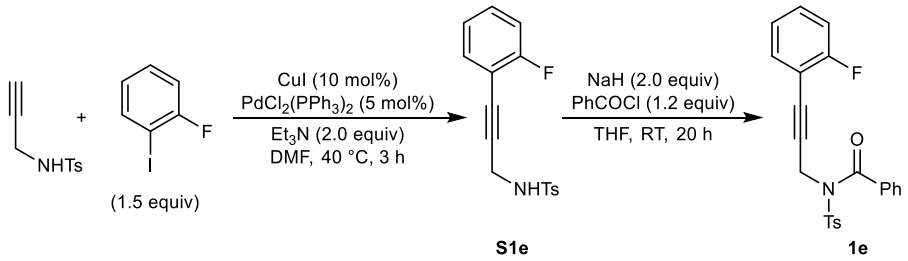
**4-Methyl-*N*-[3-(3-methylphenyl)prop-2-yn-1-yl]benzenesulfonamide (S1d).** To a stirred solution of $PdCl_2(PPh_3)_2$ (168 mg, 0.240 mmol) and CuI (91.4 mg, 0.480 mmol) in DMF (6 mL) was added freshly degassed $Et_3N$ (1.3 mL, 9.33 mmol) and 3-iodotoluene (0.92 mL, 7.17 mmol) under a nitrogen atmosphere. A solution of r-Methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.00 g, 4.78 mmol) in DMF (4 mL) was added and the resulting solution was stirred at 40 °C for 4.5 h. The reaction was quenched with 50% brine (100 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (2 × 100 mL), dried ($MgSO_4$), filtered and concentrated in

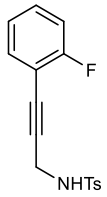
*vacuo*. The residue was purified by column chromatography (20% EtOAc/petroleum ether) to give the title compound as a white solid (861 mg, 60%). $R_f$ = 0.41 (40% EtOAc/petroleum ether); m.p. 108-109 °C ($Et_2O$); IR 3275 (NH), 2923, 1597, 1484, 1431, 1324, 1153, 1090, 1057, 814 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.87-7.77 (2H, m, Ar**H**), 7.31-7.27 (2H, m, Ar**H**), 7.17-7.04 (2H, m, Ar**H**), 7.01-6.86 (2H, m, Ar**H**), 4.64 (1H, t, *J* = 6.2 Hz, N**H**), 4.07 (2H, d, *J* = 6.2 Hz, C$\mathbf{H}_2$), 2.37 (3H, s, ArC$\mathbf{H}_3$), 2.29 (3H, s, ArC$\mathbf{H}_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 143.9 (C), 138.0 (C), 137.0 (C), 132.3 (CH), 129.8 (2 × CH), 129.6 (CH), 128.8 (CH), 128.2 (CH), 127.7 (2 × CH), 122.0 (C), 85.1 (C), 82.9 (C), 34.0 ($CH_2$), 21.6 ($CH_3$), 21.3 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{17}H_{17}NNaO_2S]^+$ $[M+Na]^+$: 322.0872, found 322.0875.



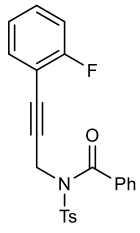

***N*-[3-(3-Methylphenyl)prop-2-yn-1-yl]-*N*-tosylbenzamide (1d).** A solution of the *N*-tosyl propargyl amine **S1d** (500 mg, 1.67 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 80.1 mg, 3.33 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Benzoyl chloride (0.23 mL, 2.01 mmol) was added dropwise and the resulting solution was stirred at room temperature for 20 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (2% to 14% EtOAc/petroleum ether) to give the title compound as a yellow oil (655 mg, 97%). $R_f$ = 0.46 (40% EtOAc/petroleum ether); IR 2921, 1687 (C=O), 1598, 1485, 1355, 1239, 1165, 1069, 948, 783 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (2H, m, Ar**H**), 7.60-7.57 (2H, m, Ar**H**), 7.53-7.48 (1H, m, Ar**H**), 7.43-7.38 (2H, m, Ar**H**), 7.29-7.26 (2H, m, Ar**H**), 7.22-7.11 (4H, m, Ar**H**), 4.80 (2H, s, C$\mathbf{H}_2$), 2.41 (3H, s, ArC$\mathbf{H}_3$), 2.33 (3H, s, ArC$\mathbf{H}_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.9 (C), 145.0 (C), 138.2 (C), 135.9 (C), 134.3 (C), 132.4 (CH), 131.9 (CH), 129.8 (CH), 129.5 (2 × CH), 129.2 (2 × CH), 128.9 (CH), 128.6 (2 × CH), 128.4 (CH), 128.0 (2 × CH), 122.0 (C), 85.4 (C), 83.5 (C), 39.0 ($CH_2$), 21.8 ($CH_3$), 21.4 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{24}H_{21}NO_3SNa]^+$ $[M+Na]^+$: 426.1134, found 426.1149.

**Preparation of Substrate 1e**



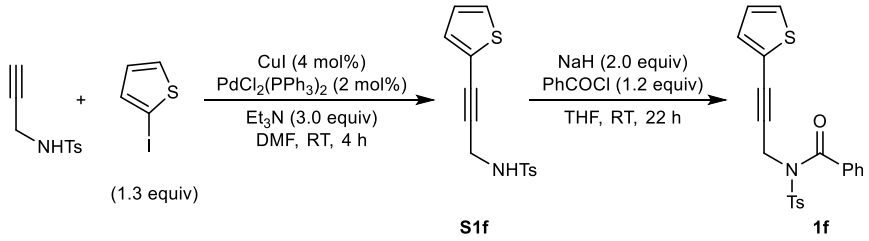
***N*-[3-(2-Fluorophenyl)prop-2-yn-1-yl]-4-methylbenzenesulfonamide (S1e).** To a stirred solution of $PdCl_2(PPh_3)_2$ (168 mg, 0.240 mmol) and CuI (91.4 mg, 0.480 mmol) in DMF (6 mL) was added freshly degassed $Et_3N$ (1.3 mL, 9.33 mmol) and 2-fluoroiodobenzene (0.84 mL, 7.20 mmol) under a nitrogen atmosphere. A solution of 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.00 g, 4.80 mmol) in DMF (4 mL) was added and the resulting solution was stirred at 40 °C for 3 h. The reaction was quenched with 50% brine (100 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (2 × 100 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (20% to 30% EtOAc/petroleum ether) to give the title compound as a pale brown solid (778 mg, 53%). $R_f$ = 0.35 (40% EtOAc/petroleum ether); m.p. 125-126 °C ($Et_2O$); IR 3283 (NH), 1597, 1490, 1428, 1326, 1255, 1213, 1150, 813, 763 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) δ 8.17-8.14 (1H, m, N**H**), 7.73 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.43-7.37 (1H, m, Ar**H**), 7.34-7.31 (2H, m, Ar**H**), 7.25-7.08 (3H, m, Ar**H**), 4.00 (2H, d, *J* = 5.3 Hz, C**H**$_2$), 2.28 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, DMSO-$d_6$) δ 161.8 (d, $J_{C\text{-}F}$ = 249.6 Hz, C), 142.8 (C), 137.8 (C), 133.4 (CH), 130.8 (d, $J_{C\text{-}F}$ = 8.1 Hz, CH), 129.4 (2 × CH), 126.8 (2 × CH), 124.5 (d, $J_{C\text{-}F}$ = 3.5 Hz, CH), 115.6 (d, $J_{C\text{-}F}$ = 20.6 Hz, CH), 110.1 (d, $J_{C\text{-}F}$ = 15.4 Hz, C), 90.4 (d, $J_{C\text{-}F}$ = 3.2 Hz, C), 76.6 (C), 32.6 ($CH_2$), 20.9 ($CH_3$); $^{19}F$ NMR (376 MHz, $CDCl_3$) δ –110.1 (s); HRMS (ESI) Exact mass calculated for $[C_{16}H_{14}FNO_2SNa]^+$ [M+Na]$^+$: 326.0621, found 326.0620.

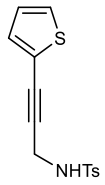


***N*-[3-(2-Fluorophenyl)prop-2-yn-1-yl]-*N*-tosylbenzamide (1e).** A solution of the *N*-tosyl propargyl amine **S1e** (500 mg, 1.65 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 79.2 mg, 3.30 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Benzoyl chloride (0.23 mL, 1.98 mmol) was added dropwise and the resulting solution was stirred at room temperature for 20 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (10% to 35% EtOAc/petroleum ether) to give the title compound as an orange solid (514 mg, 77%). $R_f$ = 0.49 (40% EtOAc/petroleum ether); m.p. 100-101 °C ($Et_2O$); IR

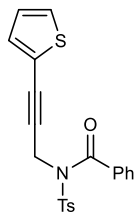
1692 (C=O), 1492, 1350, 1314, 1245, 1185, 1162, 1072, 781, 752 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.99 (2H, d, *J* = 8.5 Hz, Ar**H**), 7.60-7.57 (2H, m, Ar**H**), 7.52-7.47 (1H, m, Ar**H**), 7.42-7.26 (6H, m, Ar**H**), 7.12-7.06 (2H, m, Ar**H**), 4.84 (2H, s, C**H**$_2$), 2.40 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.7 (C), 163.1 (d, $J_{C-F}$ = 252.0 Hz, C), 145.1 (C), 135.7 (C), 134.2 (C), 133.7 (CH), 131.9 (CH), 130.7 (d, $J_{C-F}$ = 8.1 Hz, CH), 129.5 (2 × CH), 129.1 (2 × CH), 128.5 (2 × CH), 127.9 (2 × CH), 124.1 (d, $J_{C-F}$ = 3.7 Hz, CH), 115.7 (d, $J_{C-F}$ = 20.64 Hz, CH), 110.8 (d, $J_{C-F}$ = 15.4 Hz, C), 89.2 (d, $J_{C-F}$ = 3.3 Hz, C), 78.6 (C), 38.8 ($CH_2$), 21.8 ($CH_3$); $^{19}F$ NMR (376 MHz, $CDCl_3$) δ –110.0 (s); HRMS (ESI) Exact mass calculated for $[C_{23}H_{18}FNO_3SNa]^+$ $[M+Na]^+$: 430.0884, found 430.0885.

**Preparation of Substrate 1f**



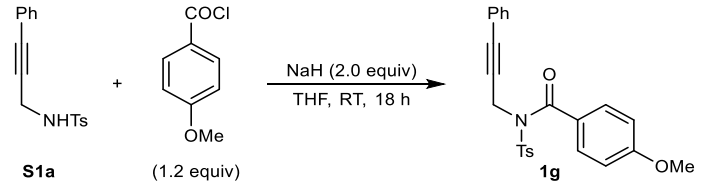

**4-Methyl-*N*-[3-(2-thienyl)prop-2-yn-1-yl]benzenesulfonamide (S1f).** To a stirred solution of $PdCl_2(PPh_3)_2$ (67.4 mg, 0.096 mmol), CuI (36.6 mg, 0.192 mmol) and *N*-tosyl propargyl amine (1.00 g, 4.80 mmol) in THF (0.2 M) was added degassed $Et_3N$ (2.0 mL, 14.4 mmol) and 2-iodothiophene (0.69 mL, 6.24 mmol) under a nitrogen atmosphere and the resulting solution was stirred at room temperature for 4 h. The reaction was filtered through celite and concentrated in *vacuo*. The residue was purified by column chromatography (30% EtOAc/petroleum ether) to give the title compound as a brown solid (860 mg, 62%). $R_f$ = 0.59 (40% EtOAc/petroleum ether); m.p. 137-138 °C ($Et_2O$); IR 3268 (NH), 1596, 1492, 1417, 1337, 1319, 1156, 1038, 813, 674 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (2H, m, Ar**H**), 7.31-7.27 (2H, m, Ar**H**), 7.21 (1H, dd, *J* = 5.1, 1.2 Hz, Ar**H**), 6.97 (1H, dd, *J* = 3.6, 1.2 Hz, Ar**H**), 6.91 (1H, dd, *J* = 5.1, 3.6 Hz, Ar**H**), 4.68 (1H, t, *J* = 6.2 Hz, N**H**), 4.09 (2H, d, *J* = 6.2 Hz, C**H**$_2$), 2.38 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.0 (C), 136.8 (C), 132.5 (CH), 129.9 (2 × CH), 127.59 (2 × CH), 127.57 (CH), 127.0 (CH), 122.1 (C), 87.2 (C), 78.2 (C), 34.1 ($CH_2$), 21.7 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{14}H_{13}NNaO_2S_2]^+$ $[M+Na]^+$: 314.0280, found 314.0278.




***N*-[3-(2-Thienyl)prop-2-yn-1-yl]-*N*-tosylbenzamide (1f).** A solution of the *N*-tosyl propargyl amine **S1f** (500 mg, 1.72 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 82.5 mg, 3.44 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for

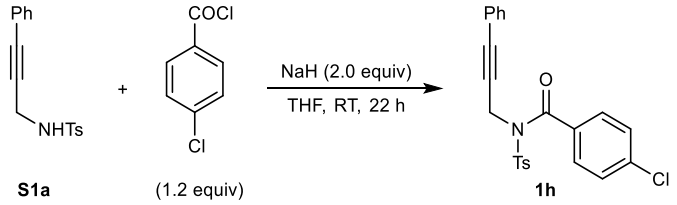
*ca.* 1 h. Benzoyl chloride (0.24 mL, 2.06 mmol) was added dropwise and the resulting solution was stirred at room temperature for 22 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (5% to 30% EtOAc/petroleum ether) to give the title compound as a yellow solid (482 mg, 70%). $R_f$ = 0.42 (40% EtOAc/petroleum ether); m.p. 103-104 °C ($Et_2O$); IR 3090, 2924, 2229 (C≡C), 1688 (C=O), 1595, 1352, 1312, 1243, 1159, 1069 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (2H, m, Ar**H**), 7.57-7.49 (3H, m, Ar**H**), 7.43-7.38 (2H, m, Ar**H**), 7.30-7.27 (3H, m, Ar**H**), 7.14 (1H, dd, *J* = 3.6, 1.2 Hz, Ar**H**), 6.98 (1H, dd, *J* = 5.2, 3.6 Hz, Ar**H**), 4.82 (2H, s, C**H**$_2$), 2.42 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.8 (C), 145.2 (C), 135.8 (C), 134.3 (C), 132.9 (CH), 131.9 (CH), 129.6 (2 × CH), 129.1 (2 × CH), 128.6 (2 × CH), 128.0 (2 × CH), 127.8 (CH), 127.1 (CH), 122.1 (C), 87.8 (C), 78.5 (C), 39.0 ($CH_2$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{21}H_{17}NO_3S_2Na]^+$ $[M+Na]^+$: 418.0542, found 418.0541.

**4-Methoxy-*N*-(3-phenylprop-2-yn-1-yl)-*N*-tosylbenzamide (1g)**



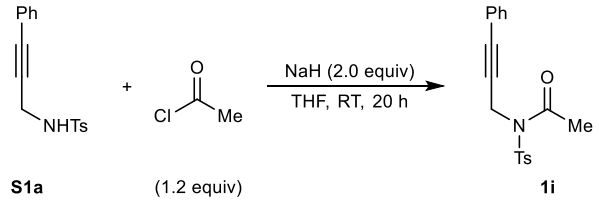

A solution of the *N*-tosyl propargyl amine **S1a** (500 mg, 1.75 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 84.0 mg, 3.50 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. 4-Methoxybenzoyl chloride (0.28 mL, 2.10 mmol) was added dropwise and the resulting solution was stirred at room temperature for 18 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (20% EtOAc/petroleum ether) to give the title compound as a white solid (415 mg, 56%). $R_f$ = 0.59 (40% EtOAc/petroleum ether); m.p. 94-95 °C ($Et_2O$); IR 2928, 2835, 1789, 1682 (C=O), 1602, 1357, 1305, 1243, 1166, 1088 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.03-7.93 (2H, m, Ar**H**), 7.70-7.62 (2H, m, Ar**H**), 7.36-7.25 (7H, m, Ar**H**), 6.94-6.87 (2H, m, Ar**H**), 4.79 (2H, s, C**H**$_2$), 3.85 (3H, s, OC**H**$_3$), 2.39 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.6 (C), 162.9 (C), 144.9 (C), 136.0 (C), 131.8 (2 × CH), 130.9 (2 × CH), 129.5 (2 × CH), 129.1 (2 × CH), 128.8 (CH), 128.4 (2 × CH), 126.2 (C), 122.2 (C), 113.9 (2 × CH), 85.1 (C), 83.8 (C), 55.6 ($CH_3$), 39.3 ($CH_2$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{24}H_{22}NO_4SNa]^+$ $[M+Na]^+$: 442.1083, found 442.1075.

**4-Chloro-*N*-(3-phenylprop-2-yn-1-yl)-*N*-tosylbenzamide (1h)**




A solution of the *N*-tosyl propargyl amine **S1a** (500 mg, 1.75 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 84.0 mg, 3.50 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. 4-Chlorobenzoyl chloride (0.27 mL, 2.10 mmol) was added dropwise and the resulting solution was stirred at room temperature for 22 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (10% EtOAc/petroleum ether) to give the title compound as a pale yellow solid (482 mg, 70%). $R_f$ = 0.61 (40% EtOAc/petroleum ether); m.p. 110-111 °C ($Et_2O$); IR 2917, 1787, 1698 (C=O), 1590, 1488, 1422, 1365, 1312, 1235, 940 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.96-7.92 (2H, m, Ar**H**), 7.55-7.52 (2H, m, Ar**H**), 7.40-7.27 (9H, m, Ar**H**), 4.78 (2H, s, C**H**$_2$), 2.41 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 169.9 (C), 145.3 (C), 138.3 (C), 135.7 (C), 132.8 (C), 131.8 (2 × CH), 129.62 (2 × CH), 129.60 (2 × CH), 129.1 (2 × CH), 129.0 (CH), 128.9 (2 × CH), 128.5 (2 × CH), 122.1 (C), 85.3 (C), 83.6 (C), 38.8 ($CH_2$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{23}H_{18}ClNO_3SNa]^+$ $[M+Na]^+$: 446.0588, found 446.0604.

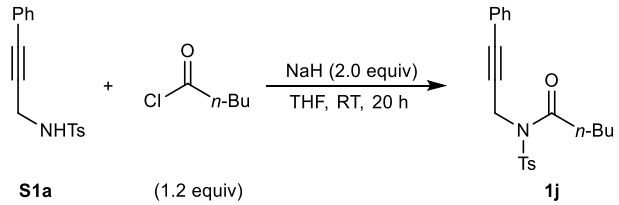
***N*-(3-Phenylprop-2-yn-1-yl)-*N*-tosylacetamide (1i)**




A solution of the *N*-tosyl propargyl amine **S1a** (500 mg, 1.75 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 84.0 mg, 3.50 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Acetyl chloride (0.15 mL, 2.10 mmol) was added dropwise and the resulting solution was stirred at room temperature for 20 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (5% to 20% EtOAc/petroleum ether) to give the title compound as a pale yellow solid (529 mg, 92). $R_f$ =

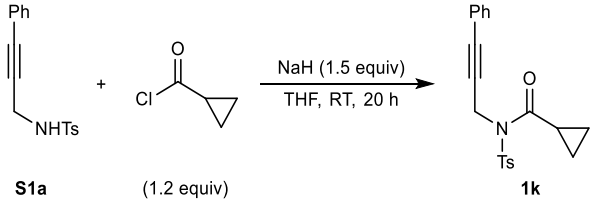
0.43 (35% EtOAc/petroleum ether); m.p. 94-96 °C ($Et_2O$); IR 2989, 1706 (C=O), 1345, 1243, 1158, 1085, 1043 864, 813, 754 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.01-7.94 (2H, m, Ar**H**), 7.37-7.29 (7H, m, Ar**H**), 4.90 (2H, s, C**H**$_2$), 2.41 (3H, s, ArC**H**$_3$), 2.37 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 169.6 (C), 145.2 (C), 136.4 (C), 131.9 (2 × CH), 129.9 (2 × CH), 128.8 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 122.3 (C), 84.3 (C), 83.8 (C), 36.5 ($CH_2$), 24.8 ($CH_3$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{18}H_{17}NO_3SNa]^+$ $[M+Na]^+$: 350.0821, measured 350.0818.

**_N_-(3-Phenylprop-2-yn-1-yl)-_N_-tosylpentanamide (1j)**



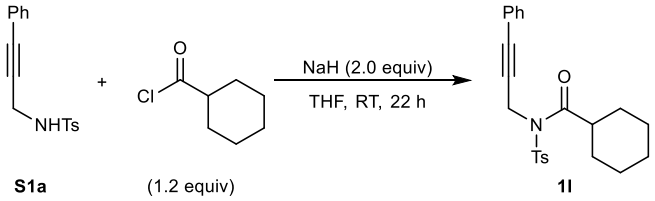

A solution of the *N*-tosyl propargyl amine **S1a** (500 mg, 1.75 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 84.0 mg, 3.50 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Valeroyl chloride (0.25 mL, 2.10 mmol) was added dropwise and the resulting solution was stirred at room temperature for 20 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (2% to 14% EtOAc/petroleum ether) to give the title compound as a yellow solid (420 mg, 65%). $R_f$ = 0.51 (40% EtOAc/petroleum ether); m.p. 53-54 °C ($Et_2O$); IR 2934, 2875, 1703 (C=O), 1343, 1173, 1147, 1087, 1052, 860, 756 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.05-7.87 (2H, m, Ar**H**), 7.40-7.27 (7H, m, Ar**H**), 4.91 (2H, s, C**H**$_2$), 2.66-2.61 (2H, m, C**H**$_2$), 2.41 (3H, s, ArC**H**$_3$), 1.65-1.50 (2H, m, C**H**$_2$), 1.37-1.16 (2H, m, C**H**$_2$), 0.84 (3H, t, *J* = 7.4 Hz, $CH_2C\mathbf{H}_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 172.6 (C), 145.0 (C), 136.6 (C), 131.8 (2 × CH), 129.7 (2 × CH), 128.8 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 122.3 (C), 84.4 (C), 84.0 (C), 36.3 ($CH_2$), 35.8 ($CH_2$), 26.5 ($CH_2$), 22.2 ($CH_2$), 21.7 ($CH_3$), 13.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{21}H_{23}NO_3SNa]^+$ $[M+Na]^+$: 392.1291, measured 392.1302.

**_N_-(3-Phenylprop-2-yn-1-yl)-_N_-tosylpentanamide (1k)**




A solution of the *N*-tosyl propargyl amine **S1a** (500 mg, 1.75 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 140 mg, 3.50 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Cyclopropanecarbonyl chloride (0.19 mL, 2.10 mmol) was added dropwise and the resulting solution was stirred at room temperature for 17 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (15% EtOAc/petroleum ether) to give the title compound as a pale yellow solid (539 mg, 87%). $R_f$ = 0.50 (40% EtOAc/petroleum ether); m.p. 106-108 °C ($Et_2O$); IR 2919, 1683 (C=O), 1596, 1490, 1355, 1156, 1043, 711, 662, 578 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.04-7.89 (2H, m, Ar**H**), 7.40-7.26 (7H, m, Ar**H**), 4.97 (2H, s, C**H**$_2$), 2.41 (3H, s, ArC**H**$_3$), 2.35 (1H, tt, *J* = 7.8, 4.6 Hz, C**H**C=O), 1.08-0.99 (2H, m, cyclopropyl**H**), 0.89-0.79 (2H, m, cyclopropyl**H**).; $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 173.3 (C), 144.9 (C), 136.8 (C), 131.8 (2 × CH), 129.7 (2 × CH), 128.7 (CH), 128.4 (2 × CH), 128.1 (2 × CH), 122.4 (C), 84.3 (C), 84.1 (C), 36.4 ($CH_2$), 21.7 ($CH_3$), 14.4 (CH), 10.6 (2 × $CH_2$); HRMS (ESI) Exact mass calculated for $[C_{20}H_{19}NO_3SNa]^+$ $[M+Na]^+$: 376.0978, found 376.0979.

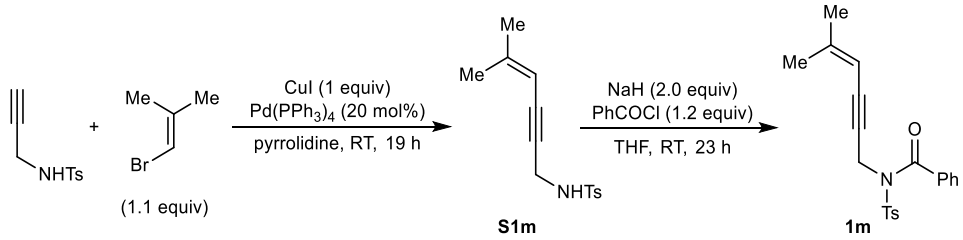
**_N_-(3-Phenylprop-2-yn-1-yl)-_N_-tosylcyclohexanecarboxamide (1l)**

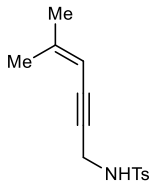



A solution of the *N*-tosyl propargyl amine **S1a** (500 mg, 1.75 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 84.0 mg, 3.50 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h.0 Cyclohexanecarbonyl chloride (0.28 mL, 2.10 mmol) was added dropwise and the resulting solution was stirred at room temperature for 22 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column

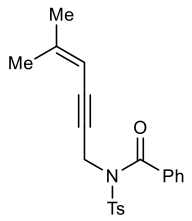
chromatography (10% EtOAc/petroleum ether) to give the title compound as a yellow solid (692 mg, >99%). $R_f$ = 0.57 (40% EtOAc/petroleum ether); m.p. 94-95 °C ($Et_2O$); IR 2935, 1697 (C=O), 1596, 1511, 1353, 1294, 1163, 1134, 1085, 545 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.03-7.90 (2H, m, Ar**H**), 7.39-7.27 (7H, m, Ar**H**), 4.92 (2H, s, C**H**$_2$), 2.91 (1H, tt, *J* = 11.4, 3.3 Hz, C**H**C=O) 2.41 (3H, s, ArC**H**$_3$), 1.78-1.67 (2H, m, cyclohexyl**H**), 1.67-1.58 (3H, m, cyclohexyl**H**), 1.46-1.32 (2H, m, cyclohexyl**H**), 1.23-1.09 (3H, m, cyclohexyl**H**); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 176.1 (C), 144.9 (C), 137.0 (C), 131.8 (2 × CH), 129.7 (2 × CH), 128.8 (CH), 128.5 (2 × CH), 128.1 (2 × CH), 122.4 (C), 84.4 (C), 84.3 (C), 44.2 (CH), 36.1 ($CH_2$), 29.4 (2 × $CH_2$), 25.63 ($CH_2$), 25.60 (2 × $CH_2$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{23}H_{25}NO_3SNa]^+$ $[M+Na]^+$: 418.1444, found 418.1447.

**Preparation of Substrate 1m**



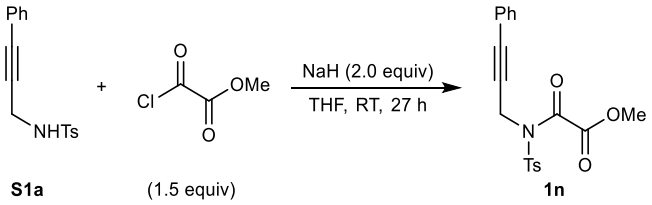




**4-Methyl-*N*-(5-methylhex-4-en-2-yn-1-yl)benzenesulfonamide (S1m).** $Pd(PPh_3)_4$ (1.11 g, 0.96 mmol) and CuI (914 mg, 4.80 mmol) were added to a flask which was sealed and purged with $N_2$. Degassed pyrrolidine (24 mL) was added and the resulting solution was purged with $N_2$ for 10 min. *N*-Tosyl propargyl amine (1.00 g, 4.80 mmol) and 1-bromo-2-methyl-1-propene (0.54 mL, 5.28 mmol) were added, and the mixture was stirred at room temperature for 19 h. The reaction was quenched with distilled water (100 mL) and extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (1% to 17% EtOAc/petroleum ether) to give the title compound as a dark brown solid (277 mg, 22%). $R_f$ = 0.46 (40% EtOAc/petroleum ether); m.p. 63-65 °C ($Et_2O$); IR 3280 (NH), 2920, 1597, 1432, 1323, 1153, 1090, 1036, 812, 667 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.80-7.72 (2H, m, Ar**H**), 7.34-7.28 (2H, m, Ar**H**), 5.01-4.99 (1H, m, $(CH_3)_2$C=C**H**), 4.93 (1H, br s, N**H**), 3.95 (2H, d, *J* = 2.1 Hz, NC**H**$_2$), 2.39 (3H, s, ArC**H**$_3$), 1.72 (3H, s, =C(C**H**$_3$)$_2$), 1.68 (3H, s, =C(C**H**$_3$)$_2$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 149.6 (C), 143.6 (C), 136.8 (C), 129.7 (2 × CH), 127.5 (2 × CH), 104.2 (CH), 85.1 (C), 82.8 (C), 34.0 ($CH_2$), 24.8 ($CH_3$), 21.6 ($CH_3$), 20.9 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{14}H_{17}NO_2SNa]^+$ $[M+Na]^+$: 286.0872, found 286.0872.




***N*-(5-Methylhex-4-en-2-yn-1-yl)-*N*-tosylbenzamide (1m).** A solution of the *N*-tosyl propargyl amine **S1m** (200 mg, 0.759 mmol) in THF (3 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 36.5 mg, 1.52 mmol) in THF (4 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Benzoyl chloride (0.11 mL, 0.947 mmol) was added dropwise and the resulting solution was stirred at room temperature for 23 h. The reaction was quenched with brine (10 mL) and extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (5% to 20% EtOAc/petroleum ether) to give the title compound as a pale yellow solid (156 mg, 56%). $R_f$ = 0.33 (30% EtOAc/petroleum ether); m.p. 90-91 °C ($Et_2O$); IR 2933, 1695 (C=O), 1438, 1352, 1292, 1238, 1165, 1064, 811, 725 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (2H, m, Ar**H**), 7.57-7.55 (2H, m, Ar**H**), 7.51-7.47 (1H, m, Ar**H**), 7.40-7.36 (2H, m, Ar**H**), 7.31-7.27 (2H, m, Ar**H**), 5.22-5.19 (1H, m, $(CH_3)_2C$=C**H**), 4.72 (2H, d, *J* = 2.1 Hz, C$\mathbf{H}_2$), 2.43 (3H, s, ArC$\mathbf{H}_3$), 1.81 (3H, s, =C(C$\mathbf{H}_3$)$_2$), 1.80 (3H, s, =C(C$\mathbf{H}_3$)$_2$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.8 (C), 150.5 (C), 144.9 (C), 136.0 (C), 134.3 (C), 131.8 (CH), 129.4 (2 × CH), 129.2 (2 × CH), 128.5 (2 × CH), 128.0 (2 × CH), 104.4 (CH), 85.6 (C), 83.3(C), 39.2 ($CH_2$), 25.0 ($CH_3$), 21.8 ($CH_3$), 21.2 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{21}H_{21}NO_3SNa]^+$ $[M+Na]^+$: 368.1315, found 368.1316.

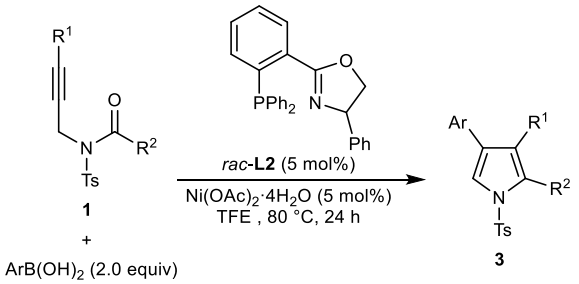
**Methyl 2-{[4-methyl-*N*-(3-phenylprop-2-yn-1-yl)phenyl]sulfonamido}-2-oxoacetate (1n)**



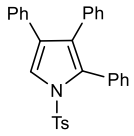

A solution of the *N*-tosyl propargyl amine **S1a** (500 mg, 1.75 mmol) in THF (7 mL) was added dropwise to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 84.0 mg, 3.50 mmol) in THF (8 mL). The resulting solution was warmed to room temperature and stirred for *ca.* 1 h. Methyl oxalyl chloride (0.24 mL, 2.60 mmol) was added dropwise and the resulting solution was stirred at room temperature for 27 h. The reaction was quenched with brine (20 mL) and extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography (3% to 10% EtOAc/petroleum ether) to give the title compound as a pale yellow solid (440 mg, 68%). $R_f$ = 0.45 (40% EtOAc/petroleum ether); m.p. 101-103 °C ($Et_2O$); IR 2958, 1758, 1682 (C=O), 1373, 1325, 1155, 866, 803, 669, 583 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.08-7.92 (2H, m, Ar**H**), 7.34-7.26 (3H, m, Ar**H**), 7.26-7.20 (2H, m, Ar**H**), 7.16-7.04 (2H, m, Ar**H**), 4.72 (2H, s,

C**H**$_2$), 3.98 (3H, s, OC**H**$_3$), 2.35 (3H, s, ArC**H**$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.8 (C), 160.3 (C), 146.2 (C), 134.7 (C), 131.8 (2 × CH), 130.1 (2 × CH), 128.8 (2 × CH), 128.7 (CH), 128.2 (2 × CH), 122.0 (C), 84.7 (C), 81.3 (C), 53.5 ($CH_3$), 34.8 ($CH_2$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{19}H_{17}NO_5SNa]^+$ $[M+Na]^+$: 394.0720, found 394.0715.

## 4. Nickel-Catalyzed Synthesis of Pyrroles: General Procedure A



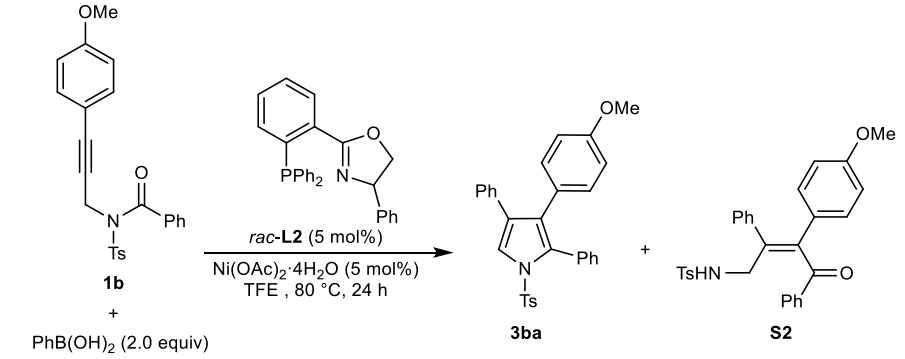

An oven-dried microwave vial fitted with a stirrer bar was charged with the appropriate substrate **1** (0.30 mmol), arylboronic acid (0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (3.7 mg, 0.015 mmol) and *rac*-**L2** (6.1 mg, 0.015 mmol). The vial was capped with a crimp cap PTFE seal and evacuated and back filled with argon (3 cycles). TFE (3 mL) which had been freshly degassed (using a stream of argon for 20 min) was added, the septum was sealed with PTFE tape, and the contents were stirred at room temperature for 10 min and then at 80 °C for 24 h. The reaction was cooled to room temperature, quenched with 50% brine (10 mL) and extracted with EtOAc (5 × 10 mL). (Extraction of the aqueous layer 5 times using EtOAc is essential for high yields.) The combined organic layers were dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography using EtOAc/petroleum ether to give the pyrrole **3**.




**2,3,4-Triphenyl-1-tosyl-1*H*-pyrrole (3aa).** [10] The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (125 mg, 93%). $R_f$ = 0.57 (40% EtOAc/petroleum ether); m.p. 193-194 °C ($Et_2O$); IR 3138, 3059, 2922, 1597, 1365, 1192, 1168, 1101, 1071, 731 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.64 (1H, s, Ar**H**), 7.32-7.28 (2H, m, Ar**H**), 7.26-7.19 (4H, m, Ar**H**), 7.19-7.11 (6H, m, Ar**H**), 7.09-6.99 (5H, m, Ar**H**), 6.90-6.83 (2H, m, Ar**H**), 2.38 (3H, s, C**H**$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.9 (C), 135.9 (C), 133.9 (C), 133.5 (C), 132.8 (2 × CH), 132.3 (C), 130.6 (2 × CH), 130.3 (C), 129.6 (2 × CH), 128.6 (2 × CH), 128.4 (3 × CH), 127.84 (C), 127.79 (2 × CH), 127.7 (2 × CH), 127.3 (2 × CH), 127.1 (C), 126.8 (CH), 126.5 (CH), 120.0 (CH), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{29}H_{23}NO_2SNa]^+$ $[M+Na]^+$: 472.1374, found: 472.1335.

These data are consistent with those reported previously.[10]

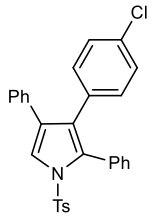
**3-(4-Methoxyphenyl)-2,4-diphenyl-1-tosyl-1*H*-pyrrole (3ba) and (*Z*)-*N*-(3-(4-methoxyphenyl)-4-oxo-2,4-diphenylbut-2-en-1-yl)-4-methylbenzenesulfonamide (S2)**



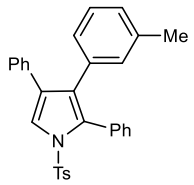

General Procedure A was followed using propargyl amide **1b** (126 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol). Purification by column chromatography (20% to 40% EtOAc/ petroleum ether) gave pyrrole **3ba** a white solid (78.1 mg, 54%) followed by alkene **S2** as a pale yellow solid that had small traces of inseparable, unidentified impurities (33.0 mg, *ca.* 23%).

*Data for* **3ba**: $R_f$ = 0.54 (40% EtOAc/petroleum ether); m.p. 167-169 °C ($Et_2O$); IR 2920, 1598, 1509, 1375, 1241, 1170, 1097, 1029, 698, 584 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, s, Ar**H**), 7.32-7.28 (2H, m, Ar**H**), 7.26-7.10 (10H, m, Ar**H**), 7.04-6.99 (2H, m, Ar**H**), 6.82-6.72 (2H, m, Ar**H**), 6.66-6.52 (2H, m, Ar**H**), 3.68 (3H, s, OC**H**$_3$), 2.38 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 158.2 (C), 144.8 (C), 135.9 (C), 134.0 (C), 132.8 (2 × CH), 132.0 (C), 131.6 (2 × CH), 130.5 (C), 129.6 (2 × CH), 128.6 (2 × CH), 128.4 (2 × CH), 128.3 (CH), 127.7 (2 × CH), 127.5 (C), 127.3 (2 × CH), 127.1 (C), 126.8 (CH), 125.7 (C), 120.0 (CH), 113.3 (2 × CH), 55.1 ($CH_3$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{30}H_{25}NO_3SNa]^+$ $[M+Na]^+$: 502.1447, found 502.1438.

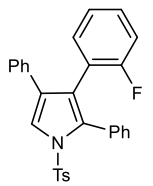
*Data for* **S2**: $R_f$ = 0.27 (40% EtOAc/petroleum ether); IR 3357 (NH), 1671, 1607, 1509, 1476, 1287, 1249, 1131, 1029, 733 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 10.14 (1H, s, N**H**), 8.12-8.04 (2H, m, Ar**H**), 7.60-7.50 (5H, m, Ar**H**), 7.09-7.05 (4H, m, Ar**H**), 6.96-6.89 (3H, m, Ar**H**), 6.72-6.67 (2H, m, Ar**H**), 6.64-6.59 (2H, m, Ar**H**), 4.54 (2H, s, C**H**$_2$), 3.70 (3H, s, |OC**H**$_3$), 2.31 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 165.6 (C), 159.3 (C), 145.1 (C), 141.0 (C), 139.3 (C), 135.3 (C), 133.4 (C), 132.4 (CH), 130.9 (2 × CH), 129.8 (2 × CH), 129.7 (2 × CH), 128.9 (2 × CH), 128.3 (C), 128.2 (2 × CH), 128.0 (2 × CH), 127.8 (2 × CH), 126.4 (CH), 117.9 (C), 113.5 (2 × CH), 62.7 ($CH_2$), 55.2 ($CH_3$), 21.7 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{30}H_{27}NO_4SNa]^+$ $[M+Na]^+$: 520.1553, found 520.1553.




**3-(4-Chlorophenyl)-2,4-diphenyl-1-tosyl-1*H*-pyrrole (3ca).** The title compound was prepared according to General Procedure A, using propargyl amide **1c** (127 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (15% EtOAc/petroleum ether) to give a white solid (134 mg, 92%). $R_f$ = 0.56 (40% EtOAc/petroleum ether); m.p. 194-196 °C ($Et_2O$); IR 2921, 1595, 1534, 1488, 1361, 1167, 1088, 1029, 592, 541 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.63 (1H, s, Ar**H**), 7.32-7.27 (3H, m, Ar**H**), 7.26-7.22 (3H, m, Ar**H**), 7.20-7.11 (6H, m, Ar**H**), 7.03-6.96 (4H, m, Ar**H**), 6.78 (2H, d, *J* = 8.5 Hz, Ar**H**), 2.38 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 145.0 (C), 135.7 (C), 133.5 (C), 132.7 (2 × CH), 132.4 (C), 132.3 (C), 132.0 (C), 131.8 (2 × CH), 130.0 (C), 129.6 (2 × CH), 128.58 (2 × CH), 128.55 (CH), 128.5 (2 × CH), 128.1 (2 × CH), 127.7 (2 × CH), 127.5 (2 × CH), 127.0 (CH), 126.8 (C), 126.5 (C), 120.1 (CH), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{29}H_{22}ClNO_2SNa]^+$ $[M+Na]^+$: 506.0952, found 506.0952.

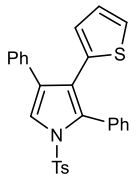



**2,4-Diphenyl-3-(3-methylphenyl)-1-tosyl-1*H*-pyrrole (3da).** The title compound was prepared according to General Procedure A, using propargyl amide **1d** (121 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (20% EtOAc/ petroleum ether) to give a yellow solid (125 mg, 90%). $R_f$ = 0.62 (40% EtOAc/petroleum ether); m.p. 153-155 °C ($Et_2O$); IR 2922, 1597, 1492, 1444, 1362, 1166, 1092, 776, 671, 591 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.64 (1H, s, Ar**H**), 7.32-7.28 (2H, m, Ar**H**), 7.26-7.10 (10H, m, Ar**H**), 7.04-6.99 (2H, m, Ar**H**), 6.95-6.83 (2H, m, Ar**H**), 6.68-6.63 (2H, m, Ar**H**), 2.38 (3H, s, C**H**$_3$), 2.06 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.8 (C), 137.1 (C), 135.9 (C), 133.9 (C), 133.3 (C), 132.7 (2 × CH), 132.2 (C), 131.3 (CH), 130.4 (C), 129.6 (2 × CH), 128.5 (2 × CH), 128.28 (3 × CH), 127.9 (C), 127.64 (3 × CH), 127.58 (CH), 127.23 (3 × CH), 127.1 (C), 126.8 (CH), 119.9 (CH), 21.7 ($CH_3$), 21.3 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{30}H_{25}NO_2SNa]^+$ $[M+Na]^+$: 486.1498, found 486.1477.

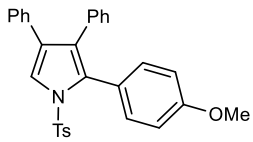



**3-(2-Fluorophenyl)-2,4-diphenyl-1-tosyl-1*H*-pyrrole (3ea).** The title compound was prepared according to General Procedure A, using propargyl amide **1e** (122 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (15% EtOAc/petroleum ether) to give a pale yellow solid (133 mg, 95%). $R_f$ = 0.59 (40% EtOAc/petroleum ether); m.p. 152-153 °C ($Et_2O$); IR 3034, 1597, 1488, 1445, 1365, 1191, 1167, 699, 670, 589 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.69 (1H, s, Ar**H**), 7.32-7.27 (2H, m, Ar**H**), 7.25-7.06 (11H, m, Ar**H**), 7.03 (2H, d, *J* = 7.1 Hz, Ar**H**), 6.91 (1H, td, *J* = 7.4, 2.0 Hz, Ar**H**), 6.88-6.79 (2H, m, Ar**H**), 2.38 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 161.6 (C), 159.2 (C), 145.0 (C), 135.7 (C), 133.8 (C), 133.5 (C), 132.8 (d, $J_{C\text{-}F}$ = 3.3 Hz, CH), 132.2

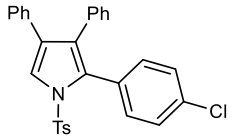
(2 × CH), 130.0 (C), 129.6 (2 × CH), 129.2 (d, $J_{C\text{-}F}$ = 8.0 Hz, CH), 128.4 (2 × CH), 127.60 (2 × CH), 127.56 (2 × CH), 127.5 (CH), 127.2 (2 × CH), 126.9 (CH), 123.7 (d, $J_{C\text{-}F}$ = 3.6 Hz, CH), 121.9 (C), 121.7 (d, $J_{C\text{-}F}$ = 16.1 Hz, C), 119.7 (CH), 115.4 (d, $J_{C\text{-}F}$ = 22.1 Hz, CH), 21.7 ($CH_3$); $^{19}$F NMR (376 MHz, $CDCl_3$) δ –112.8 (s); HRMS (ESI) Exact mass calculated for $[C_{29}H_{22}FNO_2SNa]^+$ $[M+Na]^+$: 490.1247, found 490.1238.



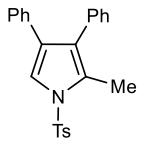

**2,4-Diphenyl-3-(2-thienyl)-1-tosyl-1*H*-pyrrole (3fa).** The title compound was prepared according to General Procedure A, using propargyl amide **1f** (119 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (10% EtOAc/petroleum ether) to give a white solid (62.7 mg, 46%). $R_f$ = 0.56 (40% EtOAc/petroleum ether); m.p. 142-143 °C ($Et_2O$); IR 3071, 1728, 1595, 1446, 1165, 1094, 775, 693, 667, 591 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, s, Ar**H**), 7.37-7.26 (8H, m, Ar**H**), 7.25-7.19 (2H, m, Ar**H**), 7.22 -7.13 (2H, m, Ar**H**), 7.15-7.07 (2H, m, Ar**H**), 7.04 (1H, dd, *J* = 5.1, 1.2 Hz, Ar**H**), 6.74 (1H, dd, *J* = 5.1, 3.6 Hz, Ar**H**), 6.50 (1H, dd, *J* = 3.6, 1.2 Hz, Ar**H**), 2.42 (3H, s, C**H**$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 145.1 (C), 135.7 (C), 134.6 (C), 133.6 (C), 132.8 (2 × CH), 132.5 (C), 130.0 (C), 129.7 (2 × CH), 128.9 (2 × CH), 128.8 (CH), 128.4 (2 × CH), 127.79 (3 × CH), 127.4 (2 × CH), 127.21 (C), 127.18 (CH), 126.5 (CH), 125.4 (CH), 121.0 (C), 120.0 (CH), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{27}H_{21}NO_2S_2Na]^+$ $[M+Na]^+$: 478.0906, found 478.0903.



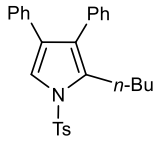

**2-(4-Methoxyphenyl)-3,4-diphenyl-1-tosyl-1*H*-pyrrole (3ga).** The title compound was prepared according to General Procedure A, using propargyl amide **1g** (126 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (10% to 15% EtOAc/petroleum ether) to give a white solid (112 mg, 78%). $R_f$ = 0.49 (40% EtOAc/petroleum ether); m.p. 169-171 °C ($Et_2O$); IR 2922, 1603, 1490, 1363, 1293, 1249, 1166, 1096, 669, 586 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, s, Ar**H**), 7.34-7.29 (2H, m, Ar**H**), 7.25-7.19 (3H, m, Ar**H**), 7.18-7.12 (4H, m, Ar**H**), 7.08-7.01 (3H, m, Ar**H**), 6.96-6.90 (2H, m, Ar**H**), 6.90-6.83 (2H, m, Ar**H**), 6.72-6.66 (2H, m, Ar**H**), 3.80 (3H, s, OC**H**$_3$), 2.38 (3H, s, ArC**H**$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.6 (C), 144.8 (C), 135.9 (C), 134.0 (C), 133.9 (2 × CH), 133.7 (C), 132.1 (C), 130.6 (2 × CH), 129.6 (2 × CH), 128.6 (2 × CH), 128.3 (2 × CH), 127.79 (C), 127.76 (2 × CH), 127.7 (2 × CH), 127.1 (C), 126.8 (CH), 126.4 (CH), 122.5 (C), 119.9 (CH), 112.8 (2 × CH), 55.3 ($CH_3$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{30}H_{25}NO_3SNa]^+$ $[M+Na]^+$: 502.1447, found 502.1447.




**2-(4-Chlorophenyl)-3,4-diphenyl-1-tosyl-1*H*-pyrrole (3ha).** The title compound was prepared according to General Procedure A, using propargyl amide **1h** (127 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (5% to 10% EtOAc/petroleum ether) to give a pale orange solid (135 mg, 93%). $R_f$ = 0.69 (40% EtOAc/petroleum ether); m.p. 205-206 °C ($Et_2O$); IR 3136, 3064, 2922, 1597, 1490, 1365, 1169, 1092, 671, 594 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.64 (1H, s, Ar**H**), 7.36-7.30 (2H, m, Ar**H**), 7.25-7.19 (3H, m, Ar**H**), 7.19-7.12 (6H, m, Ar**H**), 7.10-7.01 (3H, m, Ar**H**), 6.98-6.92 (2H, m, Ar**H**), 6.87-6.81 (2H, m, Ar**H**), 2.39 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 145.2 (C), 135.8 (C), 134.5 (C), 134.0 (2 × CH), 133.6 (C), 133.2 (C), 130.9 (C), 130.5 (2 × CH), 129.7 (2 × CH), 128.9 (C), 128.5 (2 × CH), 128.4 (2 × CH), 128.0 (2 × CH), 127.7 (2 × CH), 127.6 (2 × CH), 127.3 (C), 127.0 (CH), 126.8 (CH), 120.4 (CH), 21.8 ($CH_3$) (one carbon signal merged with others); HRMS (ESI) Exact mass calculated for $[C_{29}H_{22}ClNO_2SNa]^+$ $[M+Na]^+$: 506.0952, found 506.0955.

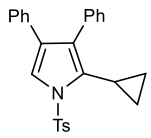



**2-Methyl-3,4-diphenyl-1-tosyl-1*H*-pyrrole (3ia).** The title compound was prepared according to General Procedure A, using propargyl amide **1i** (98.2 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (87.5 mg, 75%). $R_f$ = 0.66 (35% EtOAc/petroleum ether); IR 3057, 2921, 1597, 1359, 1308, 1173, 1158, 1092, 784, 700 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.84-7.79 (2H, m, Ar**H**), 7.52 (1H, s, Ar**H**), 7.39-7.28 (5H, m, Ar**H**), 7.24-7.18 (3H, m, Ar**H**), 7.15-7.06 (4H, m, Ar**H**), 2.46 (3H, s, C**H**$_3$), 2.31 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 145.1 (C), 136.3 (C), 134.2 (C), 133.8 (C), 130.6 (2 × CH), 130.2 (2 × CH), 128.28 (4 × CH), 128.2 (2 × CH), 128.1 (C), 127.3 (2 × CH), 127.2 (C), 126.9 (CH), 126.7 (CH), 126.5 (C), 118.8 (CH), 21.8 ($CH_3$), 11.9 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{24}H_{21}NO_2SNa]^+$ $[M+Na]^+$: 410.1185, found 410.1180.

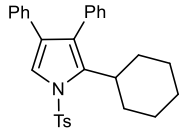



**2-Butyl-3,4-diphenyl-1-tosyl-1*H*-pyrrole (3ja).** The title compound was prepared according to General Procedure A, using propargyl amide **1j** (111 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (8% EtOAc/petroleum ether) to give a colorless oil (118 mg, 92%). $R_f$ = 0.68 (40% EtOAc/petroleum ether); IR 3031, 2957, 2929, 2870, 1734, 1597, 1365, 1171, 669, 590 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (2H, m, Ar**H**), 7.48 (1H, s, Ar**H**), 7.34-7.30 (2H, m, Ar**H**), 7.30-7.22 (3H, m, Ar**H**), 7.20-7.14 (3H, m, Ar**H**), 7.12-7.06 (4H, m, Ar**H**), 2.71-2.62 (2H, m, C**H**$_2$CH$_2$CH$_2$CH$_3$), 2.42 (3H, s, ArC**H**$_3$), 1.47-1.35 (2H, m, C**H**$_2$CH$_2$CH$_3$), 1.22-1.10 (2H, m, C**H**$_2$CH$_3$), 0.74 (3H, t, *J* = 7.3 Hz, CH$_2$C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.9 (C), 136.7 (C),

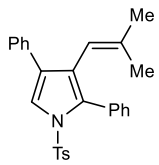
134.5 (C), 133.8 (C), 133.7 (C), 130.5 (2 × CH), 130.1 (2 × CH), 128.3 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.6 (C), 127.04 (C), 126.96 (CH), 126.9 (2 × CH), 126.6 (CH), 119.3 (CH), 33.1 ($CH_2$), 25.4 ($CH_2$), 22.6 ($CH_2$), 21.7 ($CH_3$), 13.7 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{27}H_{27}NO_2S]^+$ $[M+H]^+$: 430.1835, found 430.1828.




**2-Cyclopropyl-3,4-diphenyl-1-tosyl-1*H*-pyrrole (3ka).** The title compound was prepared according to General Procedure A, using propargyl amide **1k** (106 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (5% EtOAc/petroleum ether) to give a white solid (86.8 mg, 70%). $R_f$ = 0.64 (40% EtOAc/petroleum ether); m.p. 107-108 °C ($Et_2O$); IR 3145, 3056, 2923, 1597, 1350, 1170, 746, 699, 670, 580 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.88-7.78 (2H, m, Ar**H**), 7.50 (1H, d, *J* = 0.7 Hz, Ar**H**), 7.38-7.32 (2H, m, Ar**H**), 7.26-7.21 (3H, m, Ar**H**), 7.21-7.15 (3H, m, Ar**H**), 7.11-7.04 (4H, m, Ar**H**), 2.45 (3H, s, C**H**$_3$), 1.90-1.78 (1H, m, cyclopropyl**H**), 0.64-0.52 (2H, m, cyclopropyl**H**), 0.04-(–0.06) (2H, m, cyclopropyl**H**); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.9 (C), 136.7 (C), 134.3 (C), 133.9 (C), 132.6 (C), 130.9 (2 × CH), 130.0 (2 × CH), 128.5 (2 × CH), 128.2 (2 × CH), 127.8 (2 × CH), 127.6 (2 × CH), 127.2 (C), 126.8 (CH), 126.6 (CH), 119.7 (CH), 21.8 ($CH_3$), 8.7 (2 × $CH_2$), 7.2 (CH) (one carbon signal merged with others); HRMS (ESI) Exact mass calculated for $[C_{26}H_{23}NO_2SNa]^+$ $[M+Na]^+$: 436.1342, found 436.1333.

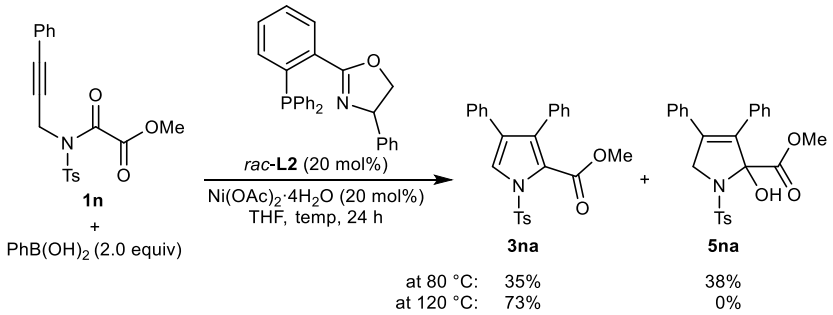



**2-Cyclohexyl-3,4-diphenyl-1-tosyl-1*H*-pyrrole (3la)**. The title compound was prepared according to a modification of General Procedure A (in that the temperature was 120 °C rather than 80 °C), using propargyl amide **1l** (119 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (1% to 5% EtOAc/petroleum ether) to give a pale orange solid (73.7 mg, 54%). $R_f$ = 0.64 (40% EtOAc/petroleum ether); m.p. 93-95 °C ($Et_2O$); IR 3155, 3056, 2924, 2853, 1598, 1446, 1167, 1092, 670, 591 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.81-7.73 (2H, m, Ar**H**), 7.57-7.50 (1H, m, Ar**H**), 7.36 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.29-7.25 (3H, m, Ar**H**), 7.21-7.10 (5H, m, Ar**H**), 7.10-7.02 (2H, m, Ar**H**), 3.21-3.00 (1H, m, C**H**), 2.46 (3H, s, ArC**H**$_3$), 1.59-1.47 (3H, m, cyclohexyl**H**), 1.45-1.33 (2H, m, cyclohexyl**H**), 1.19-1.01 (4H, m, cyclohexyl**H**), 0.91-0.74 (1H, m, cyclohexyl**H**); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 145.0 (C), 137.0 (C), 136.7 (C), 135.7 (C), 134.0 (C), 131.5 (2 × CH), 130.1 (2 × CH), 128.1 (2 × CH), 128.0 (2 × CH), 127.8 (2 × CH), 127.6 (C), 127.20 (CH), 127.17 (2 × CH), 126.6 (C), 126.4 (CH), 118.2 (CH), 37.5 (CH), 32.9 (2 × $CH_2$), 27.3 (2 × $CH_2$), 25.8 ($CH_2$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{29}H_{29}NO_2SNa]^+$ $[M+Na]^+$: 478.1811, found 478.1807.




**3-(2-Methylprop-1-en-1-yl)-2,4-diphenyl-1-tosyl-1*H*-pyrrole (3ma).** The title compound was prepared according to General Procedure A, using propargyl amide **1m** (110 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (10% EtOAc/petroleum ether) to give a white solid (127 mg, 99%). $R_f$ = 0.53 (40% EtOAc/petroleum ether); m.p. 153-154 °C ($Et_2O$); IR 3144, 3053, 2962, 2927, 1597, 1356, 1155, 695, 617, 592 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, s, Ar**H**), 7.51-7.43 (2H, m, Ar**H**), 7.38-7.26 (5H, m, Ar**H**), 7.26-7.21 (3H, m, Ar**H**), 7.15-7.05 (4H, m, Ar**H**), 5.75-5.69 (1H, m, $(CH_3)_2C$=C**H**), 2.36 (3H, s, ArC**H**$_3$), 1.58 (3H, d, *J* = 1.4 Hz, =C(C**H**$_3$)$_2$), 1.07 (3H, d, *J* = 1.2 Hz, =C(C**H**$_3$)$_2$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.7 (C), 138.1 (C), 135.8 (C), 134.6 (C), 132.8 (C), 132.1 (2 × CH), 131.2 (C), 129.5 (2 × CH), 128.5 (2 × CH), 128.2 (C), 128.0 (CH), 127.8 (2 × CH), 127.4 (2 × CH), 127.3 (2 × CH), 126.8 (CH), 125.1 (C), 120.1 (CH), 116.1 (CH), 25.4 ($CH_3$), 21.7 ($CH_3$), 19.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{27}H_{25}NO_2SNa]^+$ $[M+Na]^+$: 450.1498, found 450.1495.

**Methyl 3,4-diphenyl-1-tosyl-1*H*-pyrrole-2-carboxylate (3na) and methyl 3,4-diphenyl-1-tosyl-1*H*-pyrrole-2-carboxylate (5na)**

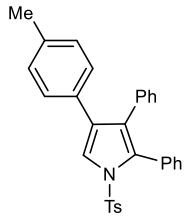



*At 80 °C:* An oven-dried microwave vial fitted with a stirrer bar was charged with propargyl amide **1n** (186 mg, 0.50 mmol), phenylboronic acid (122 mg, 1.00 mmol), $Ni(OAc)_2·4H_2O$ (24.9 mg, 0.10 mmol) and *rac*-**L2** (40.7 mg, 0.10 mmol). The vial was capped with a crimp cap PTFE seal and evacuated and back filled with argon (3 cycles). THF (5 mL) which had been freshly degassed (using stream of argon for 20 min) was added, the septum was resealed with PTFE tape, and the contents were stirred at RT for 10 min followed by 80 °C for 24 h. The reaction was cooled to room temperature and diluted with 50% brine (15 mL). The aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by column chromatography (20% EtOAc/ petroleum ether) to give pyrrole **3na** as a pale yellow solid (76.4 mg, 35%) followed by pyrroline **5na** as a yellow oil that had small traces of inseparable, unidentified impurities (85.6 mg, *ca.* 38%).

*Data* for **3na**: $R_f$ = 0.53 (40% EtOAc/petroleum ether); m.p. 201-202 °C ($Et_2O$); IR 3028, 2947, 1723 (C=O), 1596, 1338, 1230, 1118, 816, 759, 667 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.02-7.90 (2H, m, Ar**H**), 7.63 (1H, s, Ar**H**), 7.41-7.35 (2H, m, Ar**H**), 7.29-7.26 (2H, m, Ar**H**), 7.25-7.15 (4H, m, Ar**H**), 7.15-7.04 (4H, m, Ar**H**), 3.60 (3H, s, OC**H**$_3$), 2.46 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 161.5 (C), 145.4 (C), 136.1 (C), 132.9 (C), 132.8 (C), 132.7 (C), 130.1 (2 × CH), 129.8 (2 × CH), 128.6 (2 × CH), 128.4 (2 × CH), 128.2 (2 × CH), 128.0 (2 × CH), 127.7 (CH), 127.5 (C), 127.2 (CH), 123.2 (C), 123.1 (CH), 52.2 ($CH_3$), 21.9 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{25}H_{21}NO_4SNa]^+$ $[M+Na]^+$: 454.1087, found 454.1083.

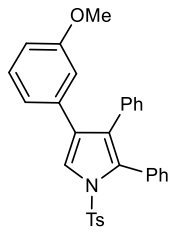
*Data* for **5na**: $R_f$ = 0.45 (40% EtOAc/petroleum ether); IR 3472 (OH), 3026, 1742, 1339, 1258, 1155, 752, 696, 667, 575 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.94-7.88 (2H, m, Ar**H**), 7.34-7.31 (2H, m, Ar**H**), 7.29-7.27 (2H, m, Ar**H**), 7.25-7.14 (6H, m, Ar**H**), 7.09-7.06 (2H, m, Ar**H**) 5.12 (1H, s, O**H**), 4.85 (1H, d, *J* = 13.5 Hz, C**H**$_2$), 4.32 (1H, d, *J* = 13.5 Hz, C**H**$_2$), 3.78 (3H, s, OC**H**$_3$), 2.42 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 171.6 (C), 143.9 (C), 136.8 (2 × C), 134.1 (C), 132.23 (C), 132.19 (C), 129.7 (2 × CH), 129.5 (2 × CH), 128.78 (CH), 128.75 (2 × CH), 128.6 (CH), 128.5 (2 × CH), 128.1 (2 × CH), 127.9 (2 × CH), 96.2 (C), 54.6 ($CH_2$), 54.2 ($CH_3$), 21.7 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{25}H_{23}NO_5SNa]^+$ $[M+Na]^+$: 472.1189, found 472.1190.

*At 120 °C:* A modification of General Procedure A (in that a 20 mol% catalyst loading was employed, the temperature was 120 °C rather than 80 °C, and THF was used as the solvent) was followed using propargyl amide **1n** (111 mg, 0.30 mmol), phenylboronic acid (73.2 mg, 0.60 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (14.9 mg, 0.06 mmol) and *rac*-**L2** (24.4 mg, 0.06 mmol) in THF (3 mL) at 120 °C. Purification by column chromatography (15% EtOAc/petroleum ether) give pyrrole **3na** as a pale yellow solid (93.7 mg, 73%).

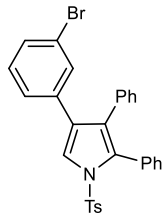



**2,3-Diphenyl-4-(4-methylphenyl)-1-tosyl-1*H*-pyrrole (3ab).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 4-methylphenylboronic acid (81.6 mg, 0.60 mmol), and purified by column chromatography (15% EtOAc/petroleum ether) to give a white solid (106 mg, 77%). $R_f$ = 0.42 (35% EtOAc/petroleum ether); m.p. 185-187 °C ($Et_2O$); IR 3066, 2920, 1368, 1186, 1169, 1099, 1075, 772, 698, 668 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, s, Ar**H**), 7.32-7.26 (3H, m, Ar**H**), 7.18-7.12 (5H, m, Ar**H**), 7.86-7.00 (8H, m, Ar**H**), 6.91-6.84 (2H, m, Ar**H**), 2.38 (3H, s, C**H**$_3$), 2.32 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.8 (C), 136.5 (C), 135.9 (C), 133.6 (C), 132.8 (2 × CH), 132.2 (C), 130.9 (C), 130.6 (2 × CH), 130.4 (C), 129.6 (2 × CH), 129.1 (2 × CH), 128.4 (2 × CH), 128.3 (CH), 127.9 (C), 127.8 (2 × CH),

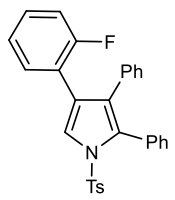
127.7 (2 × CH), 127.3 (2 × CH), 127.1 (C), 126.5 (CH), 119.8 (CH), 21.8 ($CH_3$), 21.3 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{30}H_{25}NO_2SNa]^+$ $[M+Na]^+$: 486.1498, found: 486.1493.



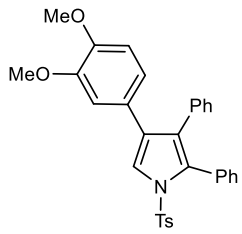

**4-(3-Methoxyphenyl)-2,3-diphenyl-1-tosyl-1*H*-pyrrole (3ac).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 3-methoxyphenylboronic acid (91.2 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (112 mg, 78%). $R_f$ = 0.42 (35% EtOAc/petroleum ether); m.p. 144-146 °C ($Et_2O$); IR 3135, 3063, 3011, 2949, 1599, 1375, 1171, 1094, 1067, 1034 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.69 (1H, s, Ar**H**), 7.34-7.26 (3H, m, Ar**H**), 7.20-7.12 (5H, m, Ar**H**), 7.09-7.01 (5H, m, Ar**H**), 6.95-6.89 (2H, m, Ar**H**), 6.85-6.81 (1H, m, Ar**H**), 6.79-6.74 (1H, m, Ar**H**), 6.70-6.65 (1H, m, Ar**H** ), 3.60 (3H, s, OC**H**$_3$), 2.39 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 159.4 (C), 144.9 (C), 135.8 (C), 135.1 (C), 133.6 (C), 132.7 (2 × CH), 132.3 (C), 130.6 (2 × CH), 130.3 (C), 129.6 (2 × CH), 129.3 (CH), 128.4 (CH), 127.9 (C), 127.8 (2 × CH), 127.7 (2 × CH), 127.3 (2 × CH), 126.9 (C), 126.6 (CH), 120.8 (CH), 120.0 (CH), 113.6 (CH), 113.1 (CH), 55.1 ($CH_3$), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{30}H_{25}NO_3SNa]^+$ $[M+Na]^+$: 502.1447, found: 502.1448.



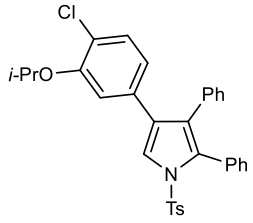

**4-(3-Bromophenyl)-2,3-diphenyl-1-tosyl-1*H*-pyrrole (3ad).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 3-bromophenylboronic acid (120.5 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (133 mg, 90%). $R_f$ = 0.42 (35% EtOAc/petroleum ether); m.p. 177-178 °C ($Et_2O$); IR 3145, 3040, 2924, 1594, 1366, 1188, 1170, 1101, 1067, 788 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.66 (1H, s, Ar**H**), 7.41 (1H, t, *J* = 1.8 Hz, Ar**H**), 7.35-7.26 (3H, m, Ar**H**), 7.25-7.23 (1H, m, Ar**H**), 7.20-7.12 (4H, m, Ar**H**), 7.11-6.97 (7H, m, Ar**H**), 6.90-6.82 (2H, m, Ar**H**), 2.38 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 145.0 (C), 136.1 (C), 135.7 (C), 133.0 (C), 132.7 (2 × CH), 132.4 (C), 131.3 (CH), 130.5 (2 × CH), 130.1 (C), 129.79 (CH), 129.76 (CH), 129.6 (2 × CH), 128.5 (CH), 127.9 (2 × CH), 127.7 (2 × CH), 127.6 (C), 127.4 (2 × CH), 127.2 (CH), 126.7 (CH), 125.5 (C), 122.4 (C), 120.2 (CH), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{29}H_{22}BrNO_2SNa]^+$ $[M+Na]^+$: 550.0447, found: 550.0441.




**4-(2-Fluorophenyl)-2,3-diphenyl-1-tosyl-1*H*-pyrrole (3ae).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 2-fluorophenylboronic acid (84.0 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (118 mg, 84%). $R_f$ = 0.42 (40% EtOAc/petroleum ether); m.p. 171-173 °C ($Et_2O$); IR 3166, 3055, 2923, 1370, 1170, 1105, 1068, 780, 752, 699 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.88 (1H, d, *J* = 1.8 Hz, Ar**H**), 7.48-7.40 (3H, m, Ar**H**), 7.37-7.25 (5H, m, Ar**H**), 7.23-7.04 (8H, m, Ar**H**), 7.01-6.90 (2H, m, Ar**H**), 2.51 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 160.15 (d, $J_{C-F}$ = 247.3 Hz, C), 144.9 (C), 135.7 (C), 133.6 (C), 132.8 (2 × CH), 131.8 (C), 131.7 (d, $J_{C-F}$ = 3.4 Hz, CH), 130.2 (C), 130.1 (2 × CH), 129.6 (2 × CH), 128.6 (d, $J_{C-F}$ = 8.1 Hz, CH), 128.4 (CH), 127.8 (2 × CH), 127.7 (2 × CH), 127.3 (2 × CH), 126.5 (CH), 123.8 (d, $J_{C-F}$ = 3.7 Hz, CH), 122.1 (d, $J_{C-F}$ = 5.4 Hz, CH), 121.6 (d, $J_{C-F}$ = 14.4 Hz, C), 120.1 (C), 115.8 (d, $J_{C-F}$ = 22.3 Hz, CH), 21.8 ($CH_3$) (one carbon signal merged with others); $^{19}F$ NMR (376 MHz, $CDCl_3$) δ –114.3 (s); HRMS (ESI) Exact mass calculated for $[C_{29}H_{22}FNO_2SNa]^+$ $[M+Na]^+$: 490.1247, found: 490.1236.

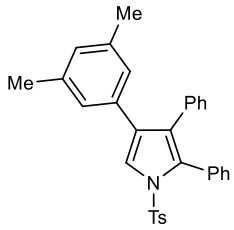



**4-(3,4-Dimethoxyphenyl)-2,3-diphenyl-1-tosyl-1*H*-pyrrole (3af).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 3,4-dimethoxyphenylboronic acid (109.2 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (103 mg, 67%). $R_f$ = 0.60 (35% EtOAc/petroleum ether); m.p. 152-154 °C ($Et_2O$); IR 3122, 3053, 2998, 2928, 2834, 1505, 1374, 1168, 1108, 762 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.65 (1H, s, Ar**H**), 7.35-7.28 (3H, m, Ar**H**), 7.20-7.14 (4H, m, Ar**H**), 7.09-7.02 (5H, m, Ar**H**), 6.96-6.91 (2H, m, Ar**H**), 6.89-6.84 (1H, m, Ar**H**), 6.83-6.78 (1H, m, Ar**H**), 6.56 (1H, d, *J* = 2.0 Hz, Ar**H**), 3.88 (3H, s, OC**H**$_3$), 3.55 (3H, s, OC**H**$_3$), 2.40 (3H, s, ArC**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 148.5 (C), 147.9 (C), 144.8 (C), 135.8 (C), 133.7 (C), 132.7 (2 × CH), 132.2 (C), 130.7 (2 × CH), 130.3 (C), 129.5 (2 × CH), 128.3 (CH), 127.9 (C), 127.8 (2 × CH), 127.6 (2 × CH), 127.3 (2 × CH), 126.7 (C), 126.5 (CH), 126.4 (C), 120.4 (CH), 119.2 (CH), 112.0 (CH), 111.1 (CH), 55.9 ($CH_3$), 55.5 ($CH_3$), 21.7 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{31}H_{27}NO_4SNa]^+$ $[M+Na]^+$: 532.1553, found: 532.1545.



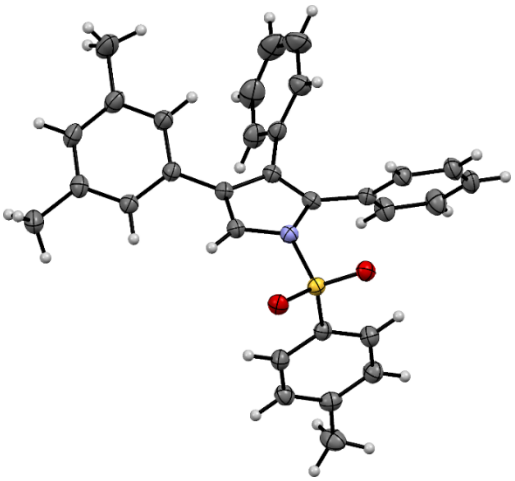

**4-(4-Chloro-3-isopropoxyphenyl)-2,3-diphenyl-1-tosyl-1*H*-pyrrole (3ag).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 3-chloro-4-isopropoxyphenylboronic acid (128.7 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a brown oil (117 mg, 72%).

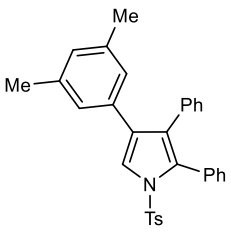
$R_f$ = 0.42 (40% EtOAc/petroleum ether); IR 3060, 2978, 2929, 1490, 1369, 1170, 1102, 907, 728, 696 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, s, Ar**H**), 7.35-7.25 (4H, m, Ar**H**), 7.21-7.12 (4H, m, Ar**H**), 7.05 (5H, m, Ar**H**), 6.94-6.85 (3H, m, Ar**H**), 6.82-6.75 (1H, m, Ar**H**), 4.52 (1H, sept, *J* = 6.1 Hz, $(CH_3)_2C\mathbf{H}$), 2.39 (3H, s, $ArC\mathbf{H}_3$), 1.37 (6H, d, *J* = 6.1 Hz, $(C\mathbf{H}_3)_2CH$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 152.6 (C), 144.9 (C), 135.7 (C), 133.2 (C), 132.7 (2 × CH), 132.3 (C), 130.5 (2 × CH), 130.2 (CH), 129.6 (2 × CH), 128.4 (CH), 127.9 (2 × CH), 127.8 (CH), 127.67 (C), 127.65 (2 × CH), 127.34 (C), 127.30 (2 × CH), 126.6 (CH), 125.6 (C), 123.9 (C), 119.6 (CH), 115.6 (CH), 72.1 (CH), 22.2 (2 × $CH_3$), 21.8 ($CH_3$) (one carbon signal merged with others); HRMS (ESI) Exact mass calculated for $[C_{32}H_{28}ClNO_3SNa]^+$ $[M+Na]^+$: 564.1371, found: 564.1376.




**4-(3,5-Dimethylphenyl)-2,3-diphenyl-1-tosyl-1*H*-pyrrole (3ah).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 3,5-dimethylphenylboronic acid (90.0 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (90.9 mg, 63%). $R_f$ = 0.60 (40% EtOAc/petroleum ether); m.p. 148-150 °C ($Et_2O$); IR 3140, 3053, 2919, 1596, 1369, 1189, 1169, 1096, 769, 690 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) 7.64 (1H, s, Ar**H**), 7.32-7.28 (2H, m, Ar**H**), 7.28-7.24 (1H, m, Ar**H**), 7.20-7.11 (4H, m, Ar**H**), 7.07-7.00 (5H, m, Ar**H**), 6.92-6.84 (3H, m, Ar**H**), 6.79 (2H, s, Ar**H**), 2.38 (3H, s, $C\mathbf{H}_3$), 2.20 (6H, s, 2 × $C\mathbf{H}_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.8 (C), 137.7 (2 × C), 135.9 (C), 133.6 (C), 132.8 (2 × CH), 132.1 (C), 130.6 (2 × CH), 130.4 (C), 129.6 (2 × CH), 128.5 (CH), 128.3 (CH), 128.0 (C), 127.7 (2 × CH), 127.6 (2 × CH), 127.3 (2 × CH), 127.2 (C), 126.43 (CH), 126.40 (2 × CH), 120.0 (CH), 21.8 ($CH_3$), 21.4 (2 × $CH_3$) (one carbon signal merged with others); HRMS (ESI) Exact mass calculated for $[C_{31}H_{27}NO_2SNa]^+$ $[M+Na]^+$: 500.1655, found: 500.1647.

Slow evaporation of a solution of **3ah** in $CDCl_3$ gave crystals that were suitable for X-ray crystallography:





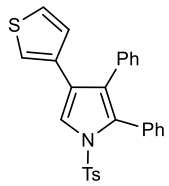

**3ah**
CCDC 1861043

**4-(Naphthalen-2-yl)-2,3-diphenyl-1-tosyl-1*H*-pyrrole (3ai).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 2-naphthylboronic acid (103.0 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (104 mg, 70%). $R_f$ = 0.42 (40% EtOAc/petroleum ether); m.p. 203-205 °C ($Et_2O$); IR 3145, 3063, 2919, 1596, 1369, 1188, 1170, 1099, 1070, 770 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (2H, m, Ar**H**), 7.73-7.65 (3H, m, Ar**H**), 7.46-7.41 (2H, m, Ar**H**), 7.36-7.27 (3H, m, Ar**H**), 7.25-7.12 (5H, m, Ar**H**), 7.10-6.99 (5H, m, Ar**H**), 6.95-6.87 (2H, m, Ar**H**), 2.39 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.9 (C), 135.8 (C), 133.6 (C), 133.5(C), 132.8 (2 × CH), 132.4 (C), 131.4 (C), 130.6 (2 × CH), 130.3 (C), 129.6 (2 × CH), 128.4 (CH), 128.0 (CH), 127.91 (C), 127.85 (2 × CH), 127.8 (CH), 127.73 (2 × CH), 127.70 (CH), 127.3 (2 × CH), 127.1 (CH), 127.0 (CH), 126.6 (CH), 126.1 (CH), 125.8 (CH), 120.3 (CH), 21.8 ($CH_3$) (two carbon signal merged with others); HRMS (ESI) Exact mass calculated for $[C_{33}H_{25}NO_2SNa]^+$ $[M+Na]^+$: 522.1498, found: 522.1502.

**5-(4,5-Diphenyl-1-tosyl-1*H*-pyrrole-3-yl)-1*H*-indole (3aj).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 5-indolylboronic acid (96.6 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a pale green solid (107 mg, 73%). $R_f$ = 0.19 (30% EtOAc/petroleum ether); m.p. 213-214 °C ($Et_2O$); IR 3409 (NH), 1596, 1365, 1188, 1168, 1098, 1087, 1066, 701, 668 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.10 (1H, br s, NH), 7.64 (1H, s, Ar**H**), 7.53-7.50 (1H, m, Ar**H**), 7.35-7.27 (3H, m, Ar**H**), 7.24-7.21 (1H, m, Ar**H**), 7.19-7.12 (5H, m, Ar**H**), 7.06-6.98 (5H, m, Ar**H**), 6.94 (1H, dd, *J* = 8.4, 1.7 Hz, Ar**H**), 6.90-6.86 (2H, m, Ar**H**), 6.50-6.46 (1H, m, Ar**H**) 2.38 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.7 (C), 136.0 (C), 135.0 (C), 133.8 (C), 132.8 (2 × CH), 132.1 (C), 130.7 (2 × CH), 129.6 (2 × CH), 128.5 (C), 128.2 (CH), 128.24 (C), 128.18 (C), 127.7 (2 × CH), 127.6 (2 × CH), 127.3 (2 × CH), 126.3 (CH), 125.6 (C), 124.6 (CH), 123.5 (CH), 120.7 (CH), 119.8 (CH), 110.8 (CH), 103.0 (CH), 21.8 ($CH_3$) (one carbon signal merged with another); HRMS (ESI) Exact mass calculated for $[C_{31}H_{24}N_2O_2SNa]^+$ $[M+Na]^+$: 511.1451, found: 511.1446.

**4-(Furan-3-yl)-2,3-diphenyl-1-tosyl-1*H*-pyrrole (3ak).** The title compound was prepared according to General Procedure C, using propargyl amide **1a** (117 mg, 0.30 mmol) and 3-furanylboronic acid (67.1 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (73.0 mg, 55%). $R_f$ = 0.61 (35% EtOAc/petroleum ether); m.p. 202-203 °C ($Et_2O$); IR 3149, 2923, 1364,

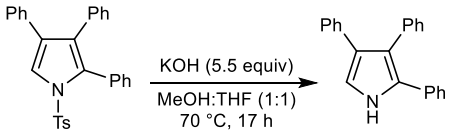
1171, 1097, 1060, 760, 695, 666, 589 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, s, Ar**H**), 7.32 (1H, t, *J* = 1.7 Hz, Ar**H**), 7.30-7.26 (2H, m, Ar**H**), 7.25-7.21 (1H, m, ArH), 7.17-7.10 (7H, m, Ar**H**), 7.04-6.98 (4H, m, Ar**H**), 6.95 (1H, t, *J* = 1.2 Hz, Ar**H**), 6.35 (1H, dd, *J* = 1.9, 0.9 Hz, Ar**H**), 2.38 (3H, s, C**H**$_3$);$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.9 (C), 142.7 (CH), 139.3 (CH), 135.8 (C), 133.8 (C), 132.6 (C), 132.5 (2 × CH), 130.6 (2 × CH), 130.1 (C), 129.6 (2 × CH), 128.3 (CH), 128.04 (C), 128.00 (2 × CH), 127.6 (2 × CH), 127.3 (2 × CH), 127.1 (CH), 119.0 (CH), 118.6 (C), 118.3 (C), 109.9 (CH), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{27}H_{21}NO_3SNa]^+$ $[M+Na]^+$: 462.1134, found: 462.1126.




**2,3-Diphenyl-4-(3-thienyl)-1-tosyl-1*H*-pyrrole (3al).** The title compound was prepared according to General Procedure A, using propargyl amide **1a** (117 mg, 0.30 mmol) and 3-thienylboronic acid (76.8 mg, 0.60 mmol), and purified by column chromatography (5% to 15% EtOAc/petroleum ether) to give a white solid (123 mg, 90%). $R_f$ = 0.42 (40% EtOAc/petroleum ether); m.p. 193-195 °C ($Et_2O$); IR 3134, 3062, 2924, 1366, 1189, 1168, 1088, 1074, 1030, 764 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.79 (1H, s, Ar**H**), 7.42-7.28 (5H, m, Ar**H**), 7.25-7.19 (6H, m, Ar**H**), 7.12-7.04 (5H, m, Ar**H**), 6.91 (1H, dd, *J* = 2.9, 1.4 Hz, Ar**H**), 2.47 (3H, s, C**H**$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.9 (C), 135.8 (C), 134.0 (C), 133.8 (C), 132.6 (2 × CH), 132.4 (C), 130.6 (2 × CH), 130.1 (C), 129.6 (2 × CH), 128.3 (CH), 128.0 (C), 127.9 (2 × CH), 127.6 (2 × CH), 127.5 (CH), 127.2 (2 × CH), 126.9 (CH), 125.2 (CH), 122.2 (C), 121.2 (CH), 119.5 (CH), 21.8 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{27}H_{21}NO_2S_2Na]^+$ $[M+Na]^+$: 478.0906, found: 478.012.

## 5. Further Transformations

### 2,3,4-Triphenyl-1*H*-pyrrole (6)[11,12]



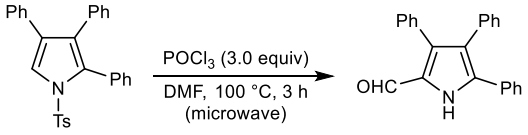

**3aa** **6**

A mixture of pyrrole **3aa** (150 mg, 0.33 mmol) and KOH (103 mg, 1.84 mmol) in THF:MeOH (1:1, 15.6 mL) was stirred at 70 °C for 17 h. The mixture was cooled to room temperature and quenched with water (10 mL) followed by addition of 1 M aqueous HCl solution (1.8 mL). The resulting mixture was extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo* to leave the title compound as a purple solid (100 mg, >99%) that required no further purification. $R_f$ = 0.46 (20% EtOAc/petroleum ether);

IR 3422, 3408, 2922, 2853, 1601, 1483, 1069, 766, 749, 692 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.32 (1H, br s, N**H**), 7.33-7.21 (15H, m, Ar**H**), 7.05 (1H, d, *J* = 2.8 Hz, Ar**H**); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 135.7 (2 × C), 133.1 (C), 131.1 (2 × CH), 129.7 (C), 128.6 (2 × CH), 128.5 (2 × CH), 128.3 (2 × CH), 128.2 (2 × CH), 127.3 (2 × CH), 126.7 (CH), 126.2 (CH), 126.0 (C), 125.7 (CH), 120.7 (C), 117 (CH); HRMS (ESI) Exact mass calculated for $[C_{22}H_{18}N]^+$ $[M+H]^+$: 296.1434, found 296.1433.

These data are consistent with those reported previously.[12]

**3,4,5-Triphenyl-1*H*-pyrrole-2-carbaldehyde (8)**[12]

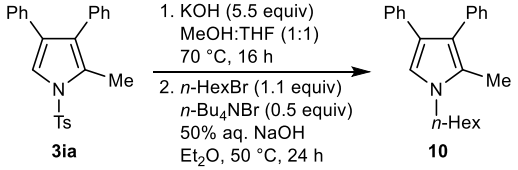



**3aa** **8**

To an oven-dried microwave vial fitted with a stirrer bar was added pyrrole **3aa** (67.4 mg, 0.15 mmol). The vial was capped with a crimp cap PTFE seal and evacuated and back filled with argon (3 cycles). DMF (0.5 mL) which had been freshly degassed (using a stream of argon for 20 min) was added. To a second vial was added DMF (1.3 mL) and the vial was cooled to 0 °C. $POCl_3$ (40 μL, 0.450 mmol) was added dropwise and the solution was stirred at 0 °C for 45 min. The resulting solution of the Vilsmeier reagent was added to the first vial *via* syringe, and the mixture was heated at 100 °C in a microwave reactor for 3 h. The reaction was cooled to room temperature, and diluted with saturated aqueous NaOAc solution (15 mL). The mixture was cooled in an ice bath, diluted with distilled water (10 mL), and the solids was collected by filtration. To the solids was added brine (50%, 7 mL) and the suspension was extracted with $CHCl_3$ (3 × 7 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was dissolved in EtOAc, and the solution was filtered through a plug of silica gel and concentrated *in vacuo* to leave the title compound as a brown solid (46 mg, 95%). $R_f$ = 0.42 (40% EtOAC/petroleum ether); IR 3273, 1624 (C=O), 1599, 1431, 1382, 1237, 823, 716, 688, 538 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.57 (1H, br s, N**H**), 9.51 (1H, s, C**H**O), 7.32-7.28 (8H, m, Ar**H**), 7.24-7.18 (5H, m, Ar**H**), 7.07-7.03 (2H, m, Ar**H**); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 180.1 (C), 136.4 (C), 136.1 (C), 133.6 (C), 132.3 (C), 131.1 (C), 131.0 (2 × CH), 130.8 (2 × CH), 129.3 (C), 128.9 (2 × CH), 128.6 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 128.0 (2 × CH), 127.6 (CH), 126.9 (CH), 124.1 (C); HRMS (ESI) Exact mass calculated for $[C_{23}H_{17}NONa]^+$ $[M+Na]^+$: 346.1202, found 346.1194.

This compound has been described previously but in that work, the $^1H$ NMR spectrum was obtained in $CD_2Cl_2$ as the solvent.[12] Our $^{13}C$ NMR data are consistent with those reported previously.[12]

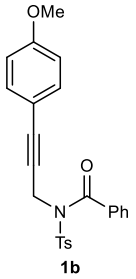
**1-Hexyl-2-methyl-3,4-diphenyl-1*H*-pyrrole (10)**[13]



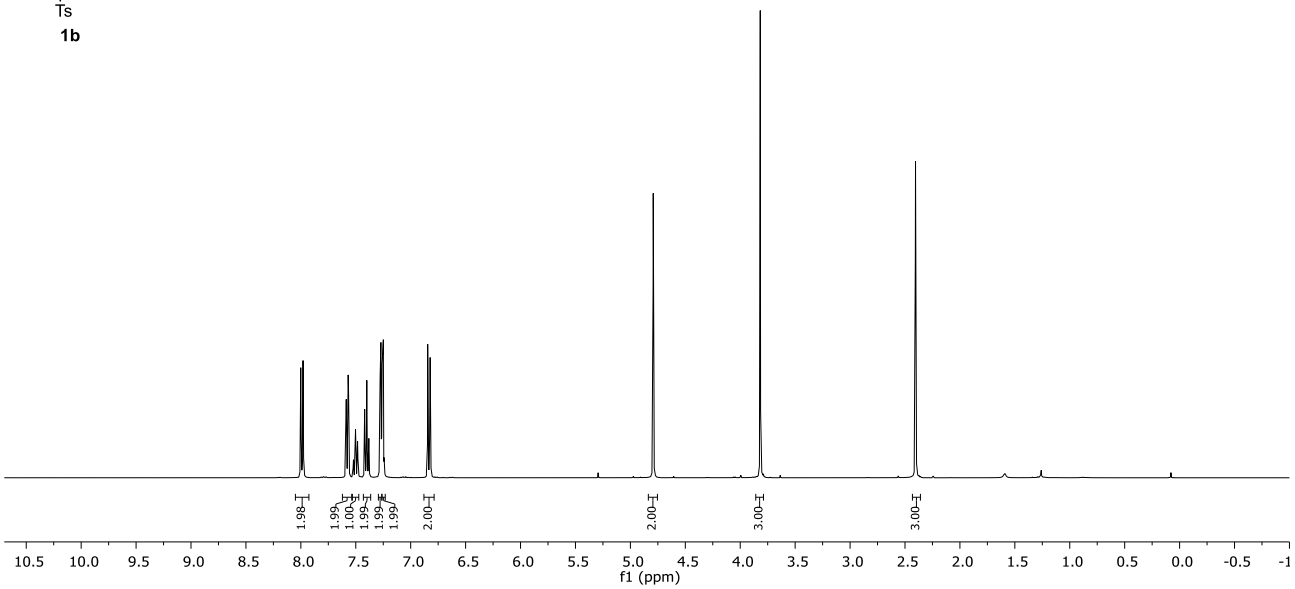

A mixture of pyrrole **3ia** (332 mg, 0.83 mmol) and KOH (256 mg, 4.57 mmol) in THF:MeOH (1:1, 33 mL) was stirred at 70 °C for 16 h. The mixture was cooled to room temperature and quenched with water (20 mL), followed by addition of 1 M aqueous HCl solution (4.6 mL). The resulting mixture was extracted with $Et_2O$ (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The crude material (168 mg) was dissolved in $Et_2O$ (4.2 mL), and *n*-$Bu_4NBr$ (134 mg, 0.42 mmol), 1-hexyl bromide (151 mg, 0.90 mmol), and 50% aqueous NaOH solution (2.1 mL) was added. The mixture was stirred at 50 °C for 24 h, cooled to room temperature, and diluted with water (20 mL). The mixture was extracted with $Et_2O$ (3 × 20 mL), and the combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The residue was purified by column chromatography on neutral alumina (0 to 1% EtOAc/*n*-pentane) to give the title compound as a colorless oil (148 mg, 56%). $R_f$ = 0.62 (20% EtOAc/petroleum ether); IR 2927, 2856, 1601, 1537, 1390, 1204, 1181, 764, 738, 697 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (2H, m, Ar**H**), 7.25-7.10 (8H, m, Ar**H**), 6.80 (1H, s, Ar**H**), 3.90-3.86 (2H, m, NC**H**$_2$), 2.26 (3H, s, ArC**H**$_3$), 1.87-1.79 (2H, m, $NCH_2C\mathbf{H}_2$), 1.47-1.33 (6H, m, $(C\mathbf{H}_2)_3CH_3$), 0.97-0.92 (3H, m, $CH_2C\mathbf{H}_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 136.7 (C), 136.2 (C), 130.7 (2 × CH), 128.11 (2 x CH), 128.08 (2 × CH), 128.06 (2 × CH), 126.6 (C), 125.6 (CH), 125.1 (CH), 122.8 (C), 120.4 (C), 118.2 (CH), 47.2 ($CH_2$), 31.6 ($CH_2$), 31.4 ($CH_2$), 26.7 ($CH_2$), 22.7 ($CH_2$), 14.2 ($CH_3$), 10.6 ($CH_3$); HRMS (ESI) Exact mass calculated for $[C_{23}H_{27}NNa]^+$ $[M+Na]^+$: 318.2216, found 318.2209.

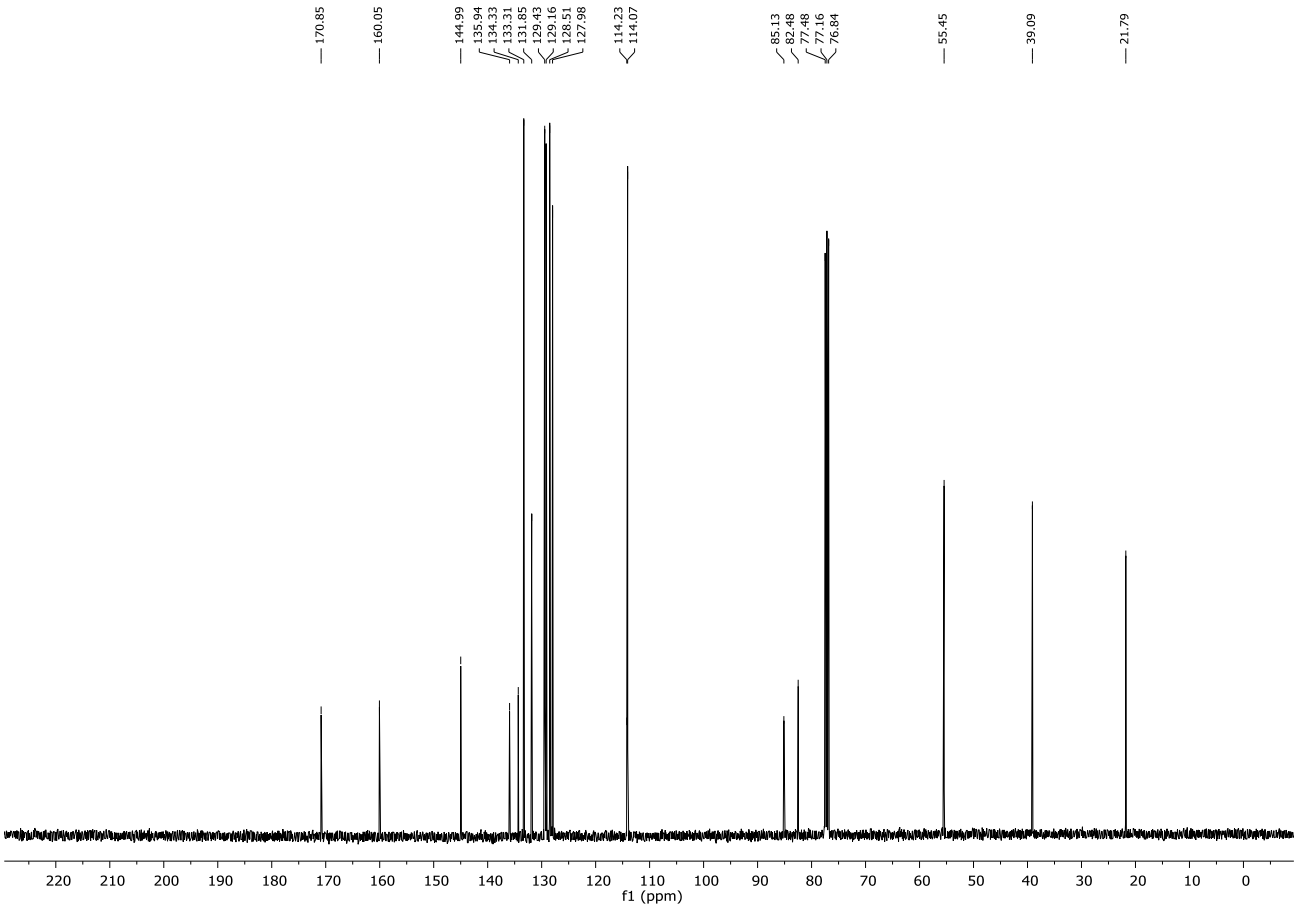
This compound has been described previously but no characterization data were reported.[13]

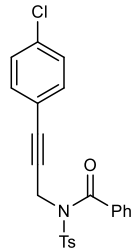
## 6. NMR Spectra



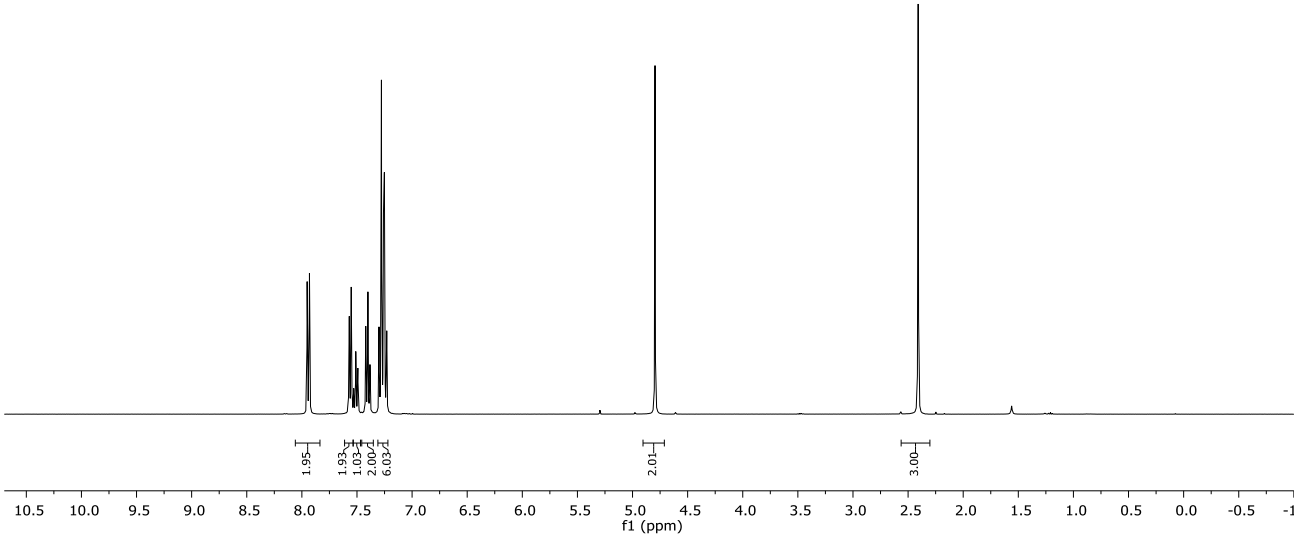

**1b**




Cl
O
N
Ph
Ts

**1c**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1.03
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2.01
3.00
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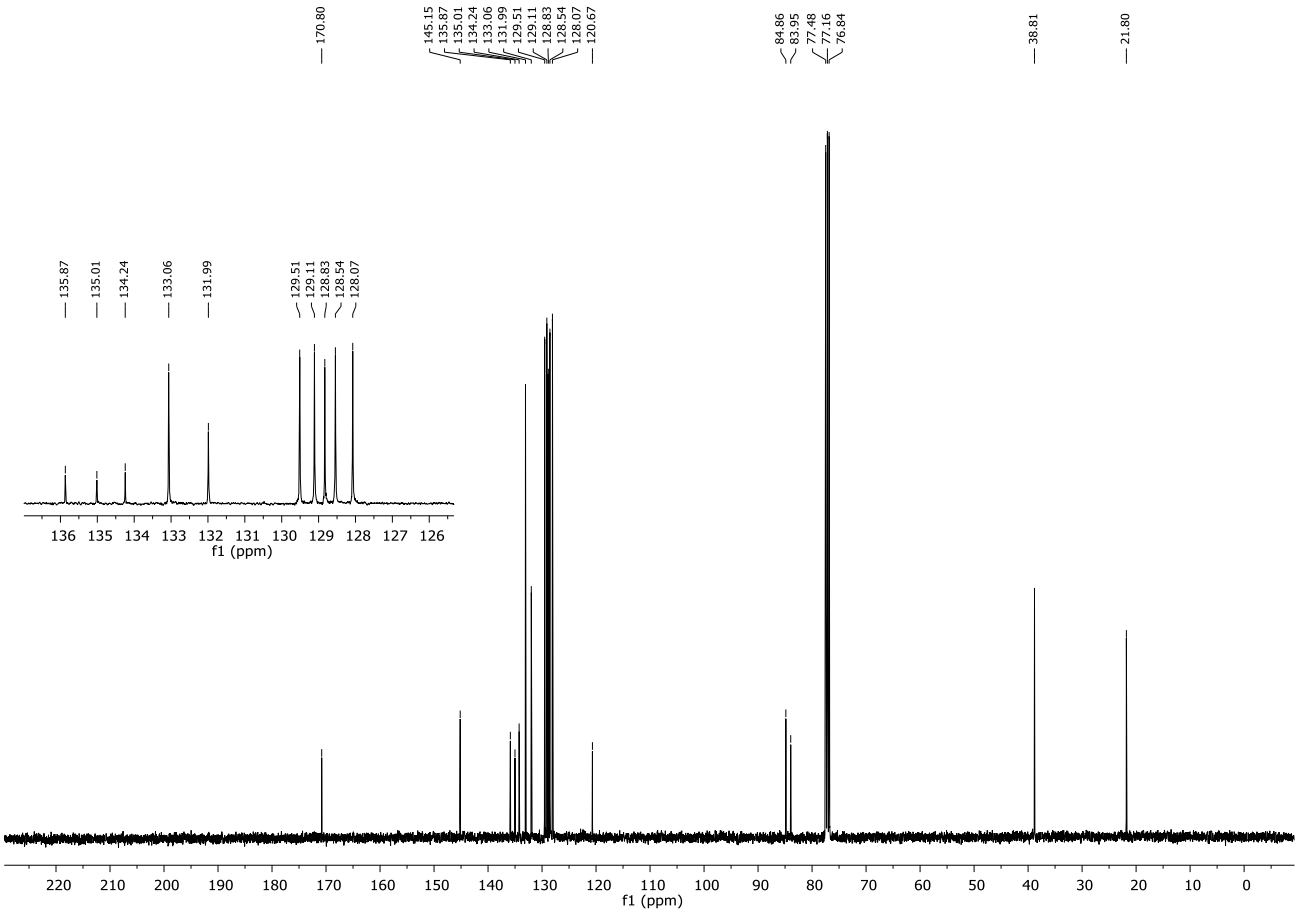
f1 (ppm)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134.24
133.06
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129.11
128.83
128.54
128.07
120.67
84.86
83.95
77.48
77.16
76.84
38.81
21.80
135.87
135.01
134.24
133.06
131.99
129.51
129.11
128.83
128.54
128.07
136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)
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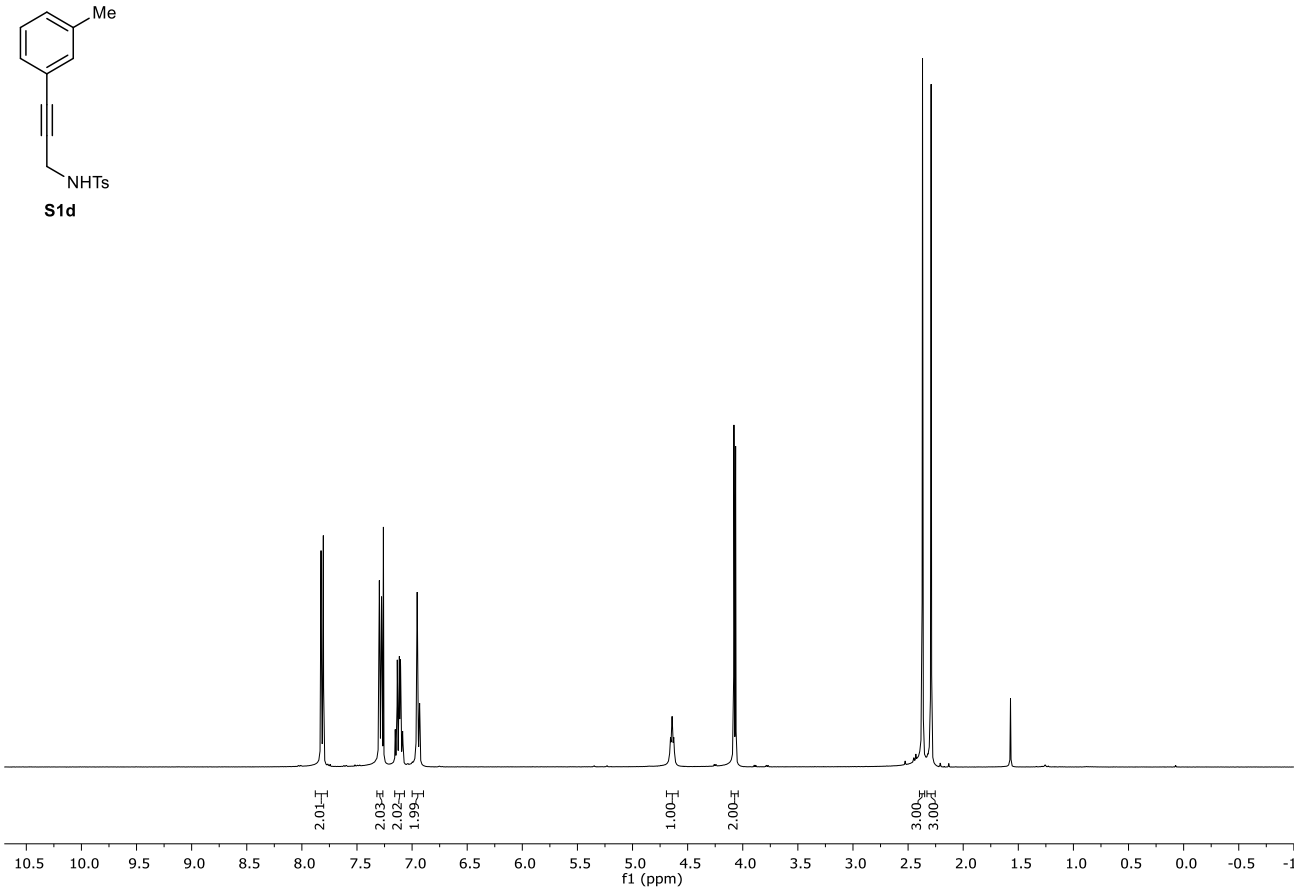
f1 (ppm)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NHTs
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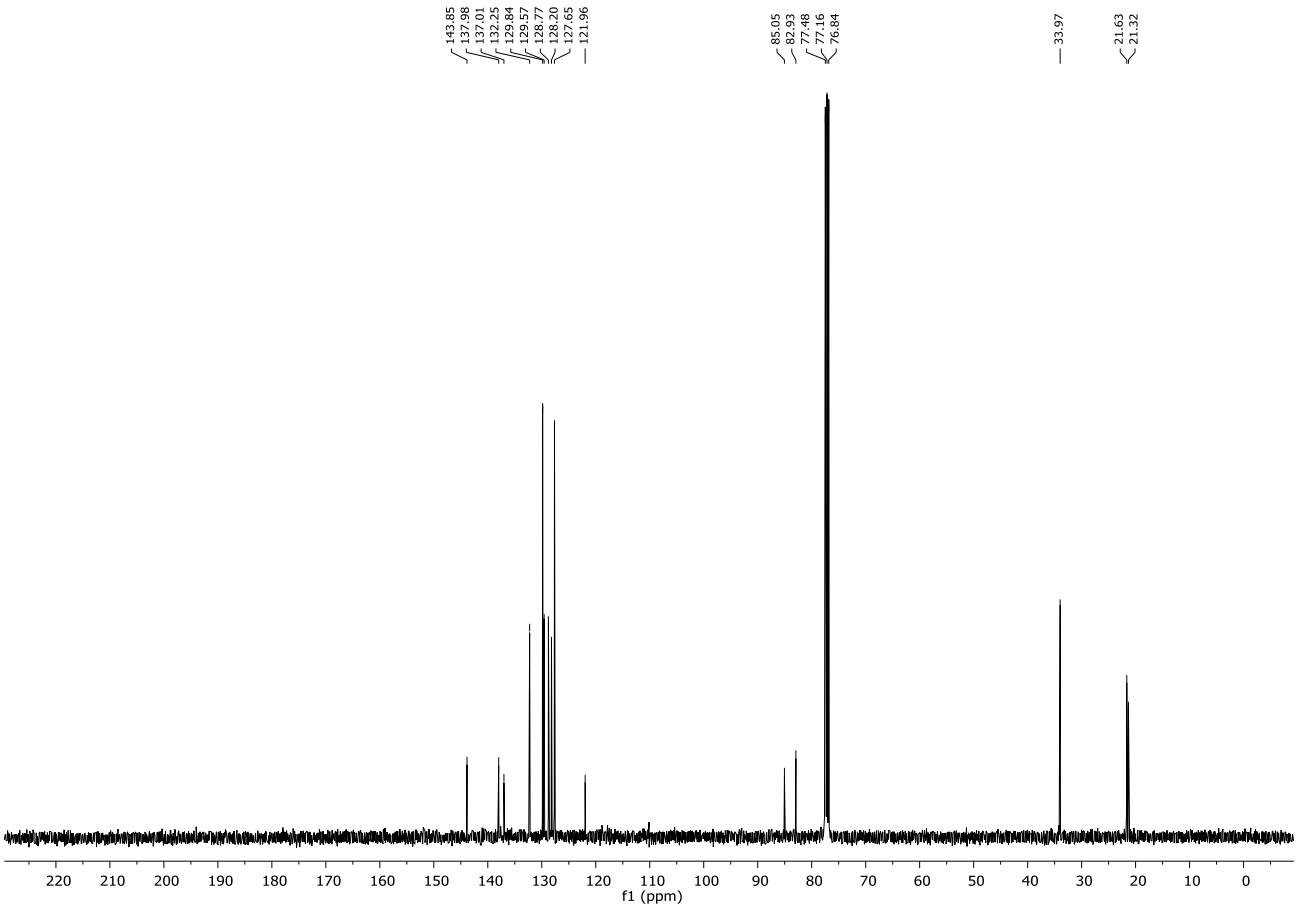
1.00
2.00
3.00
3.00
f1 (ppm)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129.57
128.77
128.20
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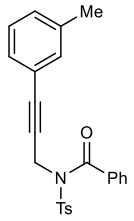
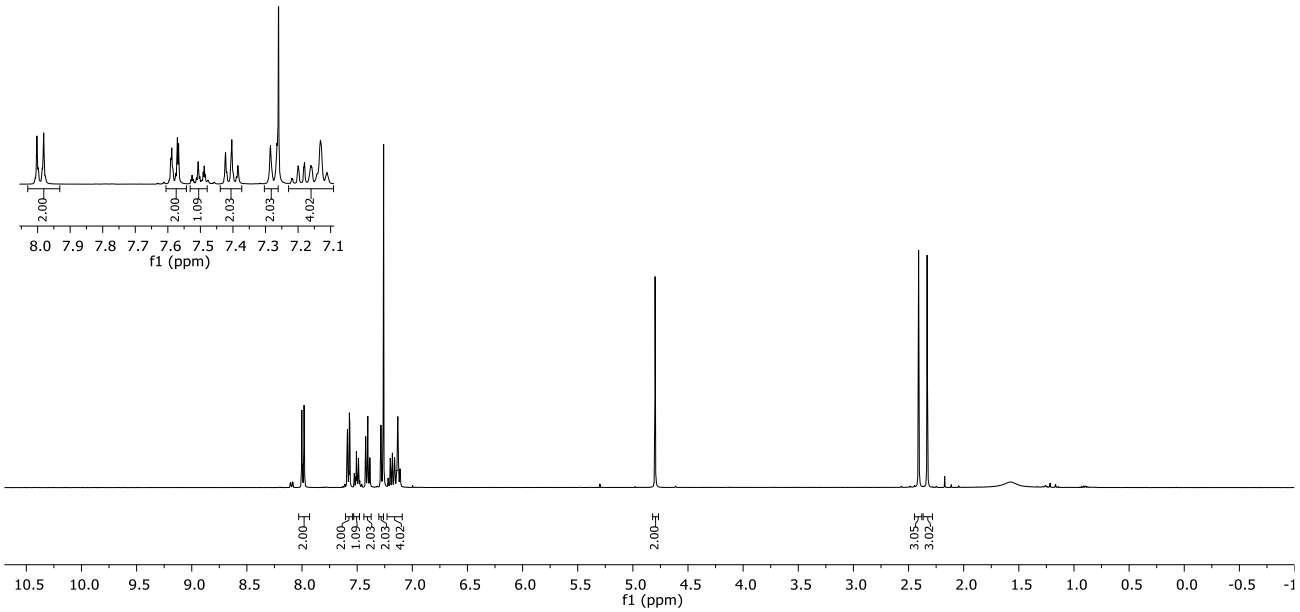
76.84
33.97
21.63
21.32
f1 (ppm)


Me
O
N
Ph
Ts

**1d**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2.03
4.02
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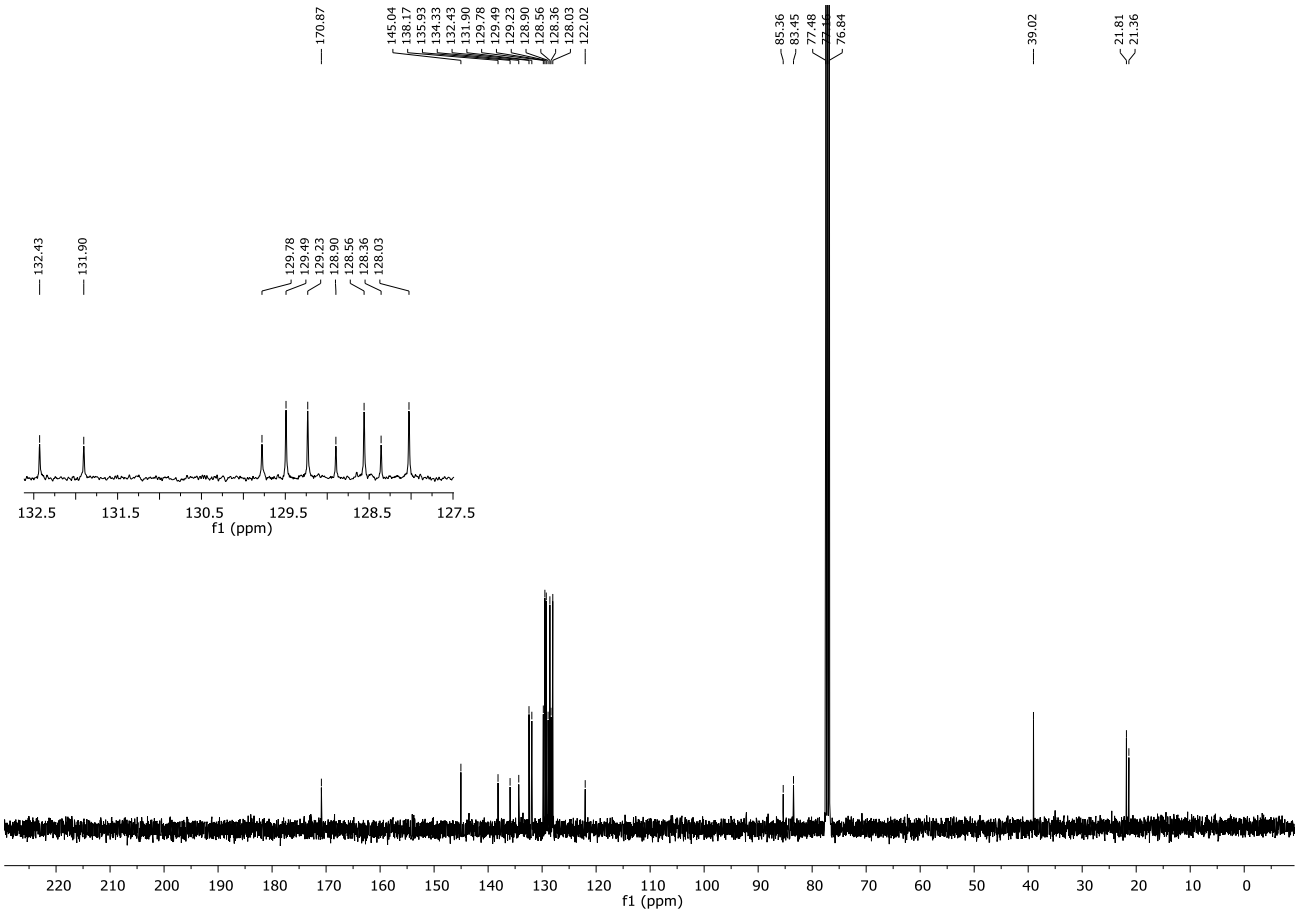
f1 (ppm)
2.00
2.00
1.09
2.03
2.03
4.02
2.00
3.05
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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128.36
128.03
122.02
85.36
83.45
77.48
76.84
39.02
21.81
21.36
132.43
131.90
129.78
129.49
129.23
128.90
128.56
128.36
128.03
132.5 131.5 130.5 129.5 128.5 127.5
f1 (ppm)
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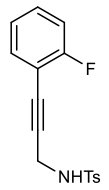
f1 (ppm)


F
NHTs

**S1e**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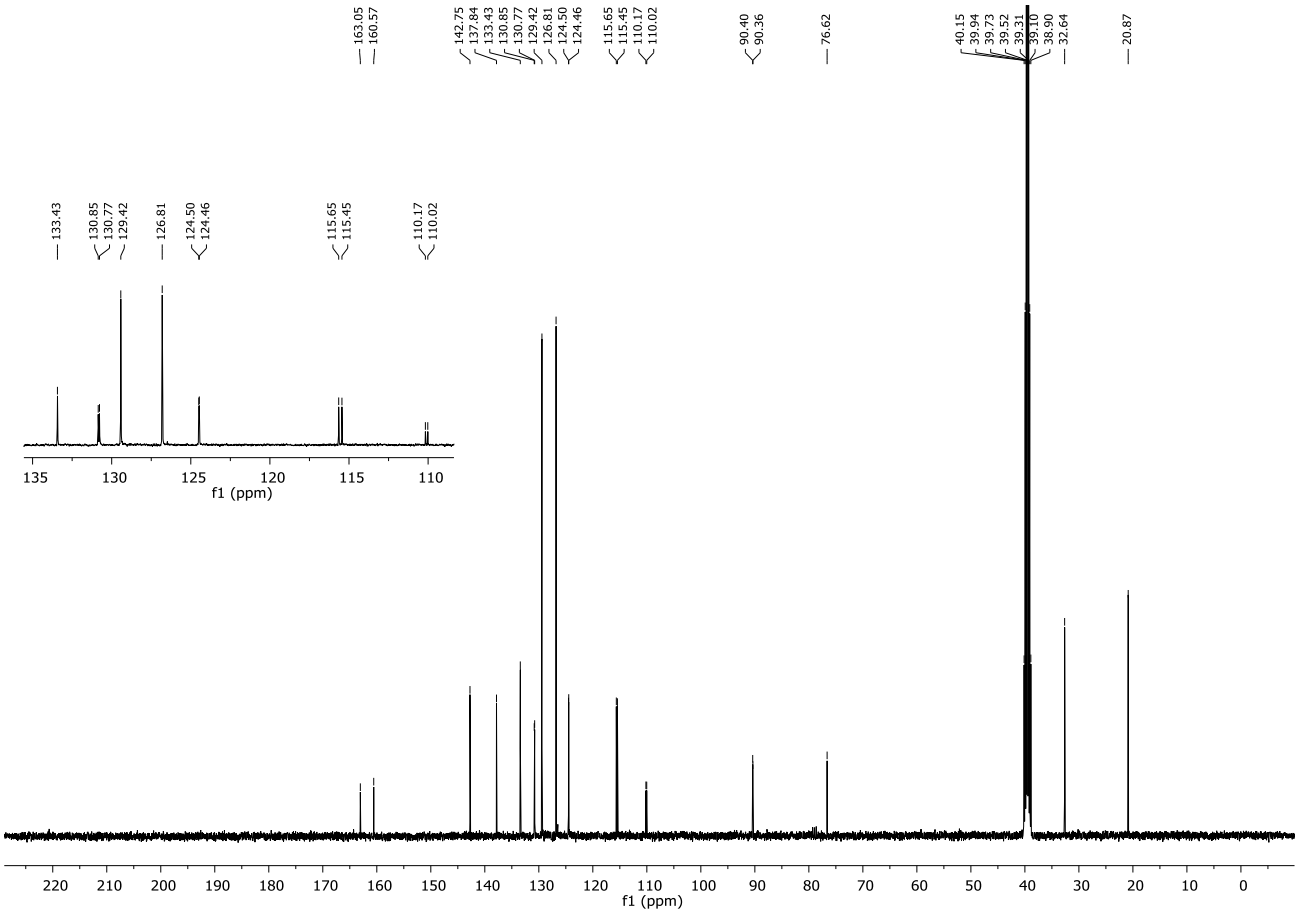
1.08
2.06
3.04
2.02
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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129.42
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124.50
124.46
115.65
115.45
110.17
110.02
90.40
90.36
76.62
40.15
39.94
39.73
39.52
39.31
39.10
38.90
32.64
20.87
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


133.43
130.85
130.77
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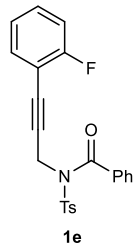
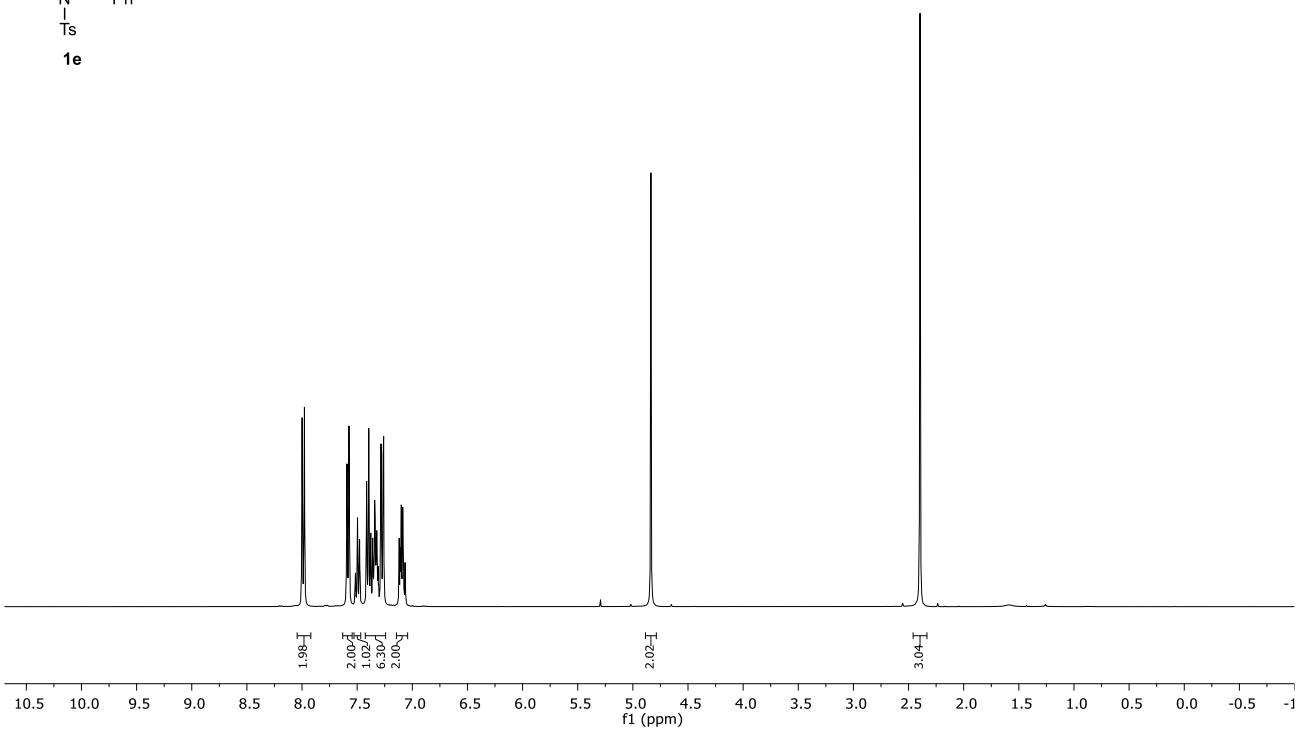
126.81
124.50
124.46
115.65
115.45
110.17
110.02
135 130 125 120 115 110
f1 (ppm)


F
O
N
Ph
Ts

**1e**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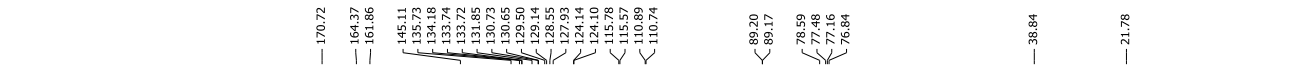
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133.72
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130.73
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129.14
128.55
127.93
124.14
124.10
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89.17
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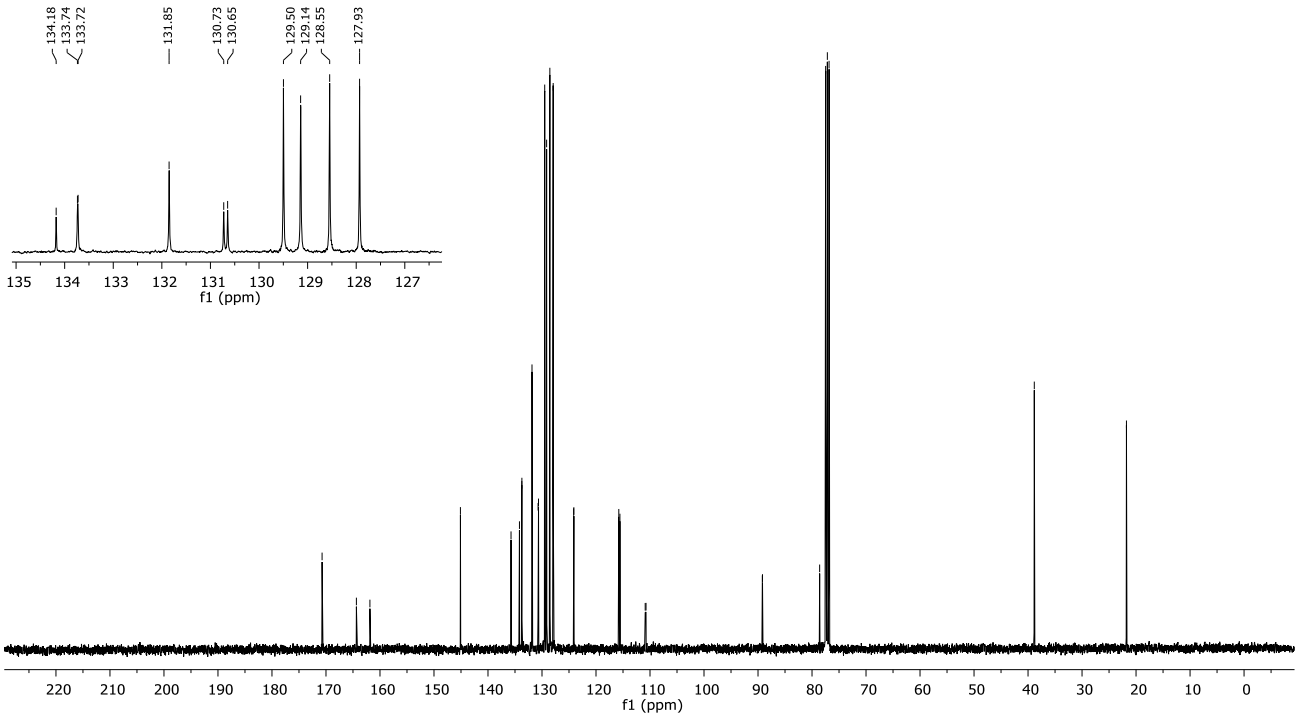
76.84
38.84
21.78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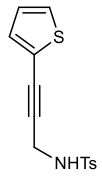
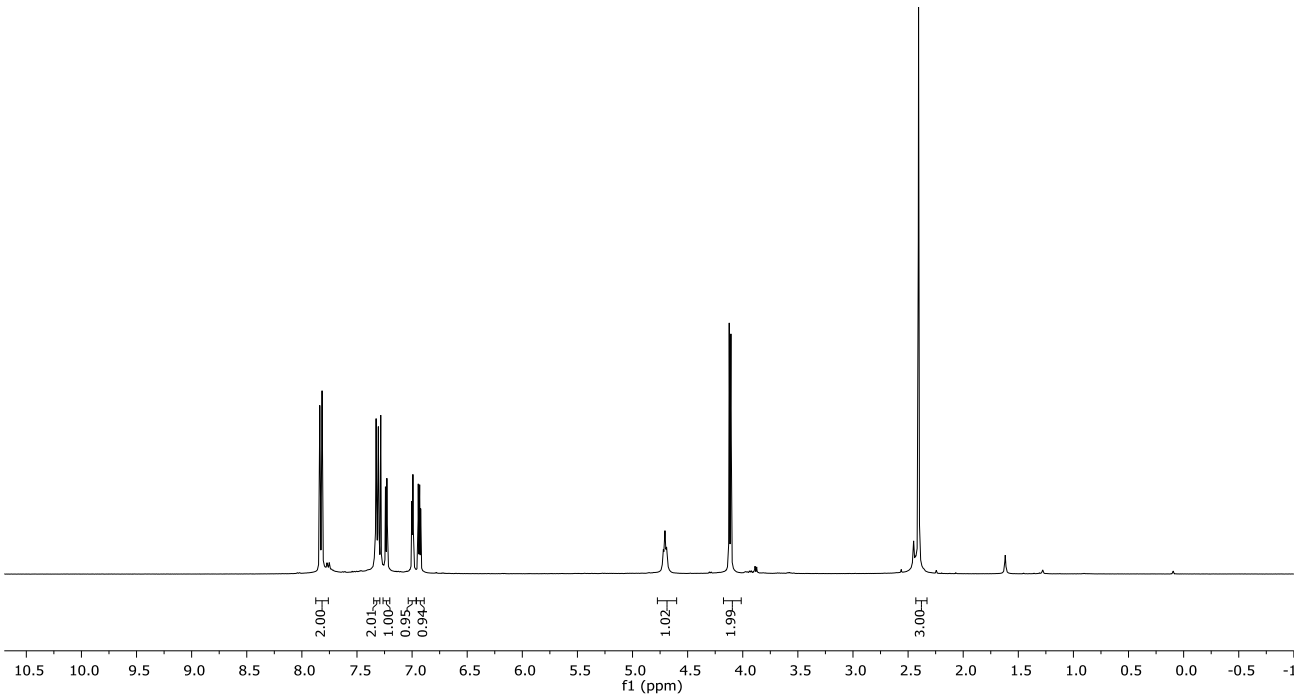
f1 (ppm)


S
NHTs

**S1f**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3.00
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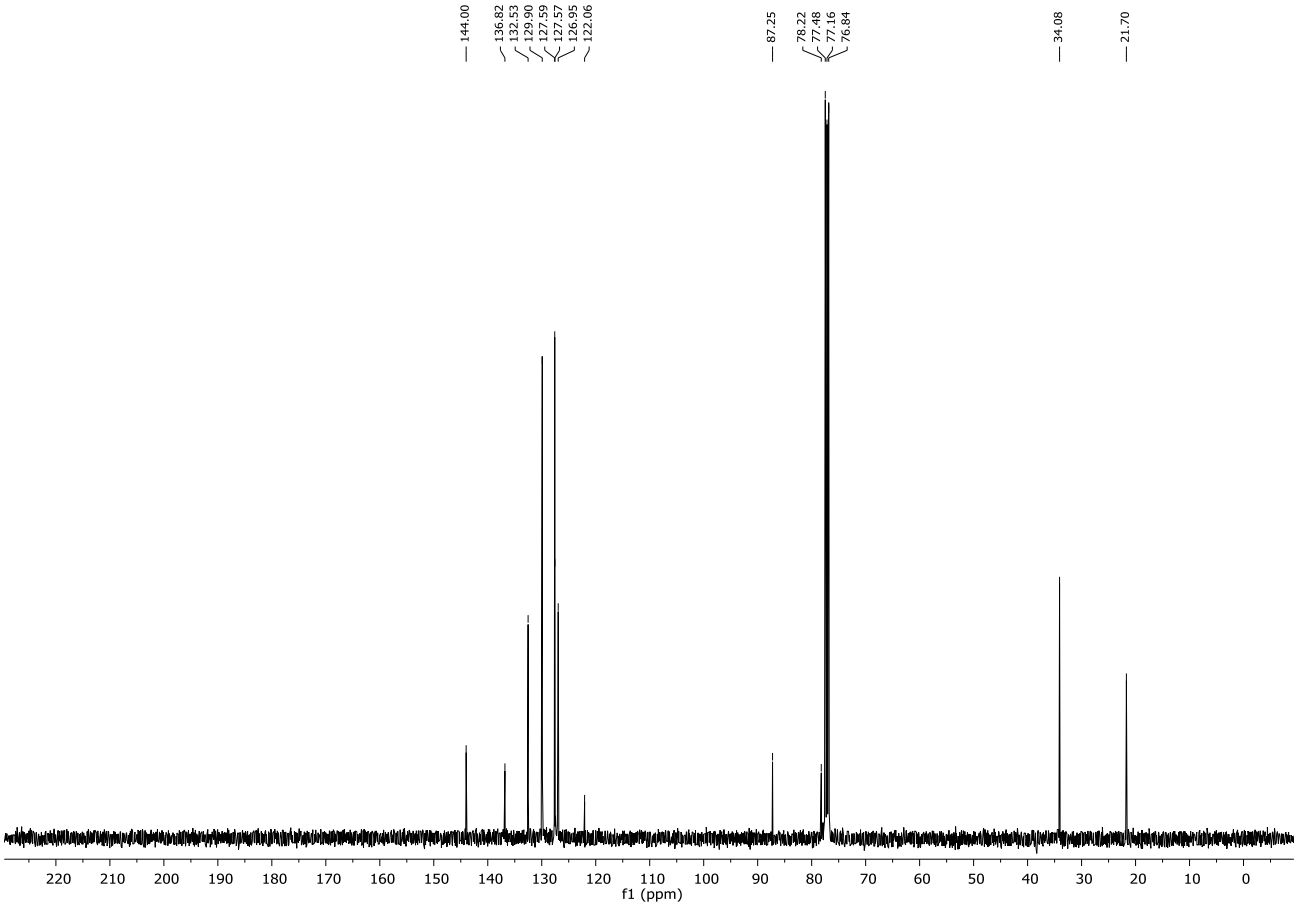
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21.70
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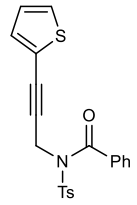
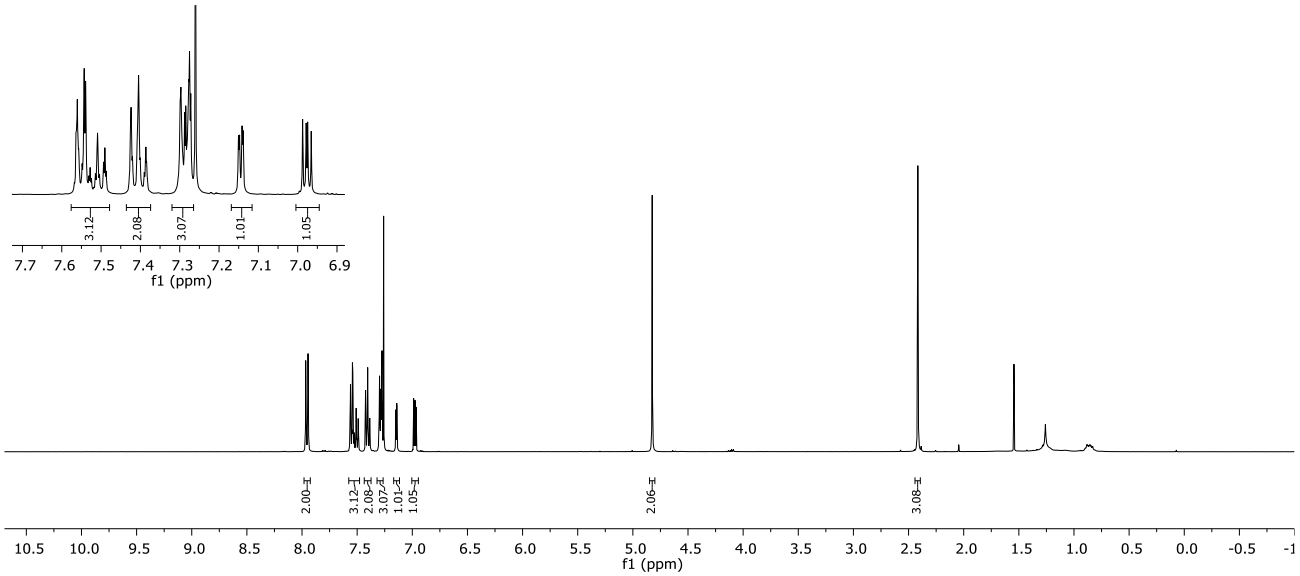
f1 (ppm)


S
O
N
Ph
Ts

**1f**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1.05
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
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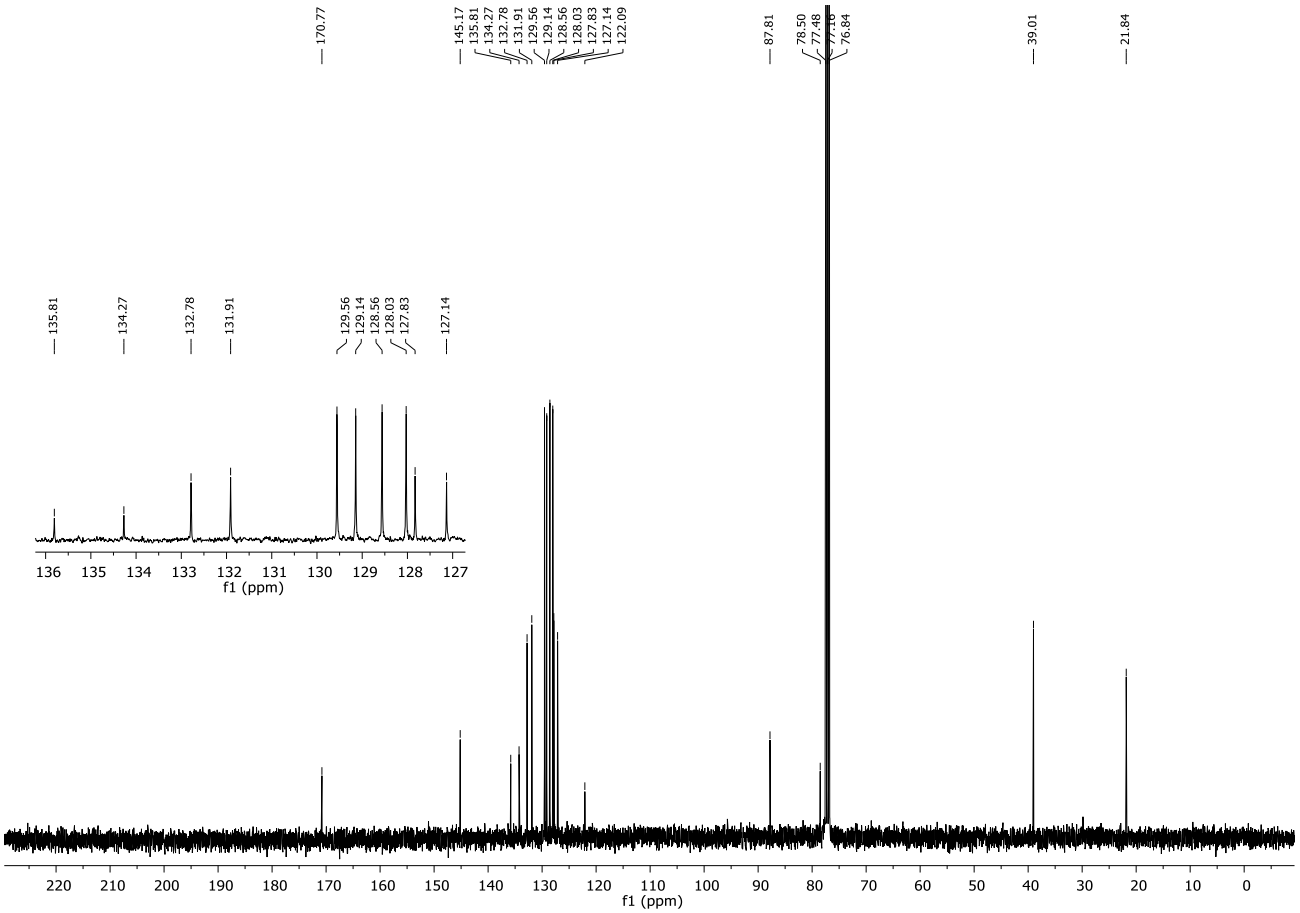
3.12
2.08
3.07
1.01
1.05
2.06
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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78.50
77.48
76.84
39.01
21.84
135.81
134.27
132.78
131.91
129.56
129.14
128.56
128.03
127.83
127.14
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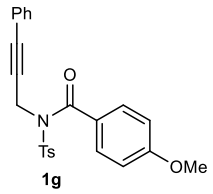
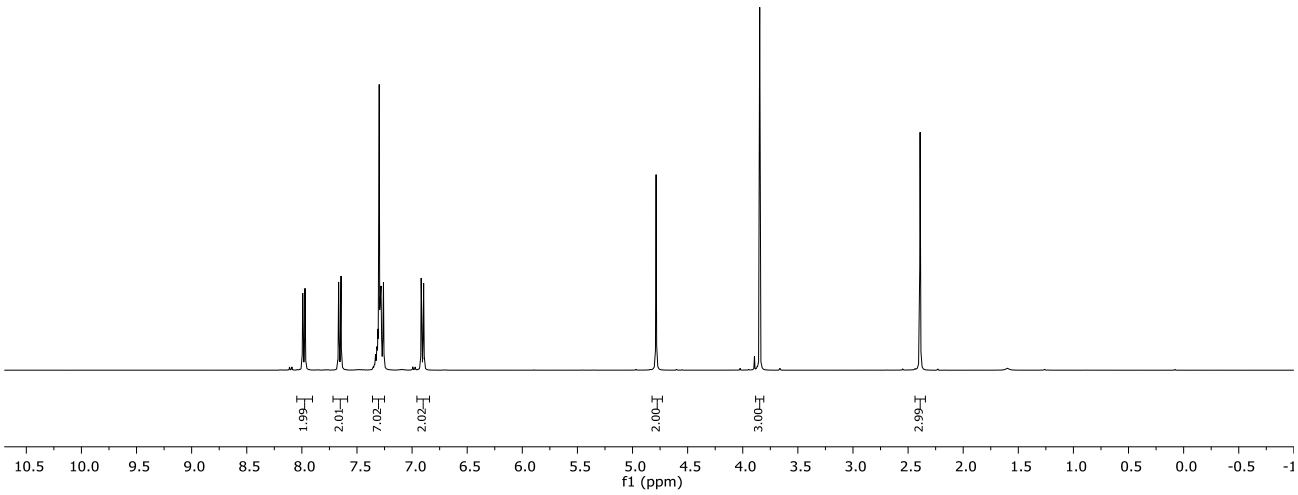
f1 (ppm)


Ph
O
N
Ts
OMe

**1g**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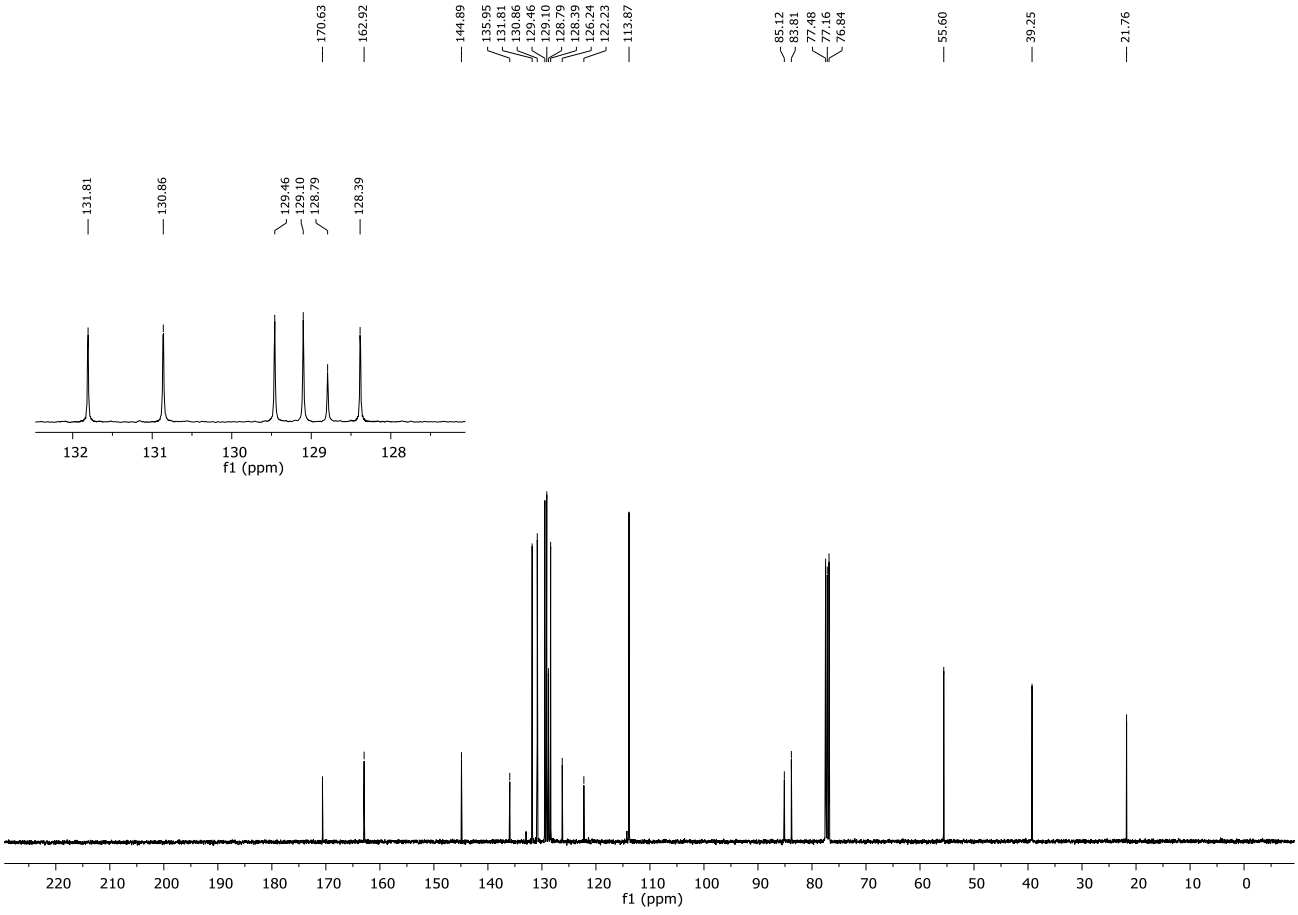
3.00
2.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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129.10
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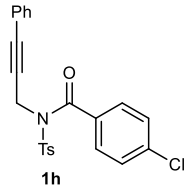
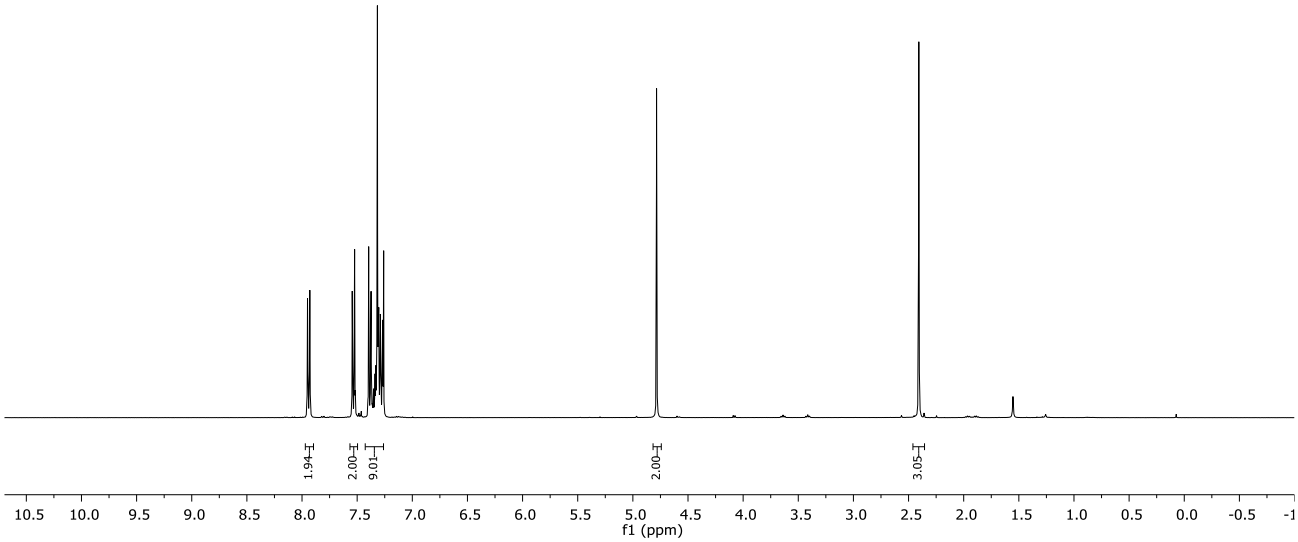
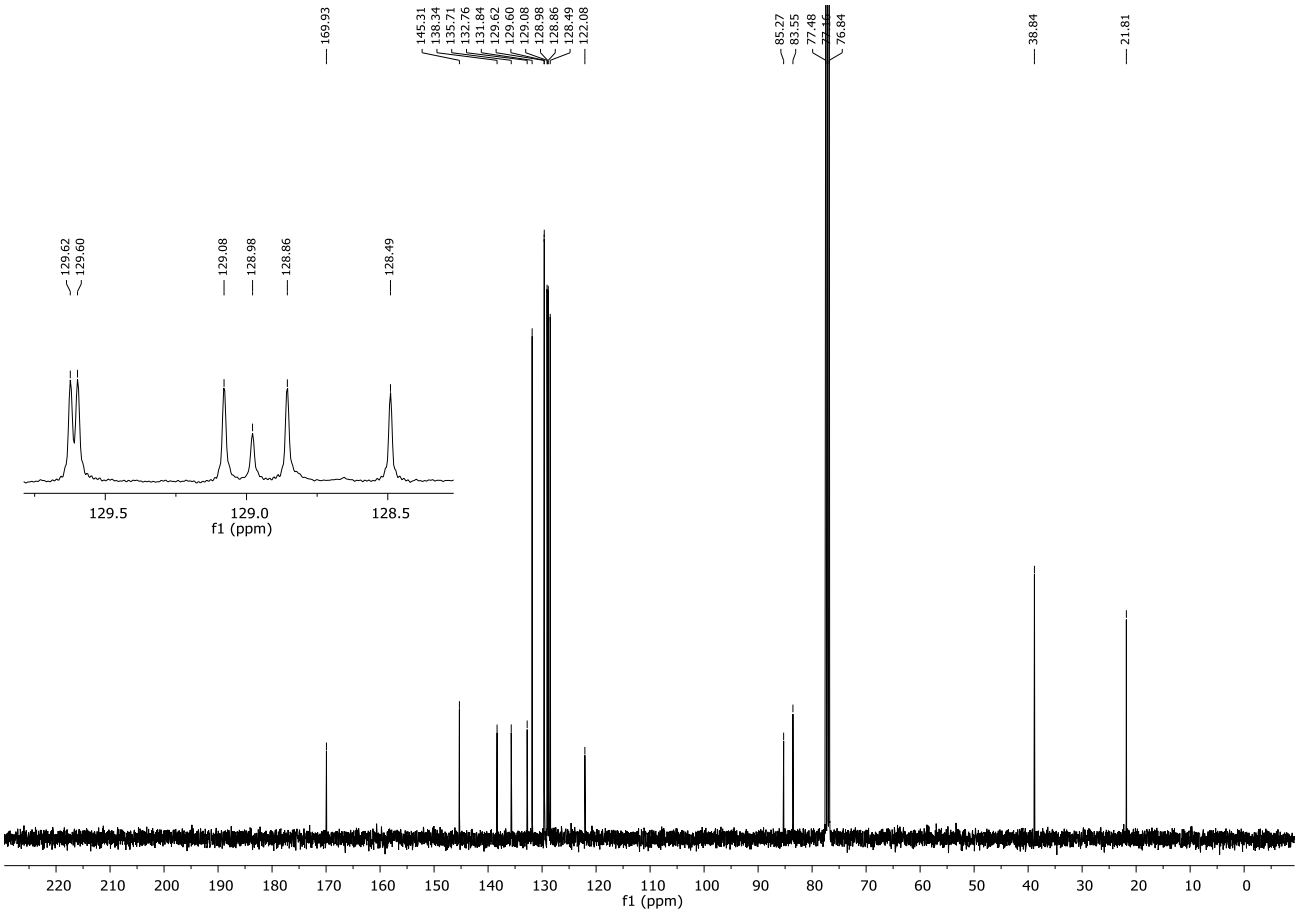
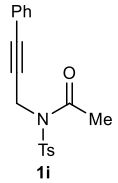
126.24
122.23
113.87
85.12
83.81
77.48
77.16
76.84
55.60
39.25
21.76
131.81
130.86
129.46
129.10
128.79
128.39
132 131 130 129 128
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
N
Ts
Cl

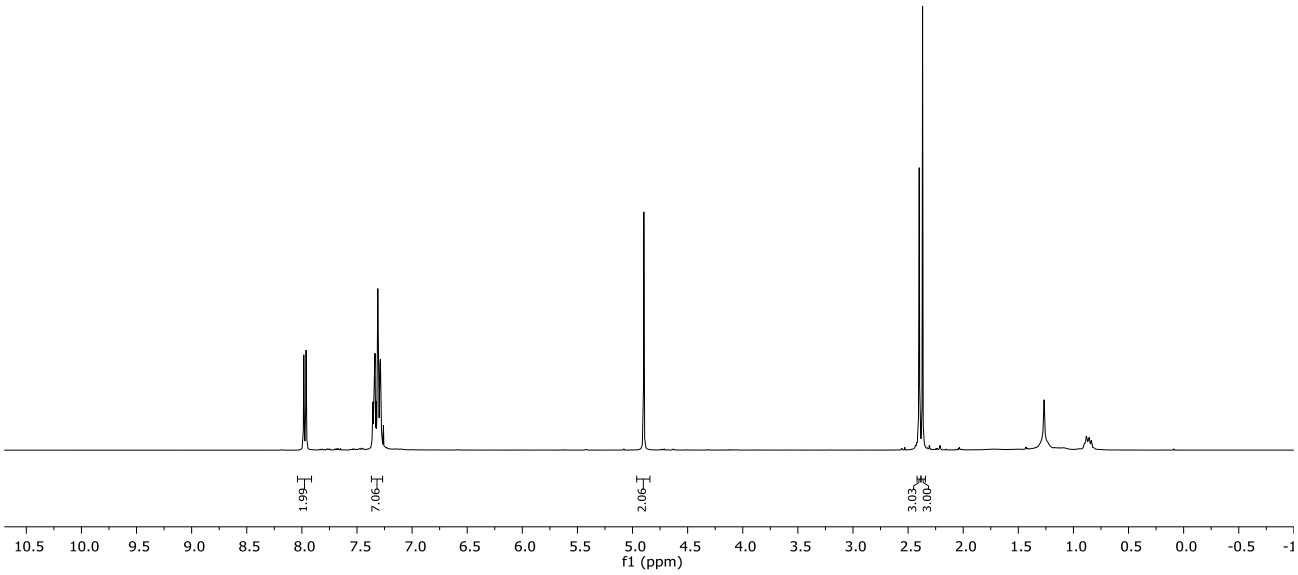
**1h**

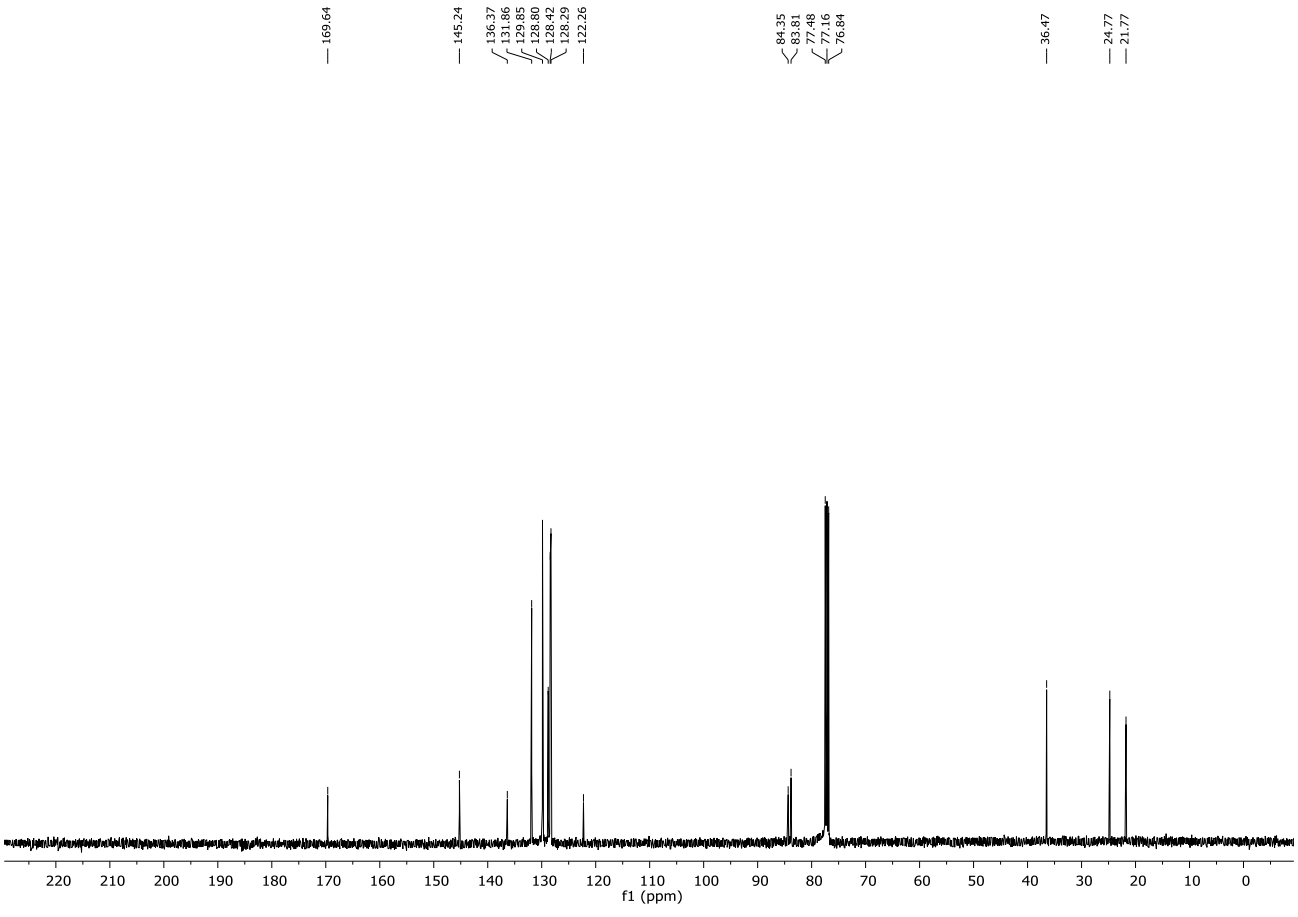

1.94
2.00
9.01
2.00
3.05
f1 (ppm)

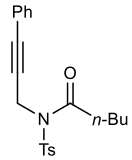

169.93
145.31
138.34
135.71
132.76
131.84
129.62
129.60
129.08
128.98
128.86
128.49
122.08
85.27
83.55
77.48
76.84
38.84
21.81
129.62
129.60
129.08
128.98
128.86
128.49
f1 (ppm)


Ph
O
N
Me
Ts

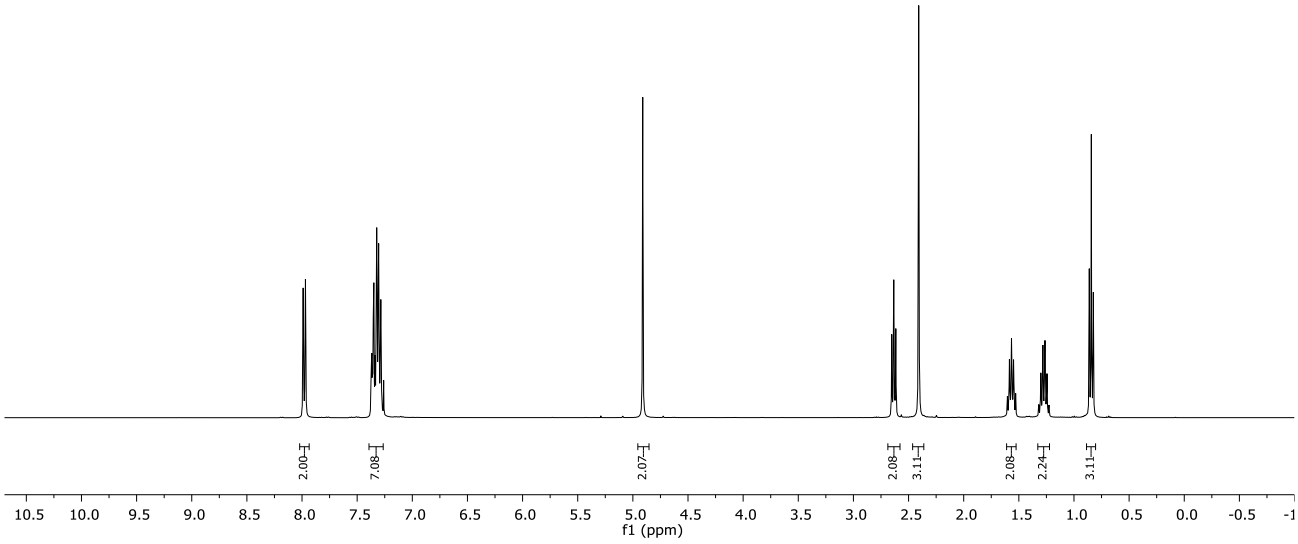
**1i**

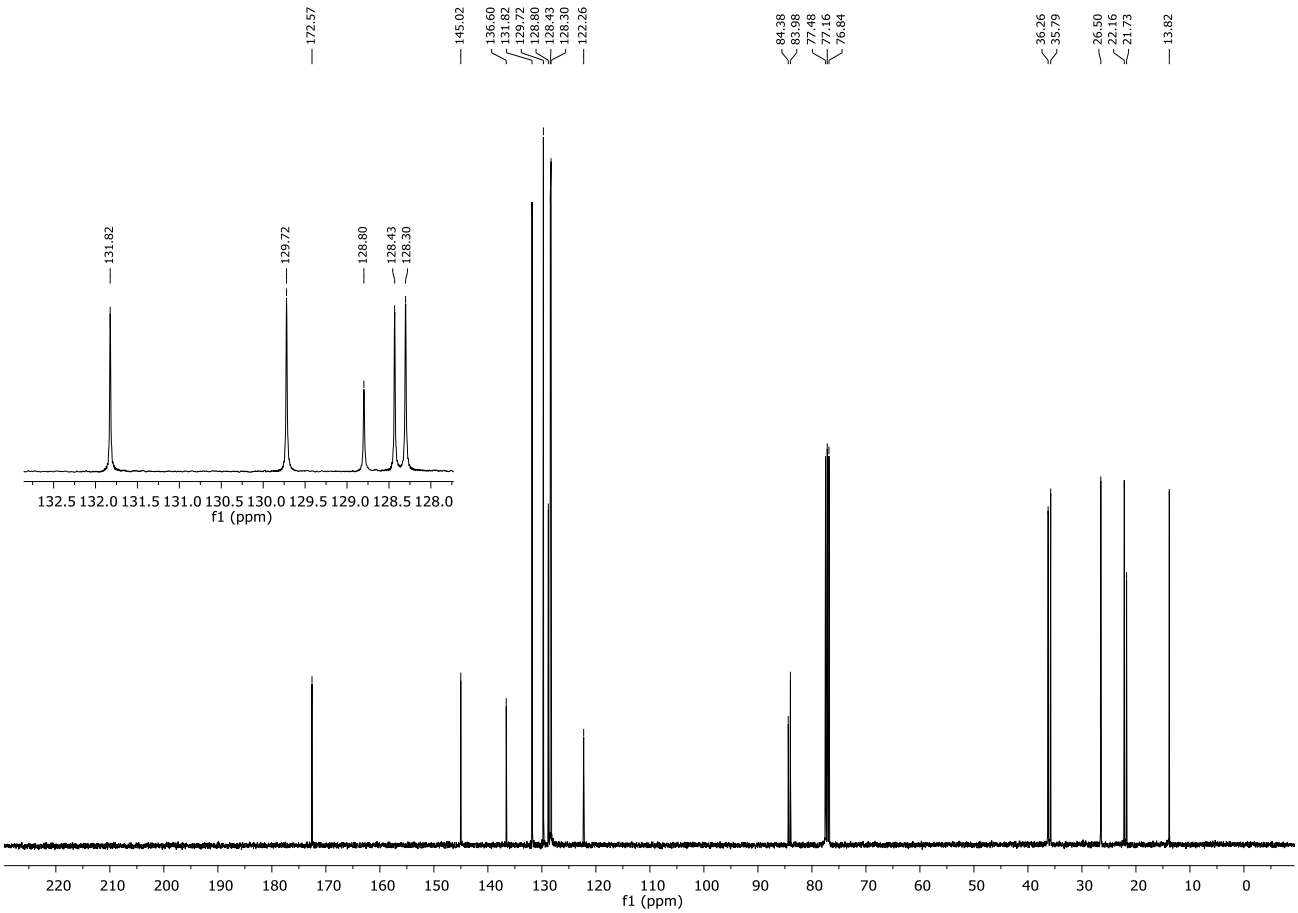

1.99
7.06
2.06
3.03
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

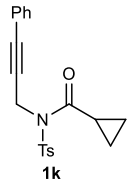

169.64
145.24
136.37
131.86
129.85
128.80
128.42
128.29
122.26
84.35
83.81
77.48
77.16
76.84
36.47
24.77
21.77
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
N
n-Bu
Ts

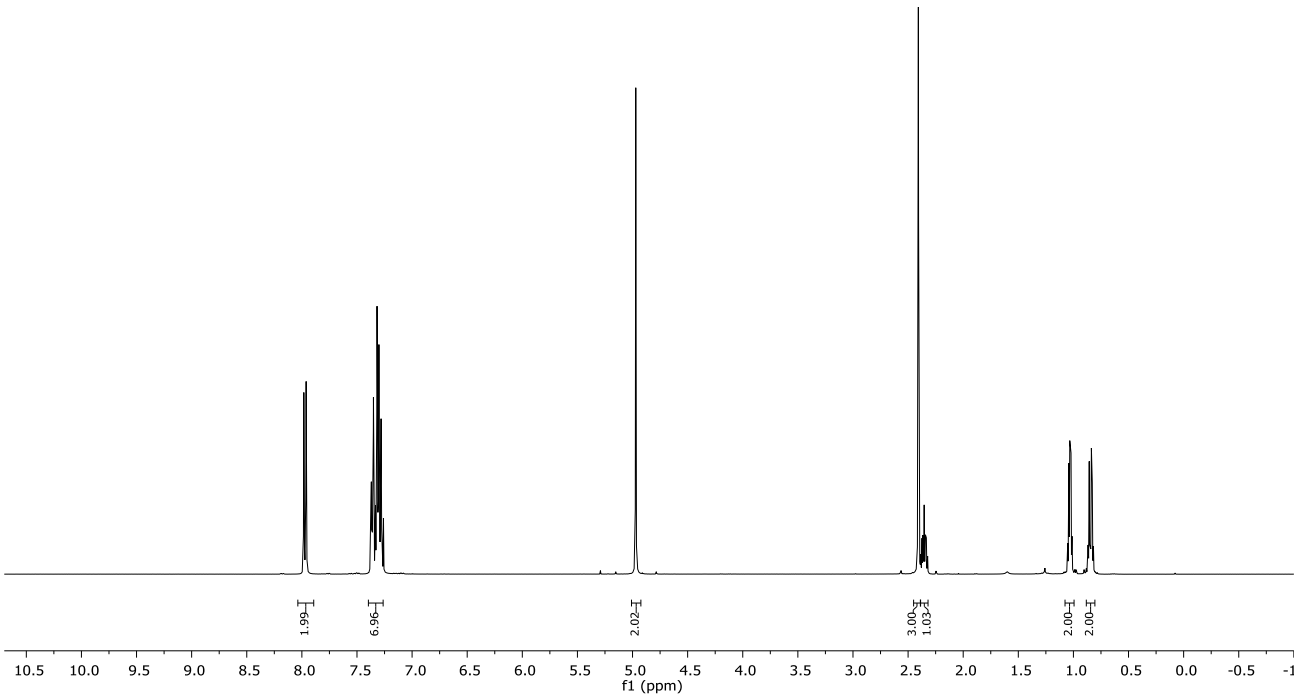
**1j**

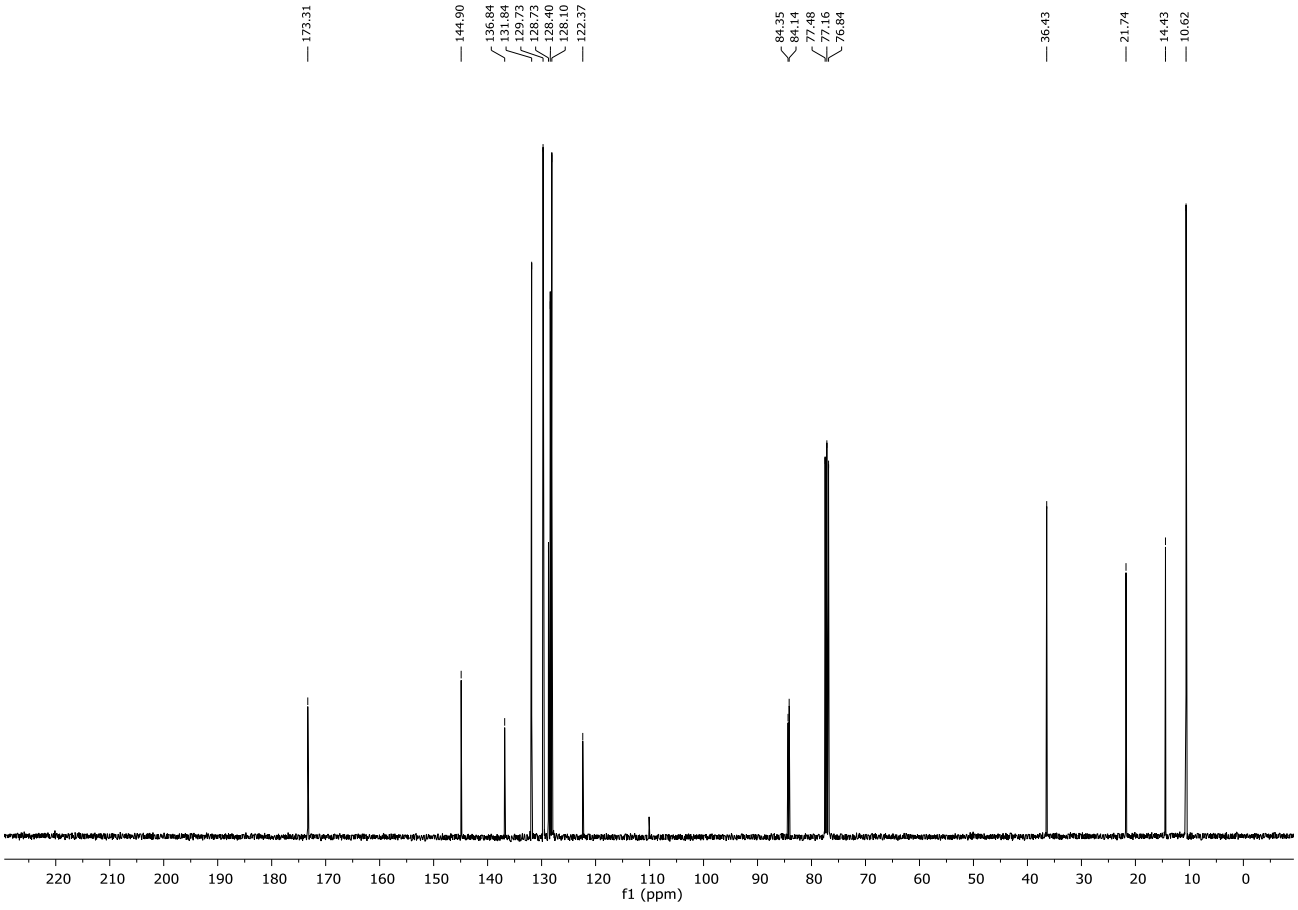

2.00
7.08
2.07
2.08
3.11
2.08
2.24
3.11
f1 (ppm)

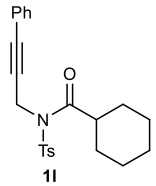

172.57
145.02
136.60
131.82
129.72
128.80
128.43
128.30
122.26
84.38
83.98
77.48
77.16
76.84
36.26
35.79
26.50
22.16
21.73
13.82
f1 (ppm)


Ph
O
N
Ts

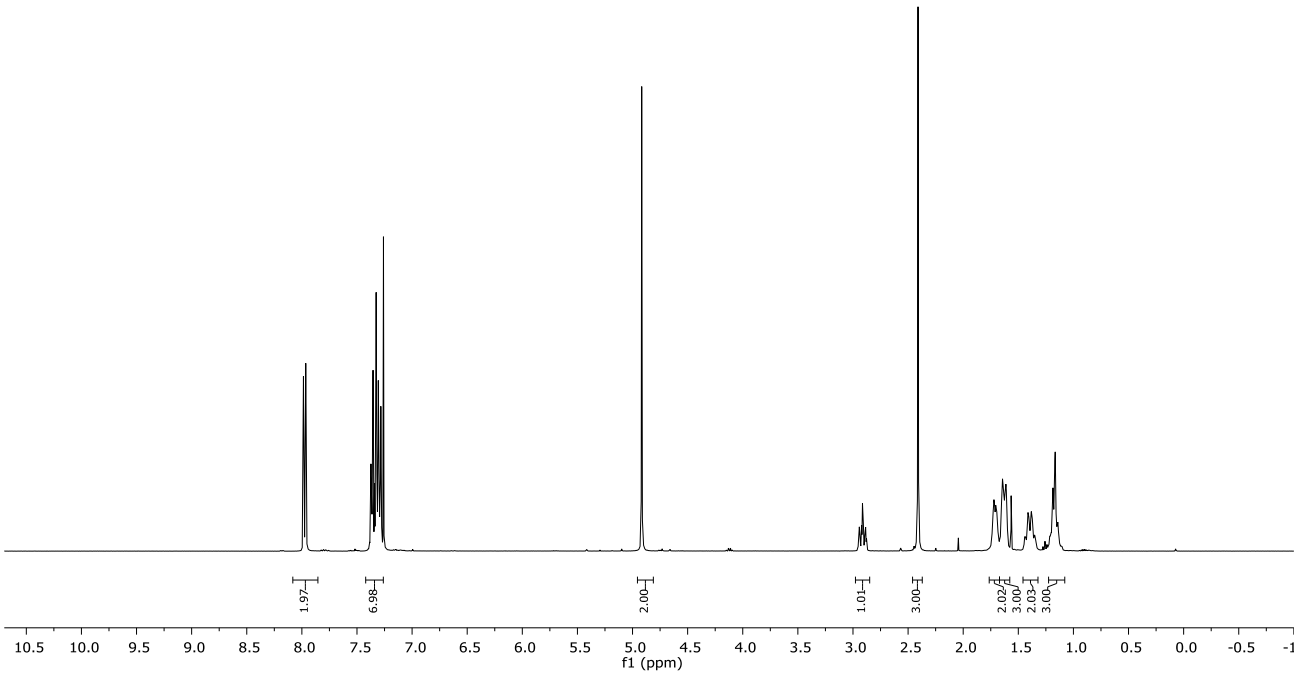
**1k**

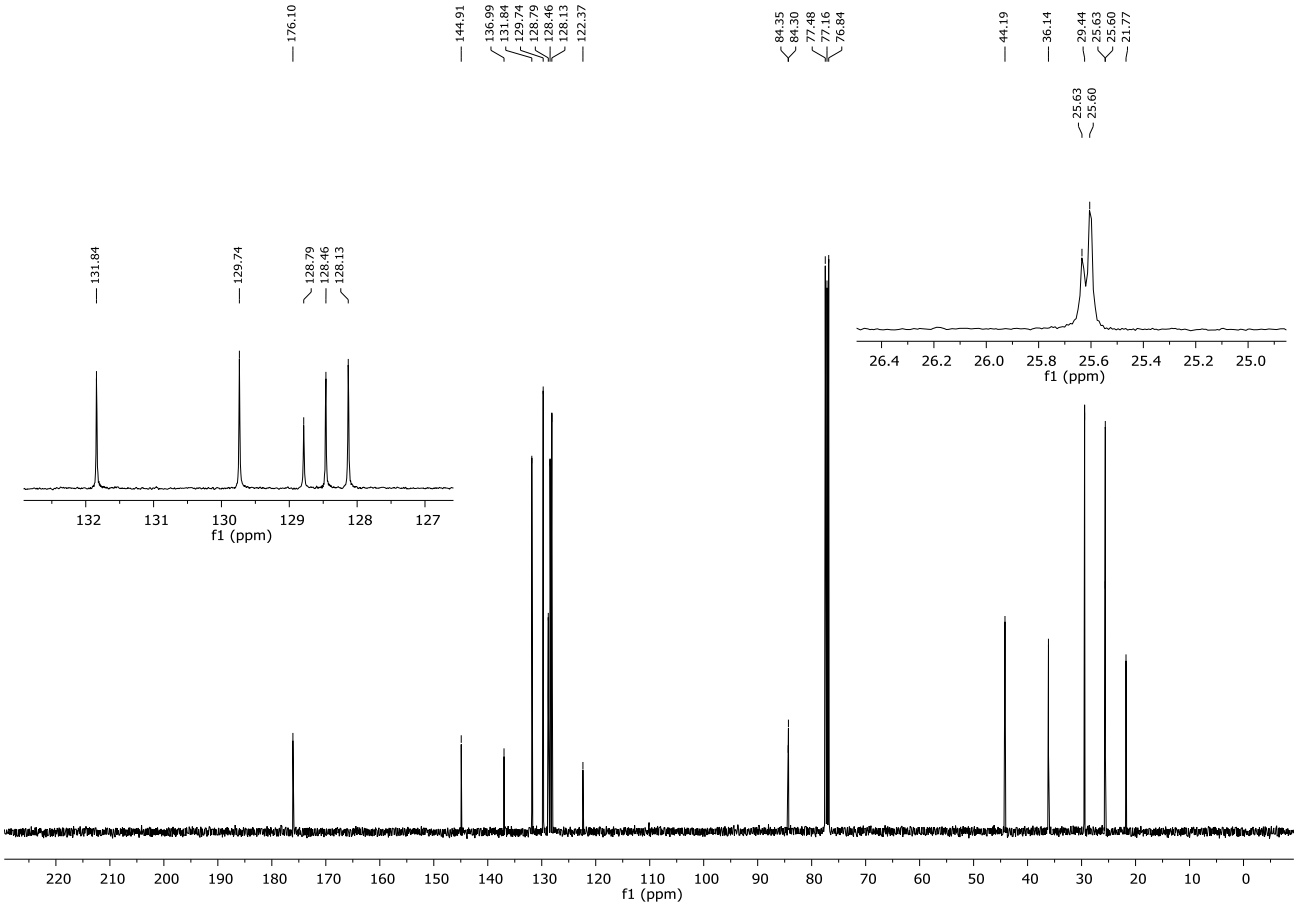

1.99
6.96
2.02
3.00
1.03
2.00
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


173.31
144.90
136.84
131.84
129.73
128.73
128.40
128.10
122.37
84.35
84.14
77.48
77.16
76.84
36.43
21.74
14.43
10.62
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
N
Ts

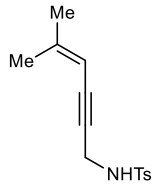
**1l**


1.97
6.98
2.00
1.01
3.00
2.02
3.00
2.03
3.00
f1 (ppm)


176.10
144.91
136.99
131.84
129.74
128.79
128.46
128.13
122.37
84.35
84.30
77.48
77.16
76.84
44.19
36.14
29.44
25.63
25.60
21.77
f1 (ppm)

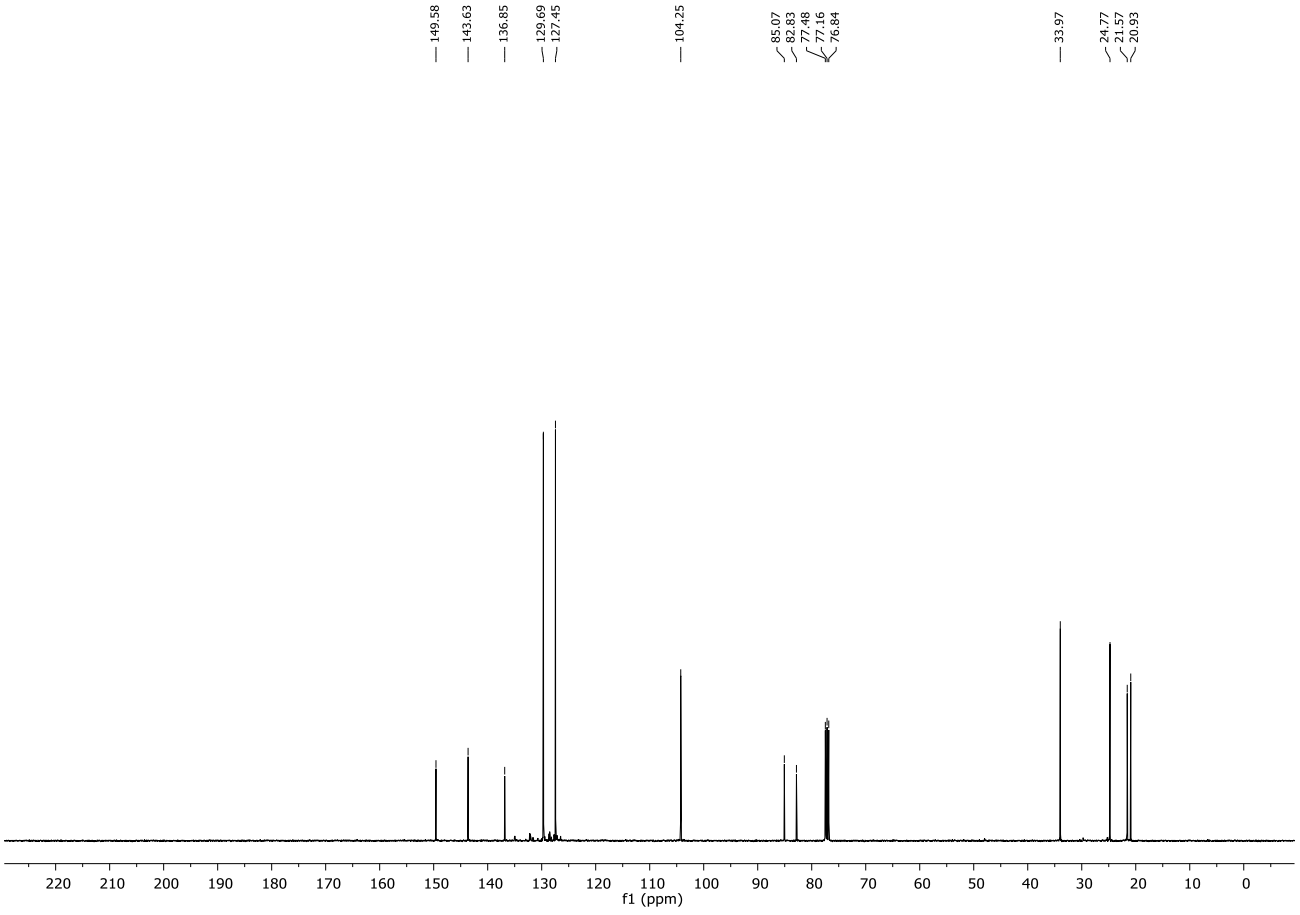

131.84
129.74
128.79
128.46
128.13
f1 (ppm)

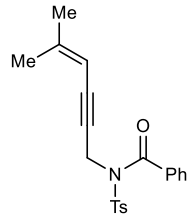

25.63
25.60
f1 (ppm)


Me
Me
NHTs

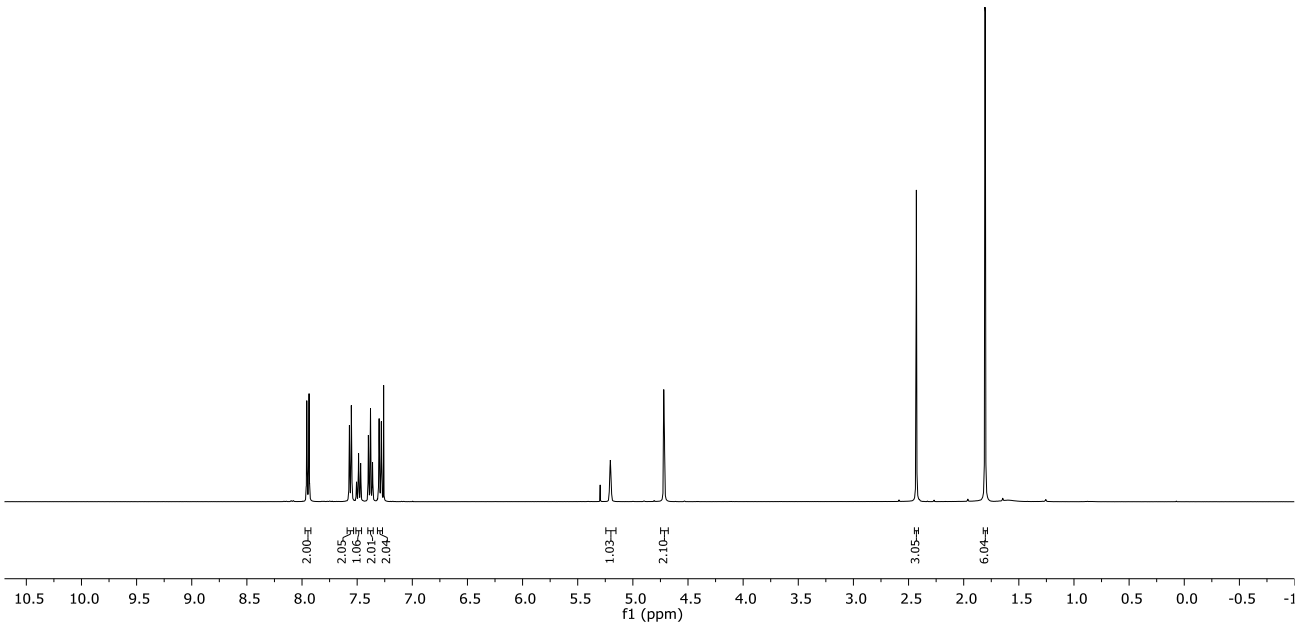
**S1m**

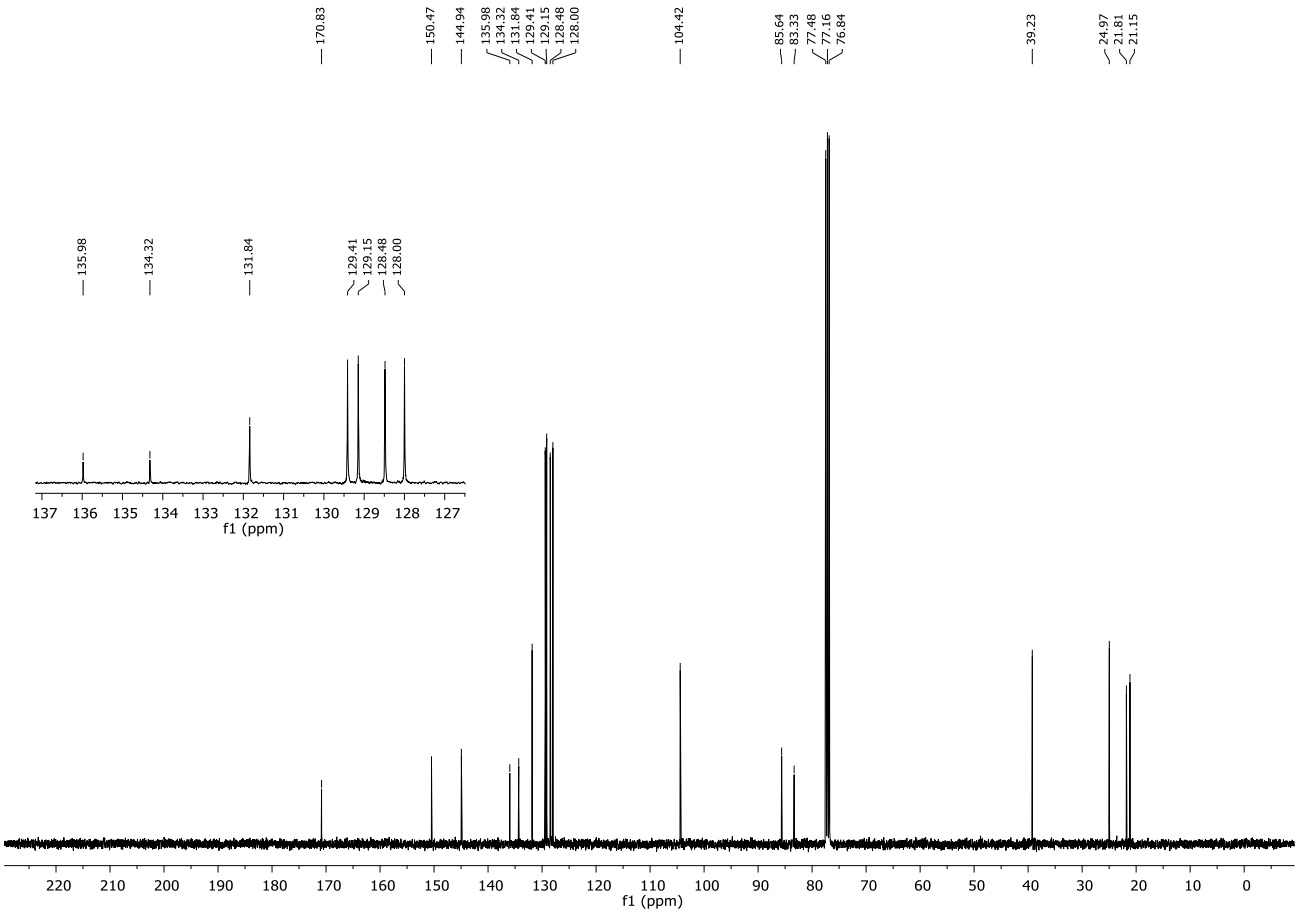

2.00
2.12
1.01
0.95
2.06
3.10
3.06
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

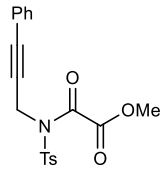

149.58
143.63
136.85
129.69
127.45
104.25
85.07
82.83
77.48
77.16
76.84
33.97
24.77
21.57
20.93
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Me
O
N
Ph
Ts

**1m**

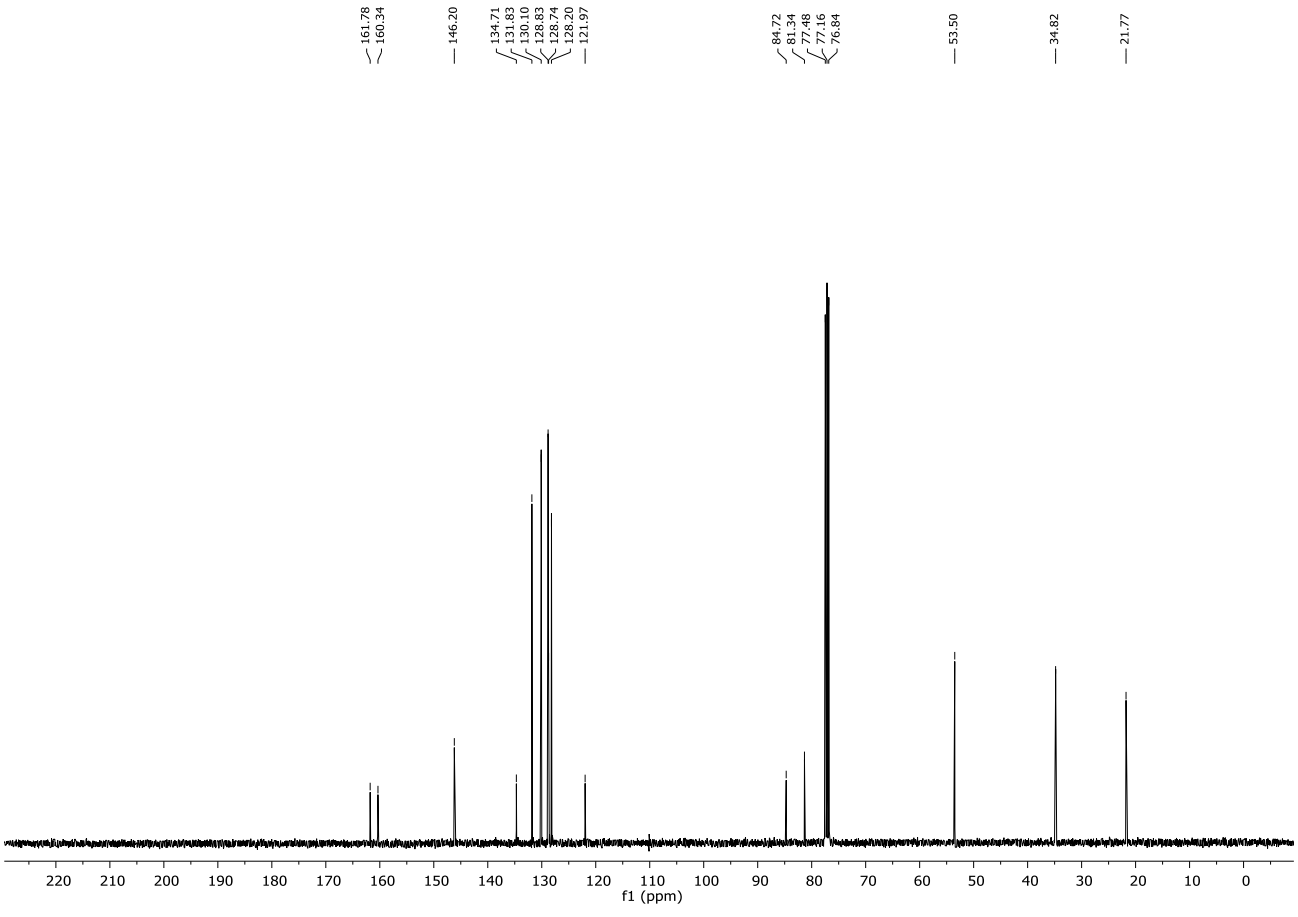

2.00
2.05
1.06
2.01
2.04
1.03
2.10
3.05
6.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

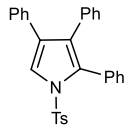

170.83
150.47
144.94
135.98
134.32
131.84
129.41
129.15
128.48
128.00
104.42
85.64
83.33
77.48
77.16
76.84
39.23
24.97
21.81
21.15
135.98
134.32
131.84
129.41
129.15
128.48
128.00
137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
OMe
N
Ts
O

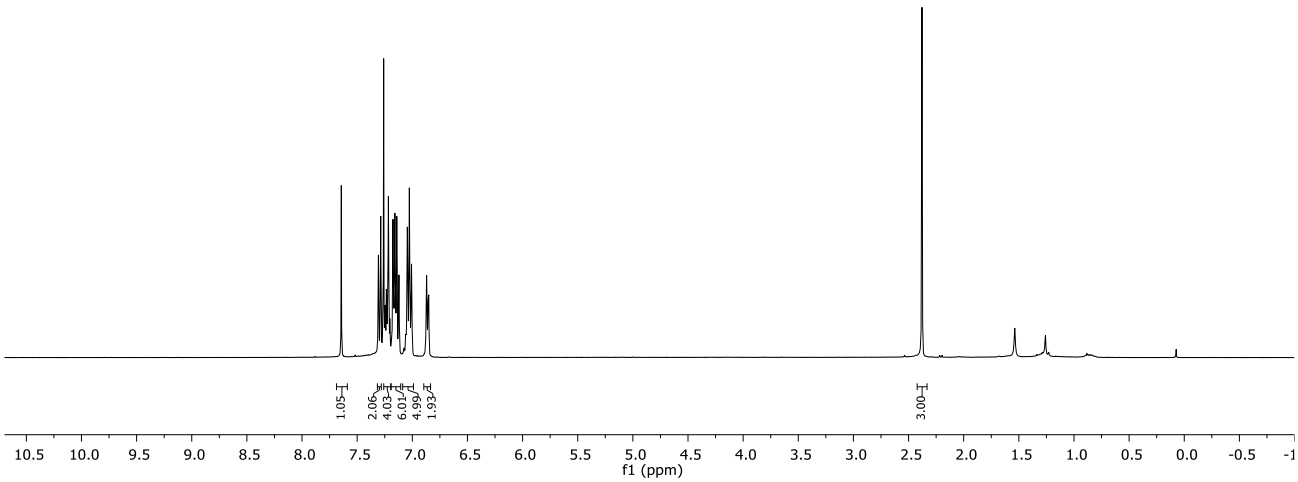
**1n**

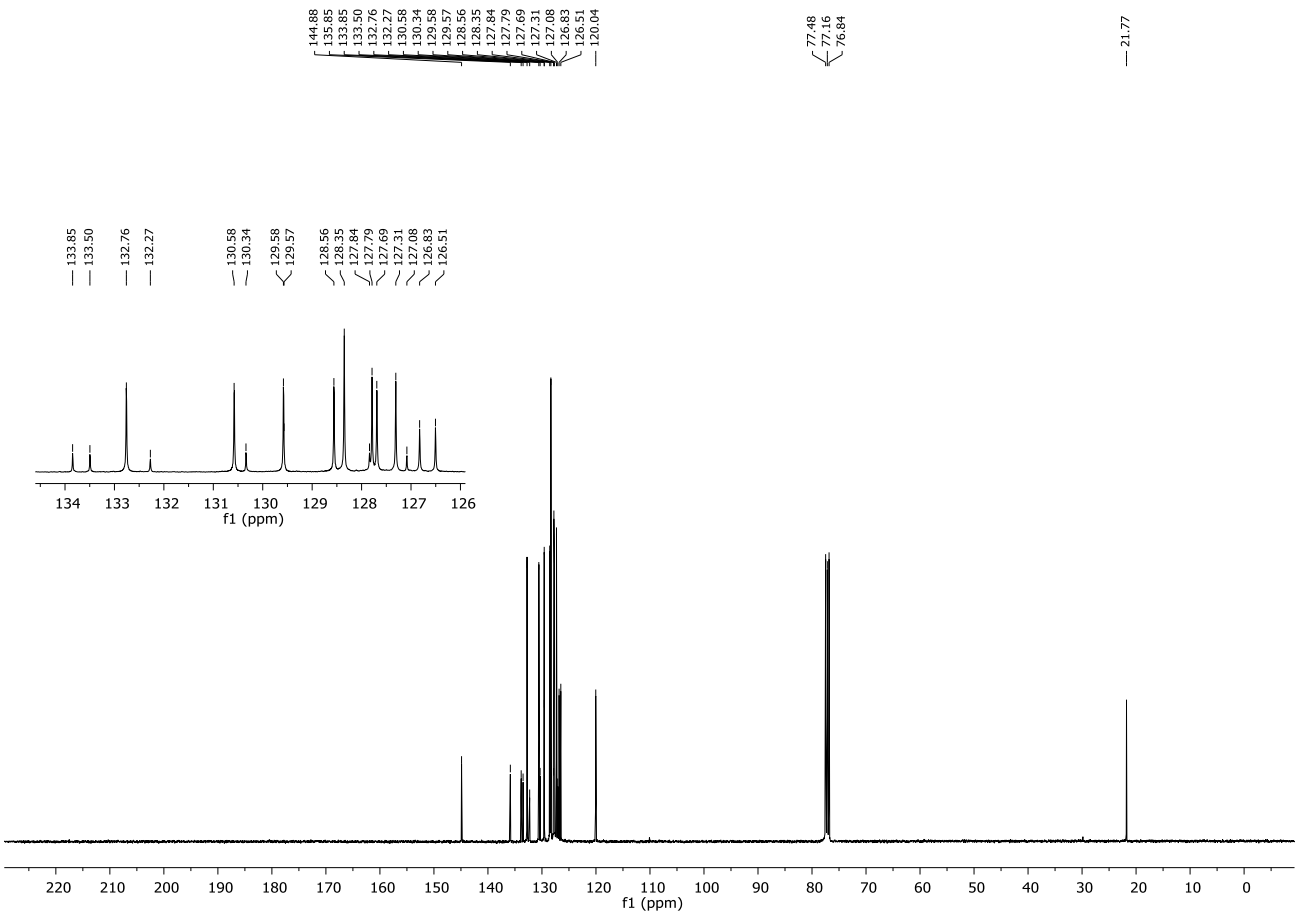

1.97
2.99
2.00
2.00
2.00
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

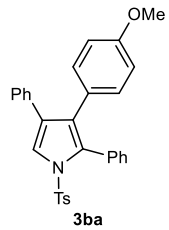

161.78
160.34
146.20
134.71
131.83
130.10
128.83
128.74
128.20
121.97
84.72
81.34
77.48
77.16
76.84
53.50
34.82
21.77
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
Ph
N
Ts

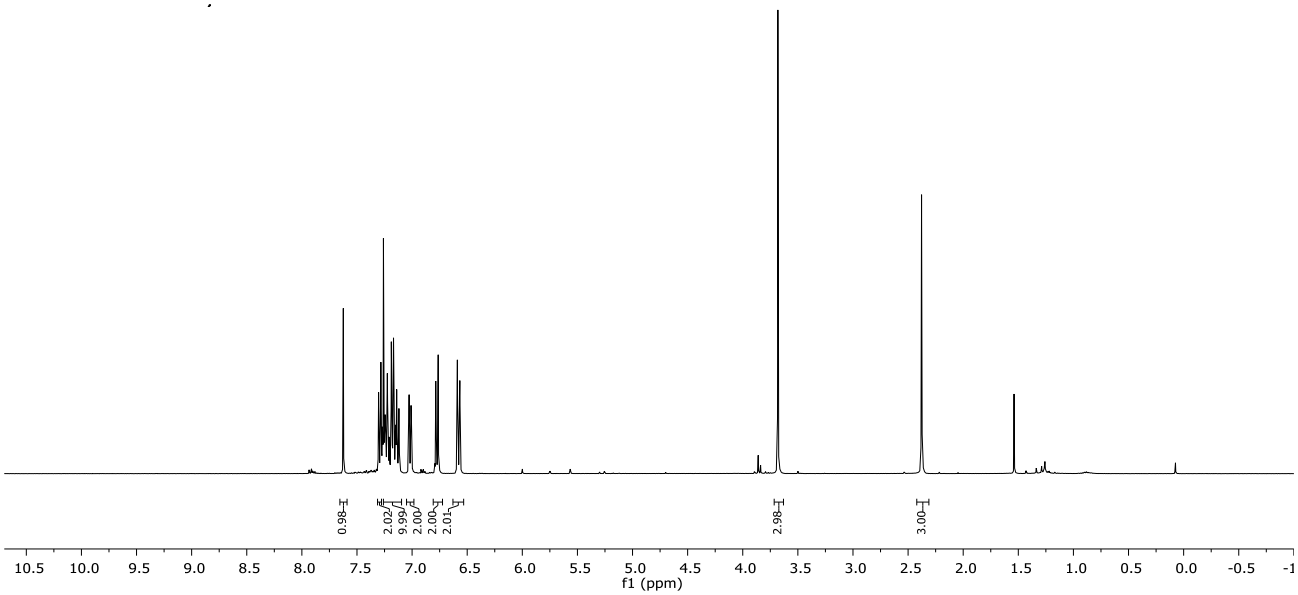
**3aa**


1.05
2.06
4.03
6.01
4.99
1.93
3.00
f1 (ppm)

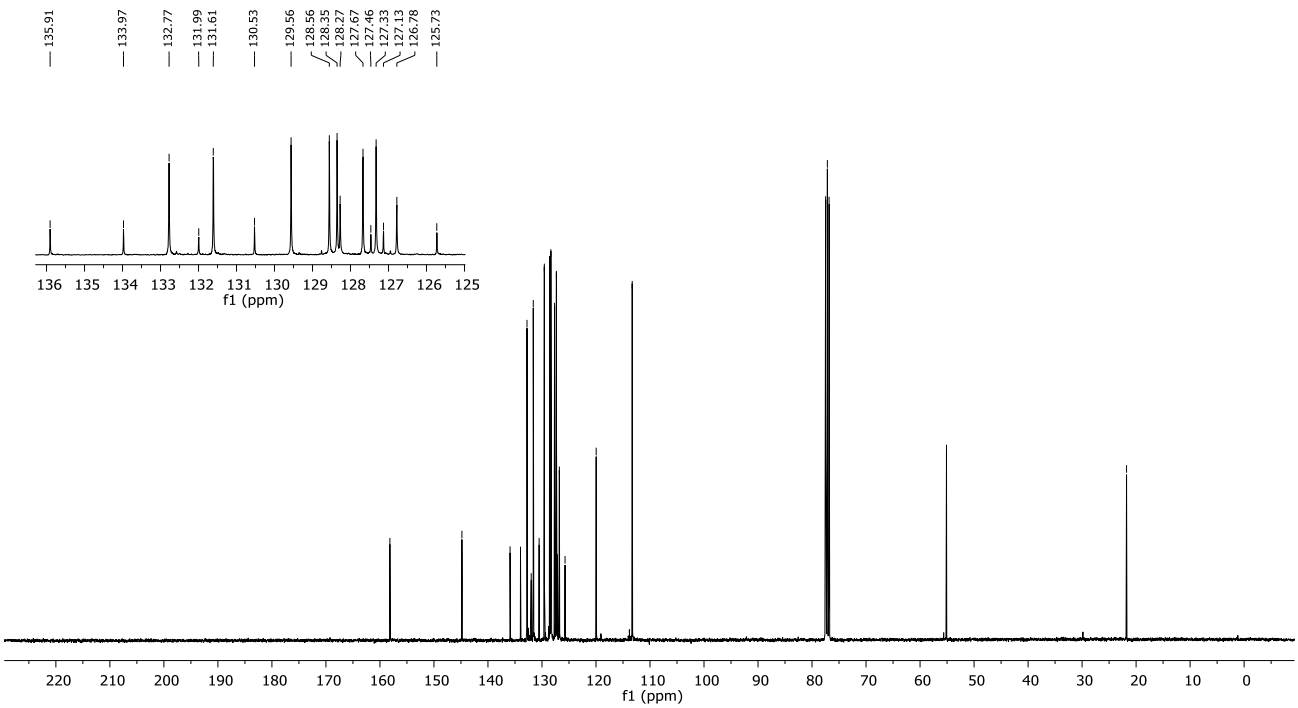

144.88
135.85
133.85
133.50
132.76
132.27
130.58
130.34
129.58
129.57
128.56
128.35
127.84
127.79
127.69
127.31
127.08
126.83
126.51
120.04
77.48
77.16
76.84
21.77
f1 (ppm)

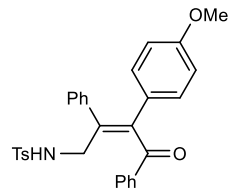

OMe
Ph
Ph
N
Ts

**3ba**

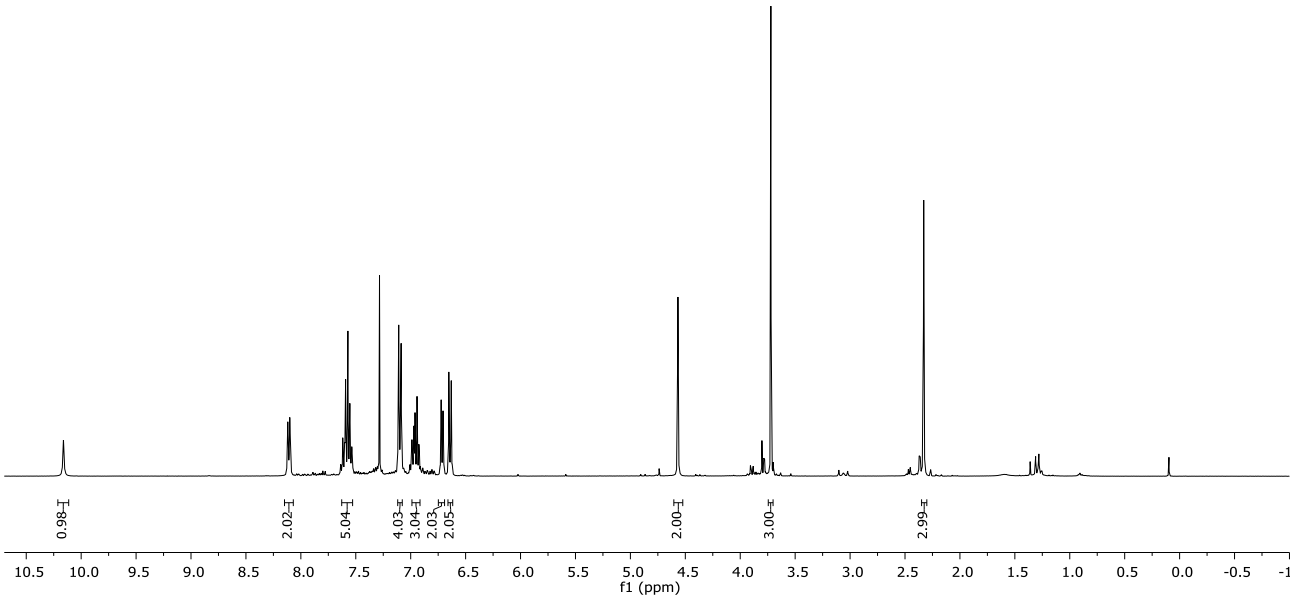

0.98
2.02
9.99
2.00
2.00
2.01
2.98
3.00
f1 (ppm)

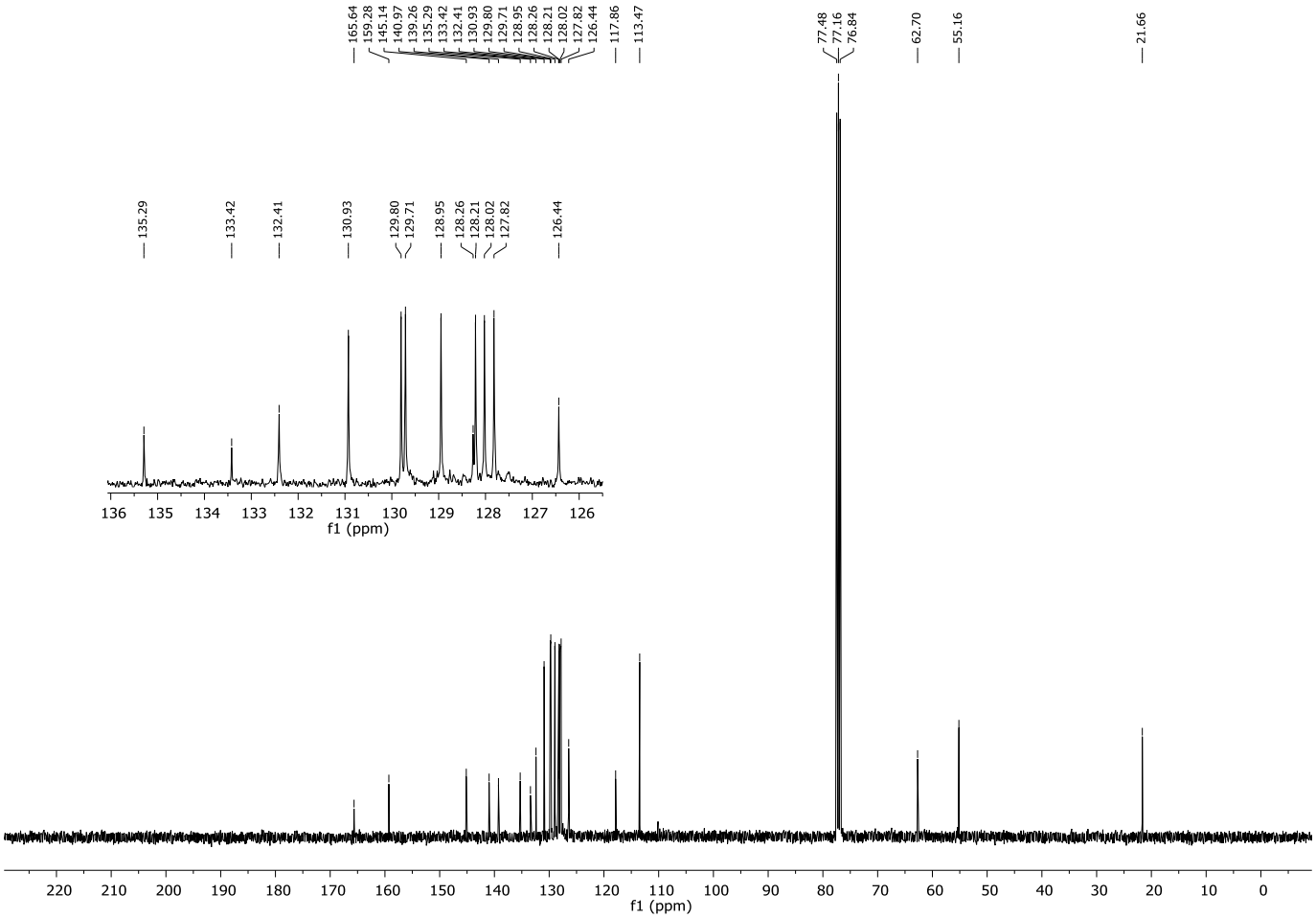

158.16
144.82
135.91
133.97
132.77
131.99
131.61
130.53
129.56
128.56
128.35
128.27
127.67
127.46
127.33
127.13
126.78
125.73
119.96
113.29
77.48
77.16
76.84
55.11
21.77

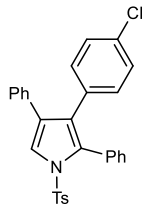

135.91
133.97
132.77
131.99
131.61
130.53
129.56
128.56
128.35
128.27
127.67
127.46
127.33
127.13
126.78
125.73
f1 (ppm)
f1 (ppm)



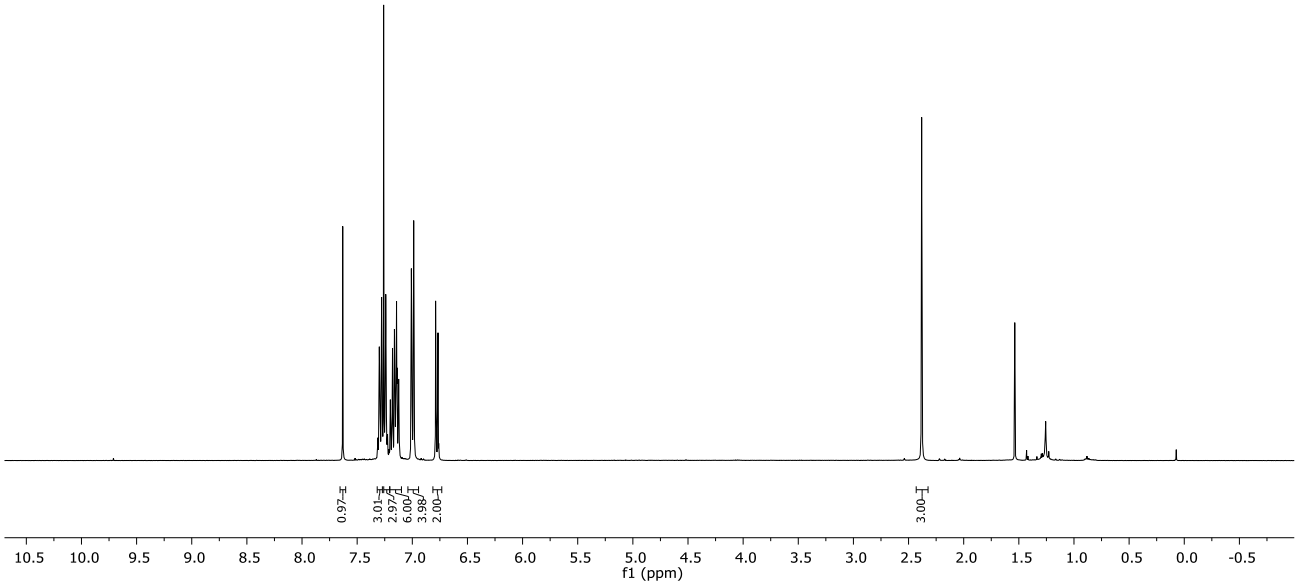

**S2**
(contains trace impurities)

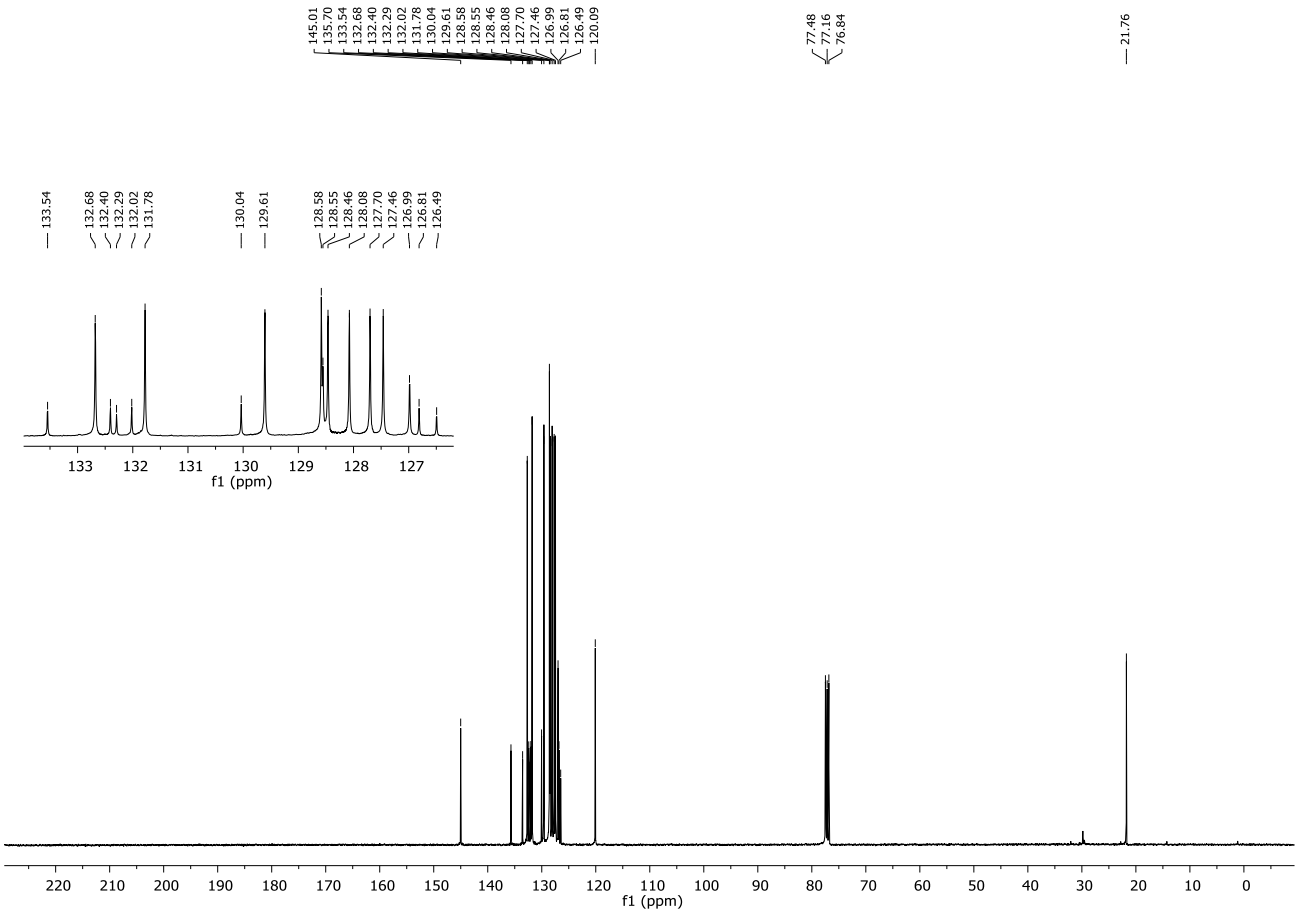


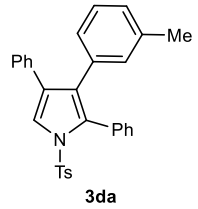




Cl
Ph
Ph
N
Ts

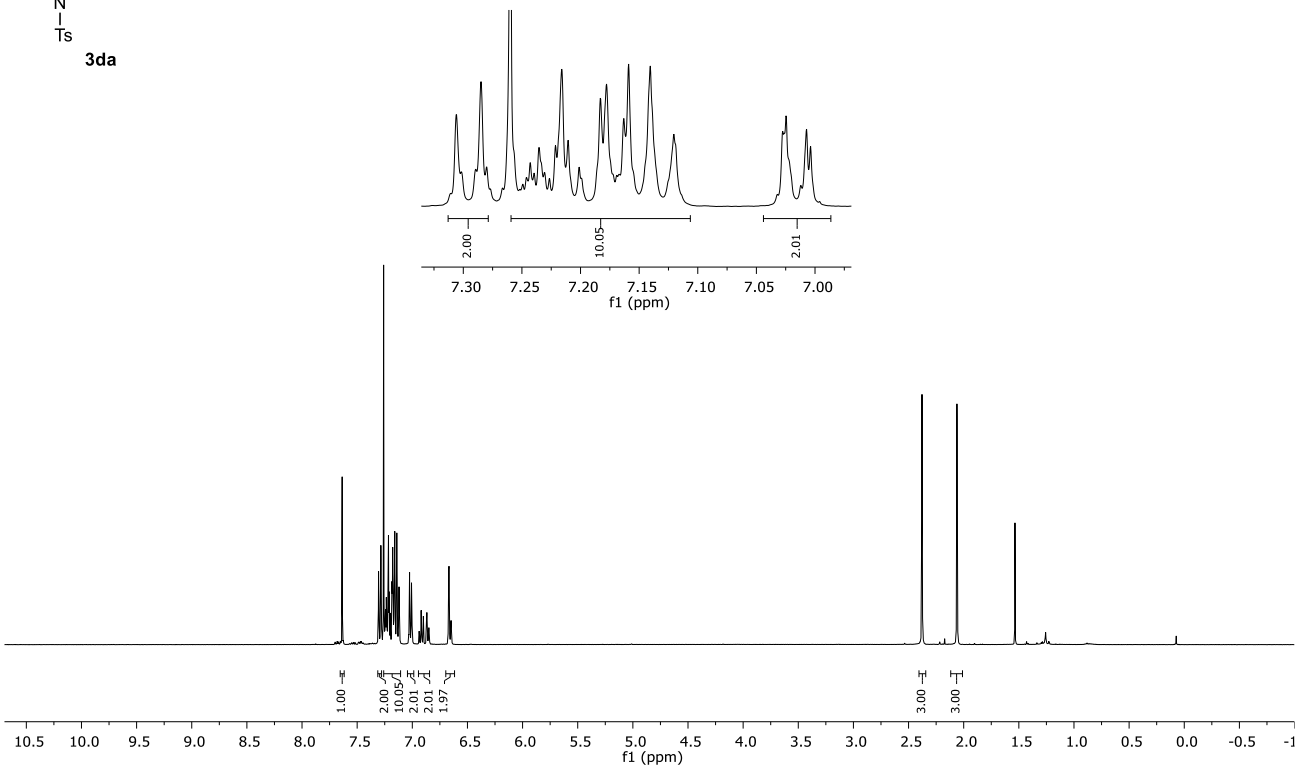
**3ca**

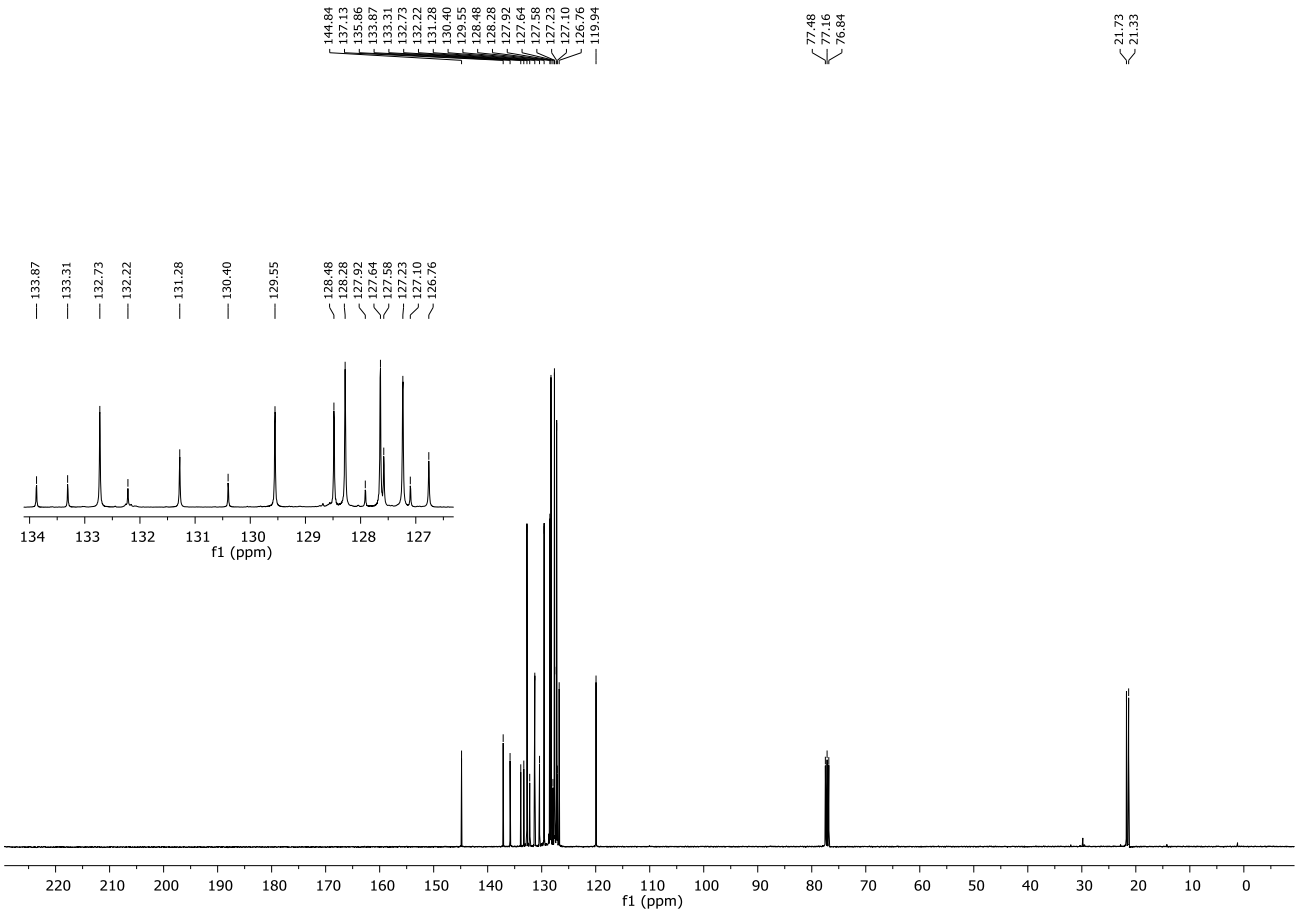

0.97
3.01
2.97
6.00
3.98
2.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

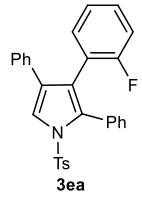

145.01
135.70
133.54
132.68
132.40
132.29
132.02
131.78
130.04
129.61
128.58
128.55
128.46
128.08
127.70
127.46
126.99
126.81
126.49
120.09
77.48
77.16
76.84
21.76
133 132 131 130 129 128 127
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Ph
Ph
N
Ts

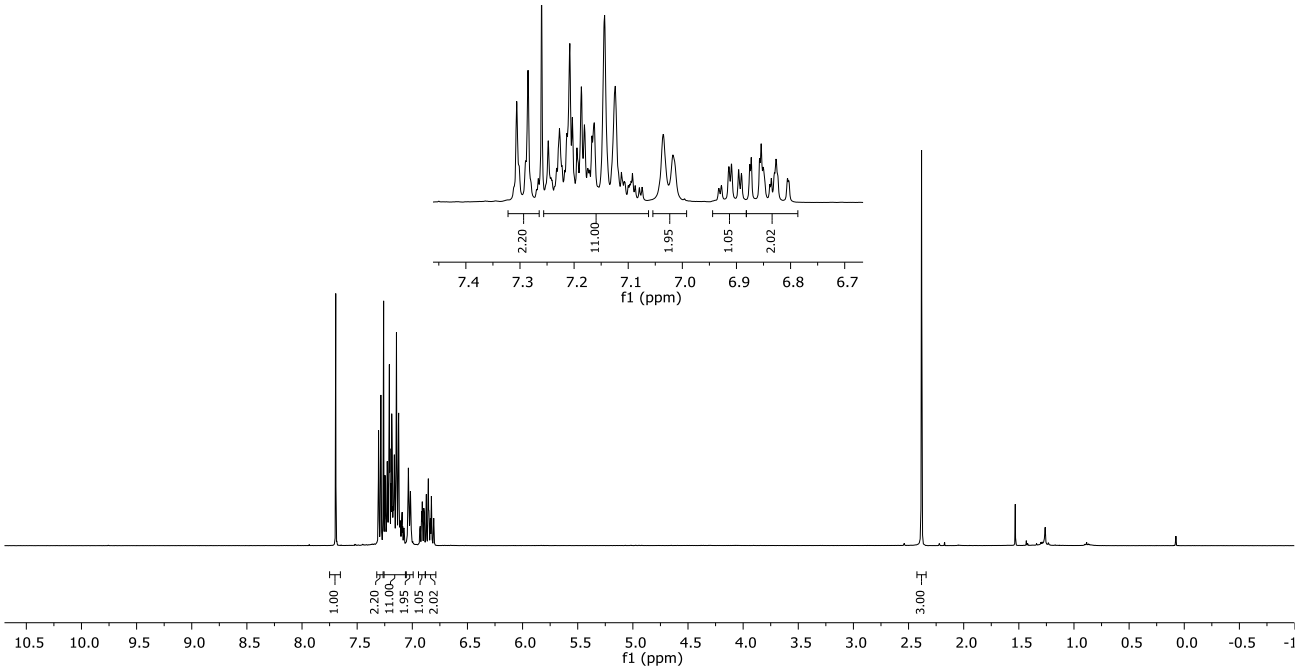
**3da**

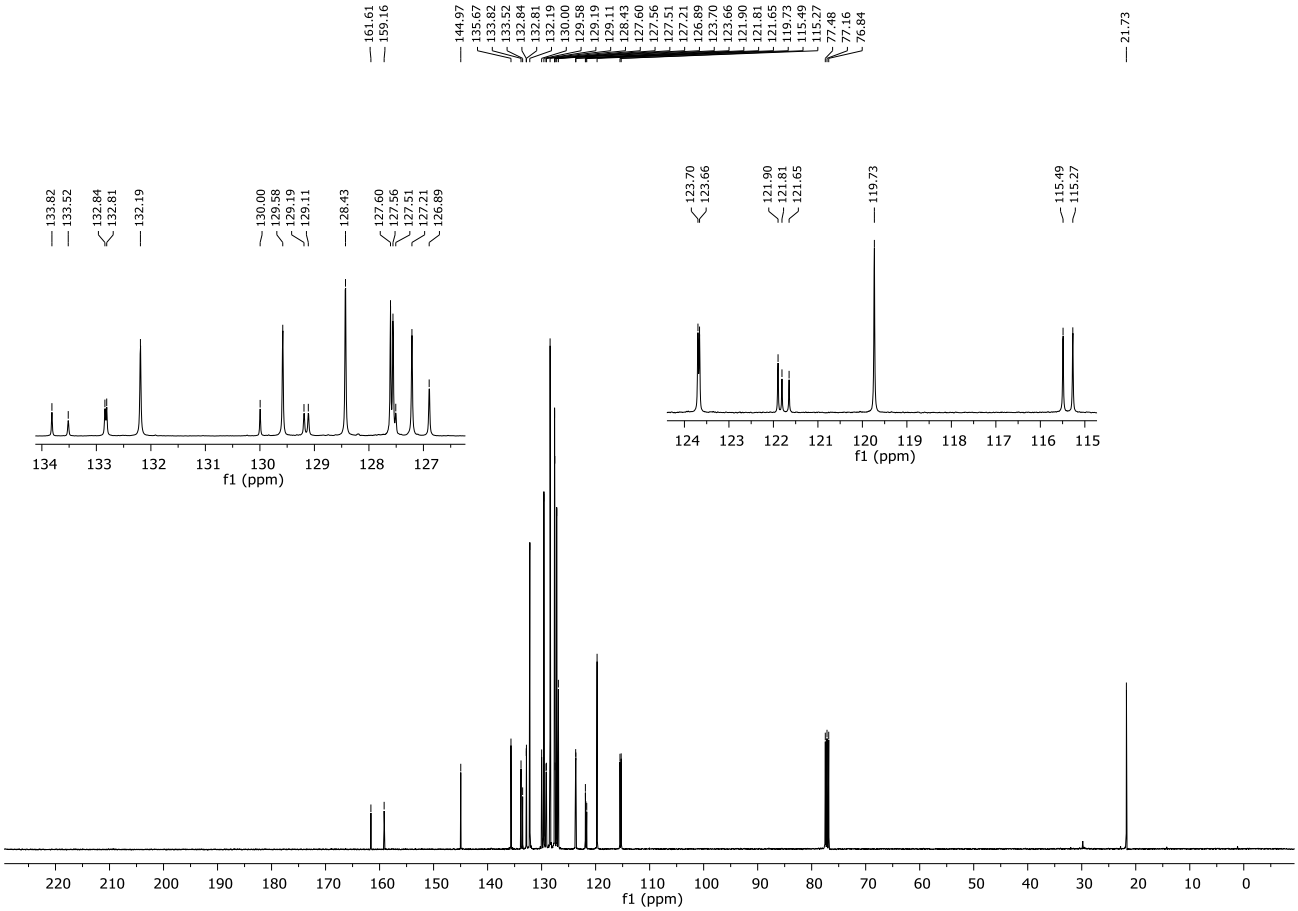

2.00
10.05
2.01
7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
1.00
2.00
10.05
2.01
2.01
1.97
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

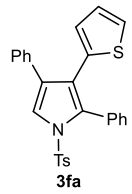

144.84
137.13
135.86
133.87
133.31
132.73
132.22
131.28
130.40
129.55
128.48
128.28
127.92
127.64
127.58
127.23
127.10
126.76
119.94
77.48
77.16
76.84
21.73
21.33
133.87
133.31
132.73
132.22
131.28
130.40
129.55
128.48
128.28
127.92
127.64
127.58
127.23
127.10
126.76
134 133 132 131 130 129 128 127
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
F
Ph
N
Ts

**3ea**

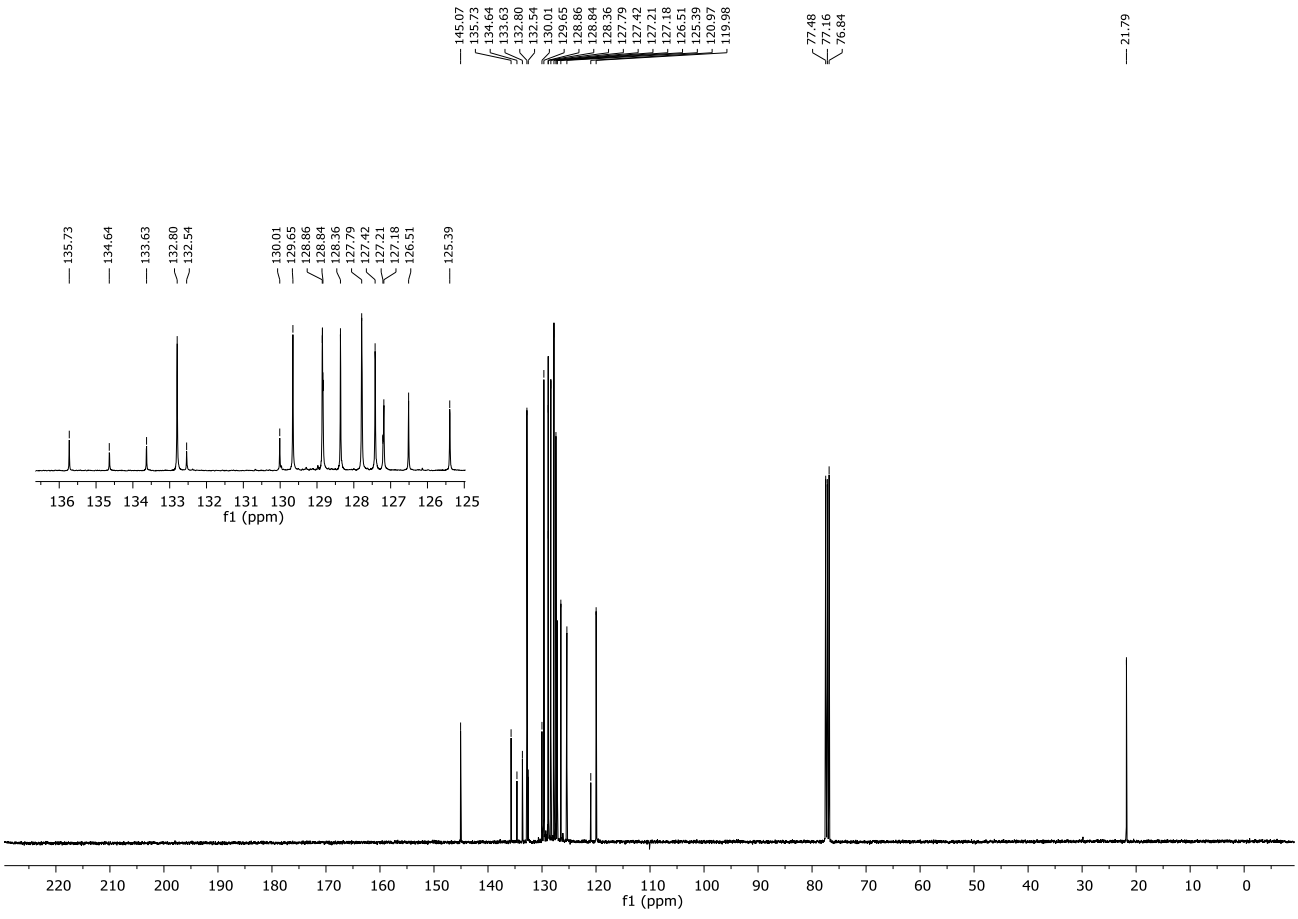

2.20
11.00
1.95
1.05
2.02
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
1.00
2.20
11.00
1.95
1.05
2.02
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

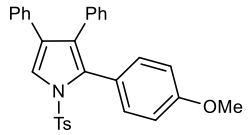

161.61
159.16
144.97
135.67
133.82
133.52
132.84
132.81
132.19
130.00
129.58
129.19
129.11
128.43
127.60
127.56
127.51
127.21
126.89
123.70
123.66
121.90
121.81
121.65
119.73
115.49
115.27
77.48
77.16
76.84
21.73
134 133 132 131 130 129 128 127
f1 (ppm)
124 123 122 121 120 119 118 117 116 115
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
S
Ph
N
Ts

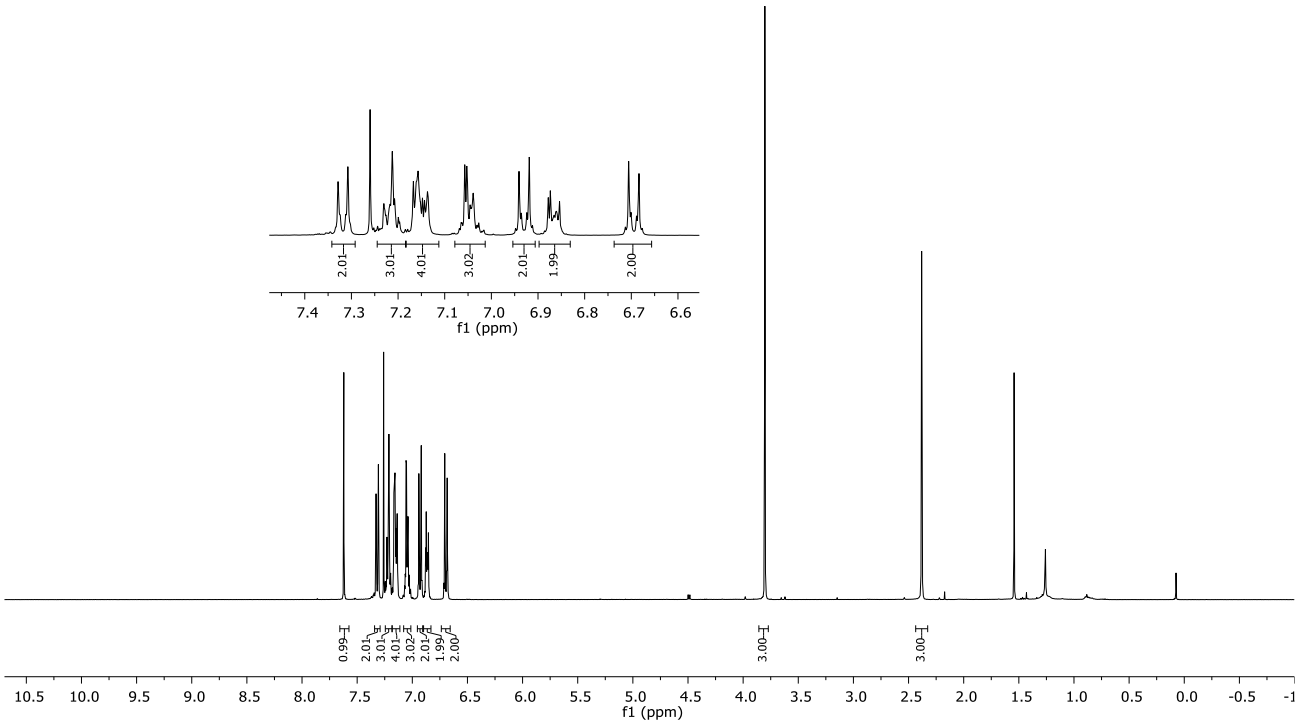
**3fa**

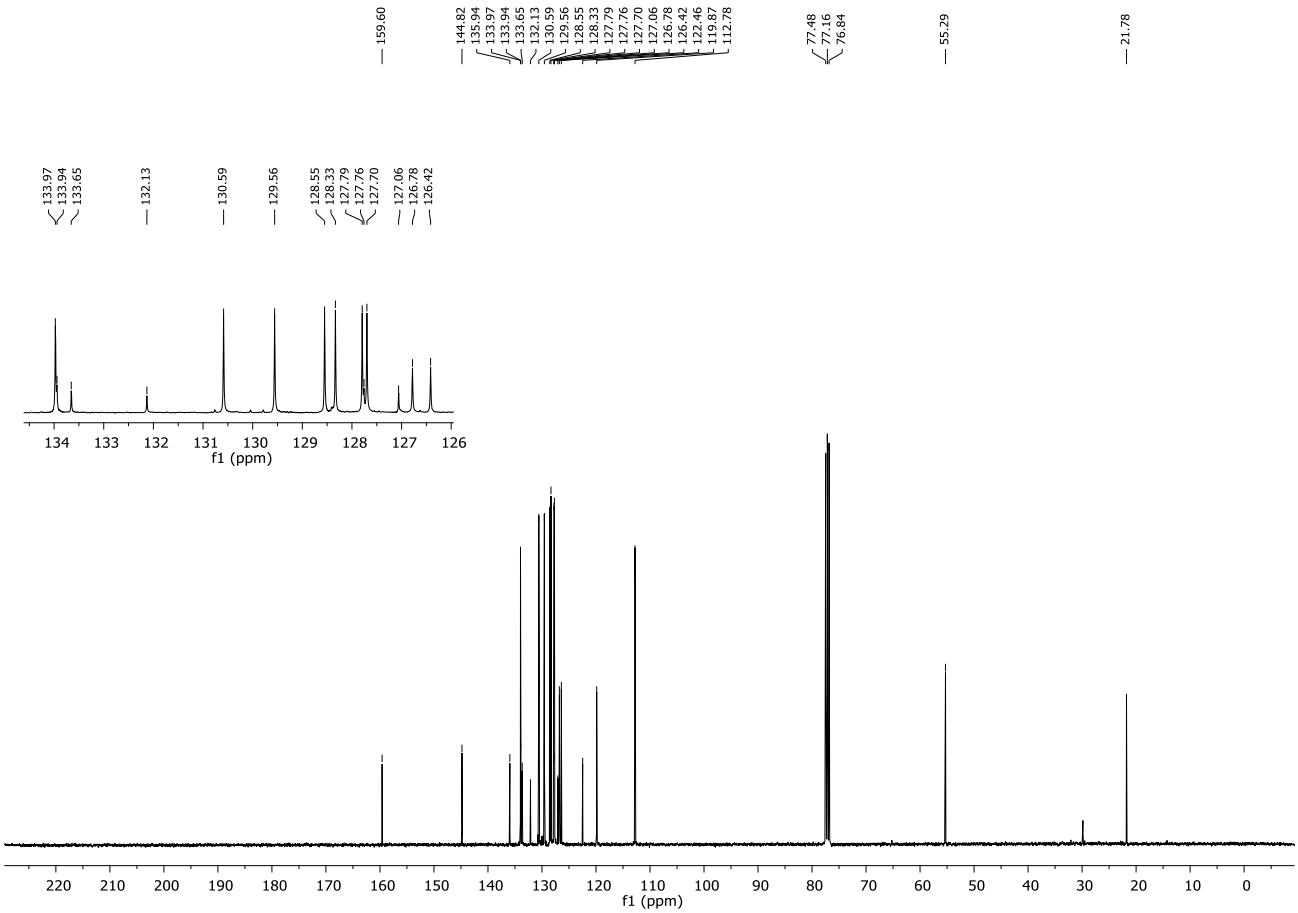

1.00
7.99
2.01
2.01
2.00
1.00
1.00
1.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

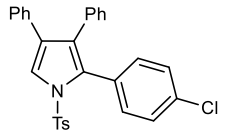

145.07
135.73
134.64
133.63
132.80
132.54
130.01
129.65
128.86
128.84
128.36
127.79
127.42
127.21
127.18
126.51
125.39
120.97
119.98
77.48
77.16
76.84
21.79
135.73
134.64
133.63
132.80
132.54
130.01
129.65
128.86
128.84
128.36
127.79
127.42
127.21
127.18
126.51
125.39
136 135 134 133 132 131 130 129 128 127 126 125
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
N
Ts
OMe

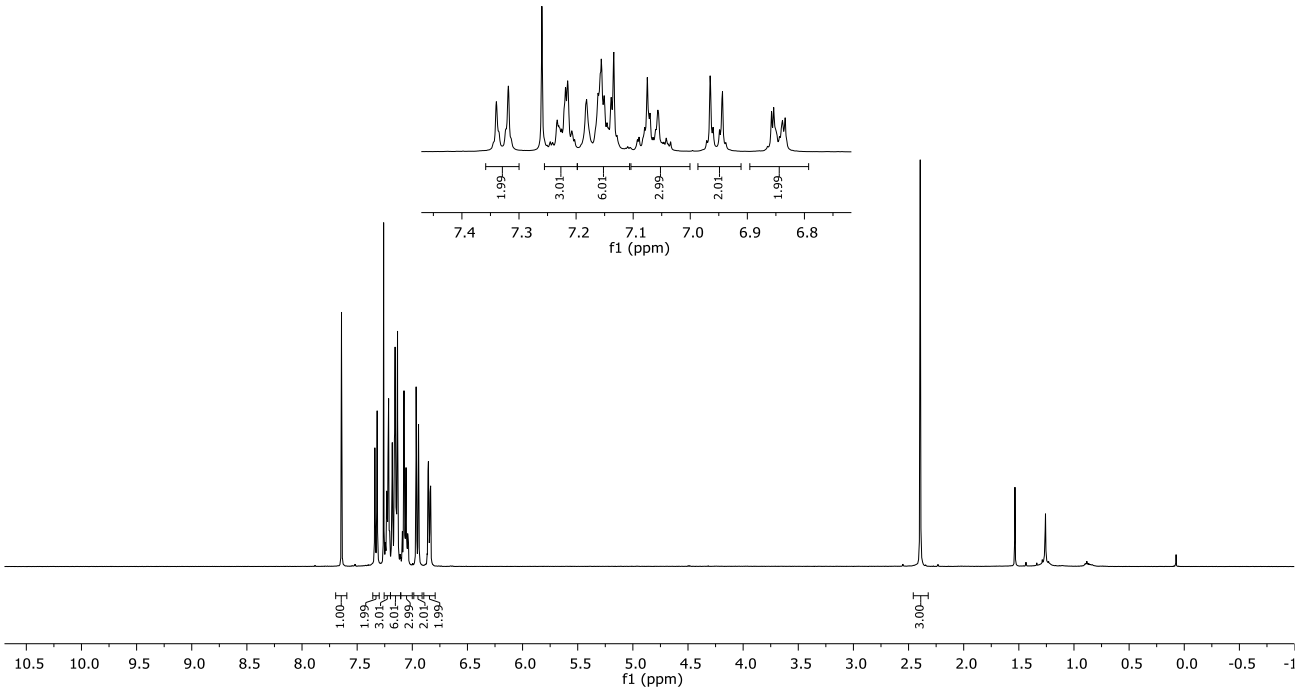
**3ga**

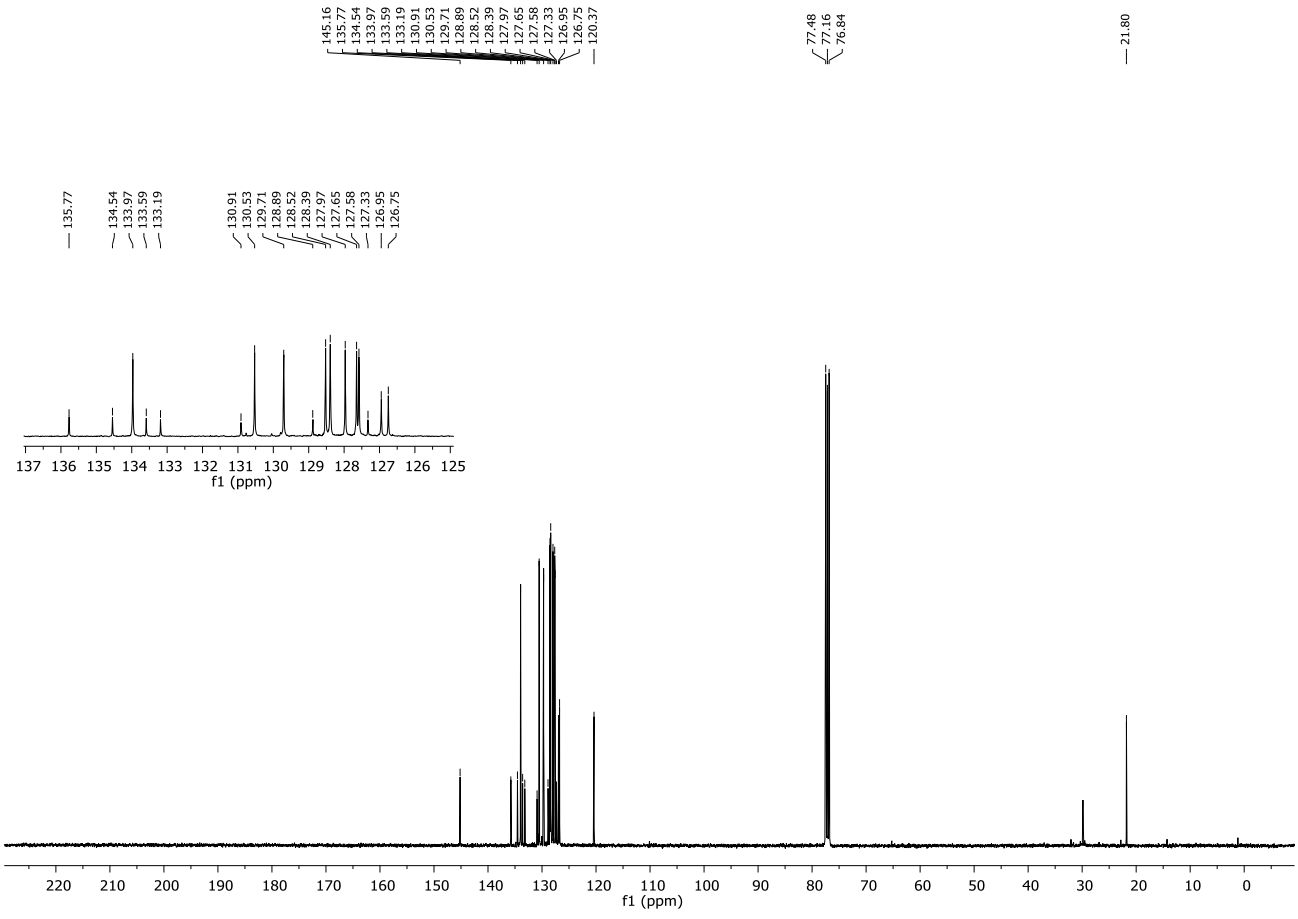

2.01
3.01
4.01
3.02
2.01
1.99
2.00
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
0.99
2.01
3.01
4.01
3.02
2.01
1.99
2.00
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

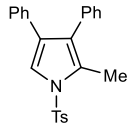

159.60
144.82
135.94
133.97
133.94
133.65
132.13
130.59
129.56
128.55
128.33
127.79
127.76
127.70
127.06
126.78
126.42
122.46
119.87
112.78
77.48
77.16
76.84
55.29
21.78
133.97
133.94
133.65
132.13
130.59
129.56
128.55
128.33
127.79
127.76
127.70
127.06
126.78
126.42
134 133 132 131 130 129 128 127 126
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
N
Ts
Cl

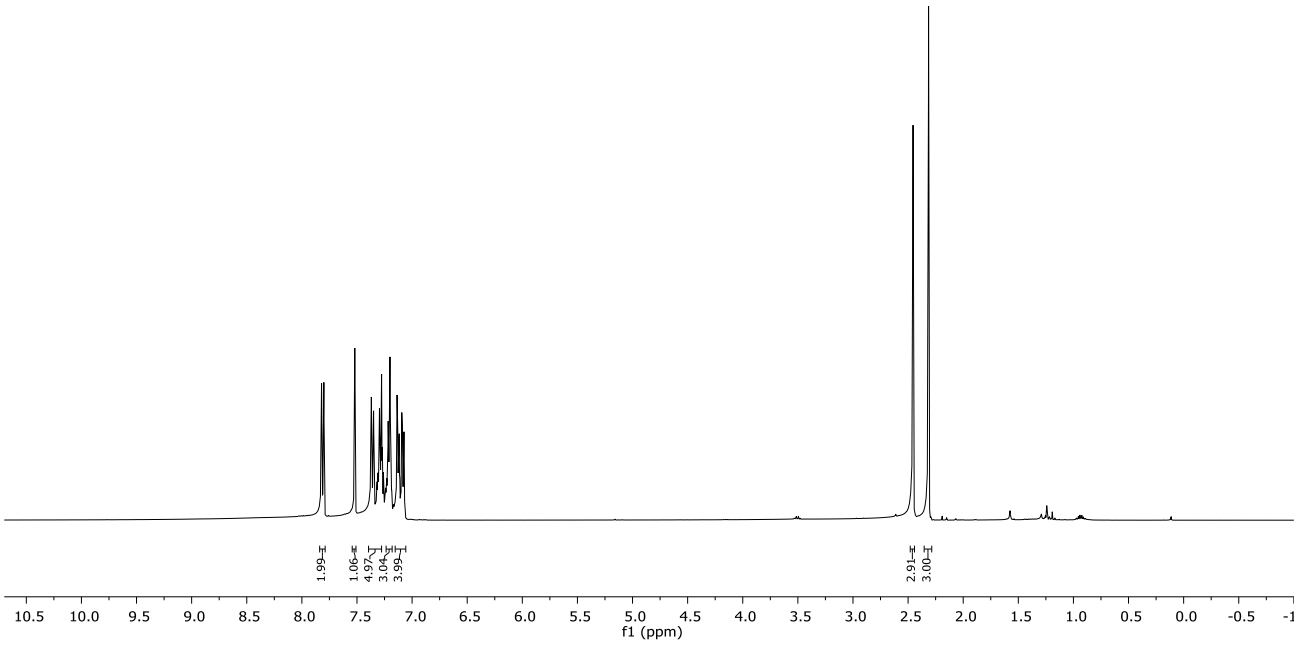
**3ha**

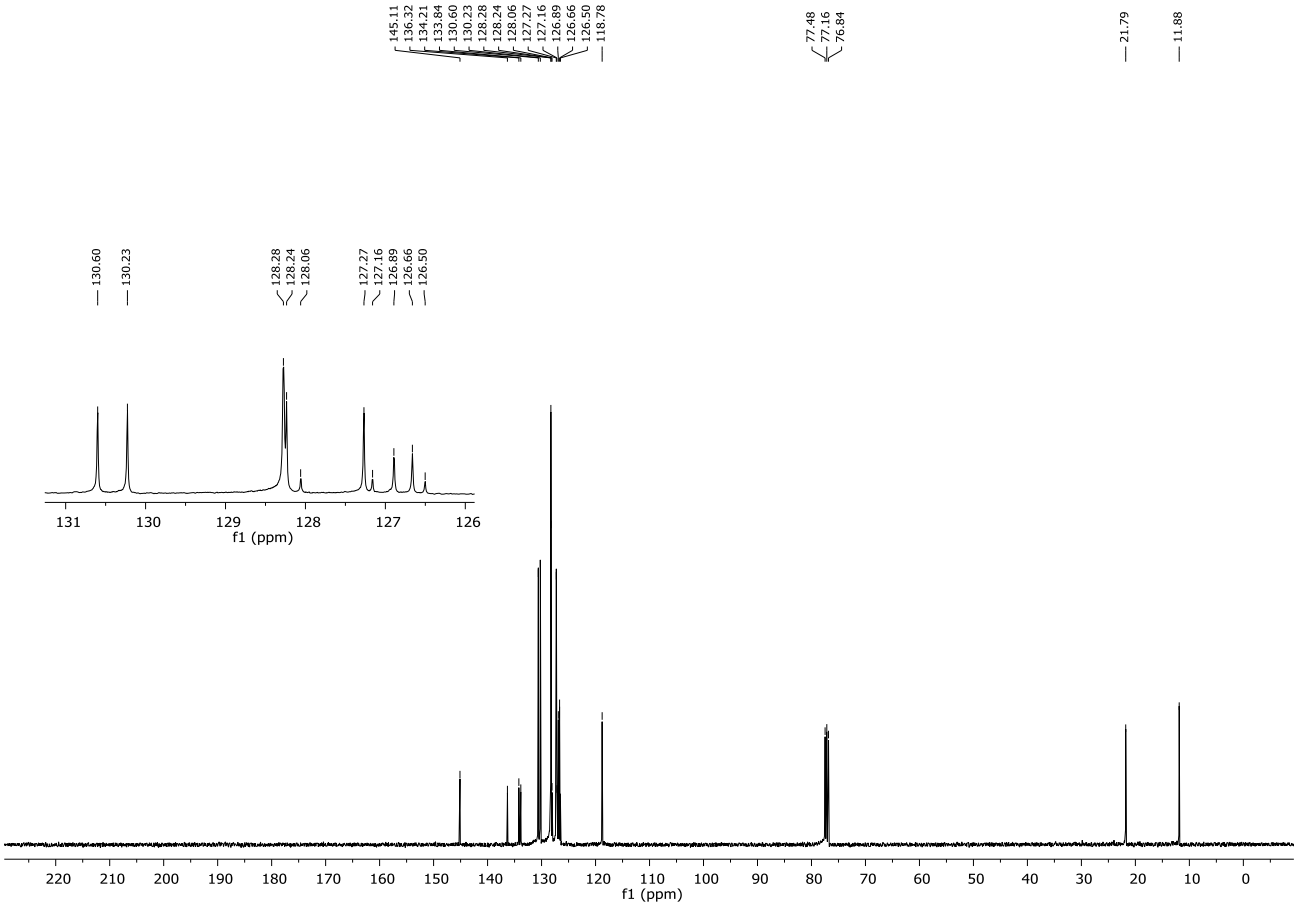

1.99
3.01
6.01
2.99
2.01
1.99
7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00
1.99
3.01
6.01
2.99
2.01
1.99
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

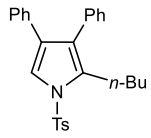

145.16
135.77
134.54
133.97
133.59
133.19
130.91
130.53
129.71
128.89
128.52
128.39
127.97
127.65
127.58
127.33
126.95
126.75
120.37
77.48
77.16
76.84
21.80
135.77
134.54
133.97
133.59
133.19
130.91
130.53
129.71
128.89
128.52
128.39
127.97
127.65
127.58
127.33
126.95
126.75
137 136 135 134 133 132 131 130 129 128 127 126 125
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
Me
N
Ts

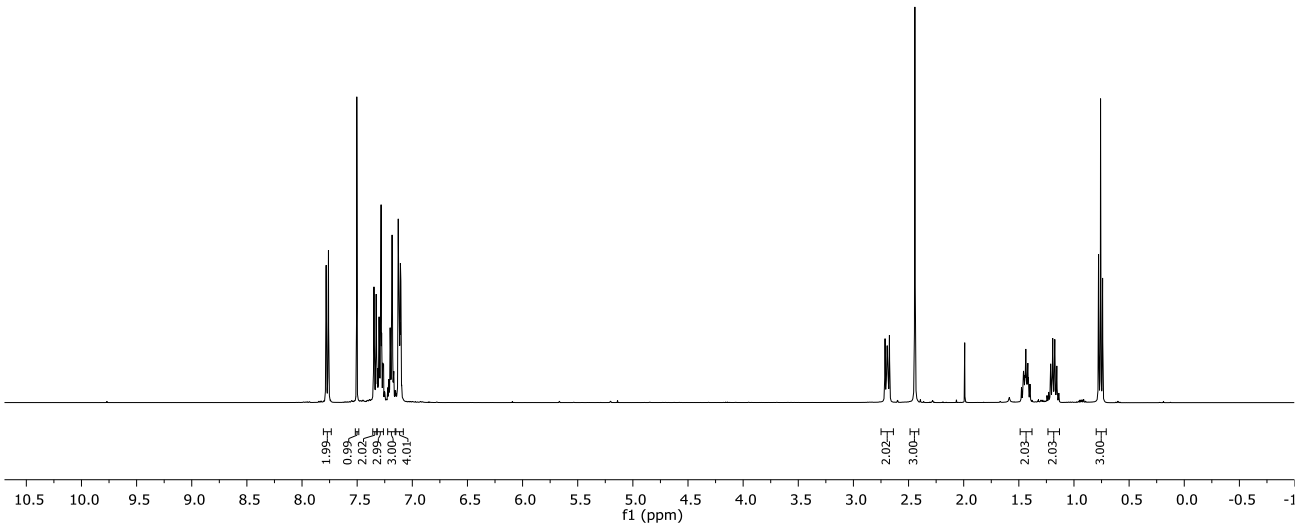
**3ia**

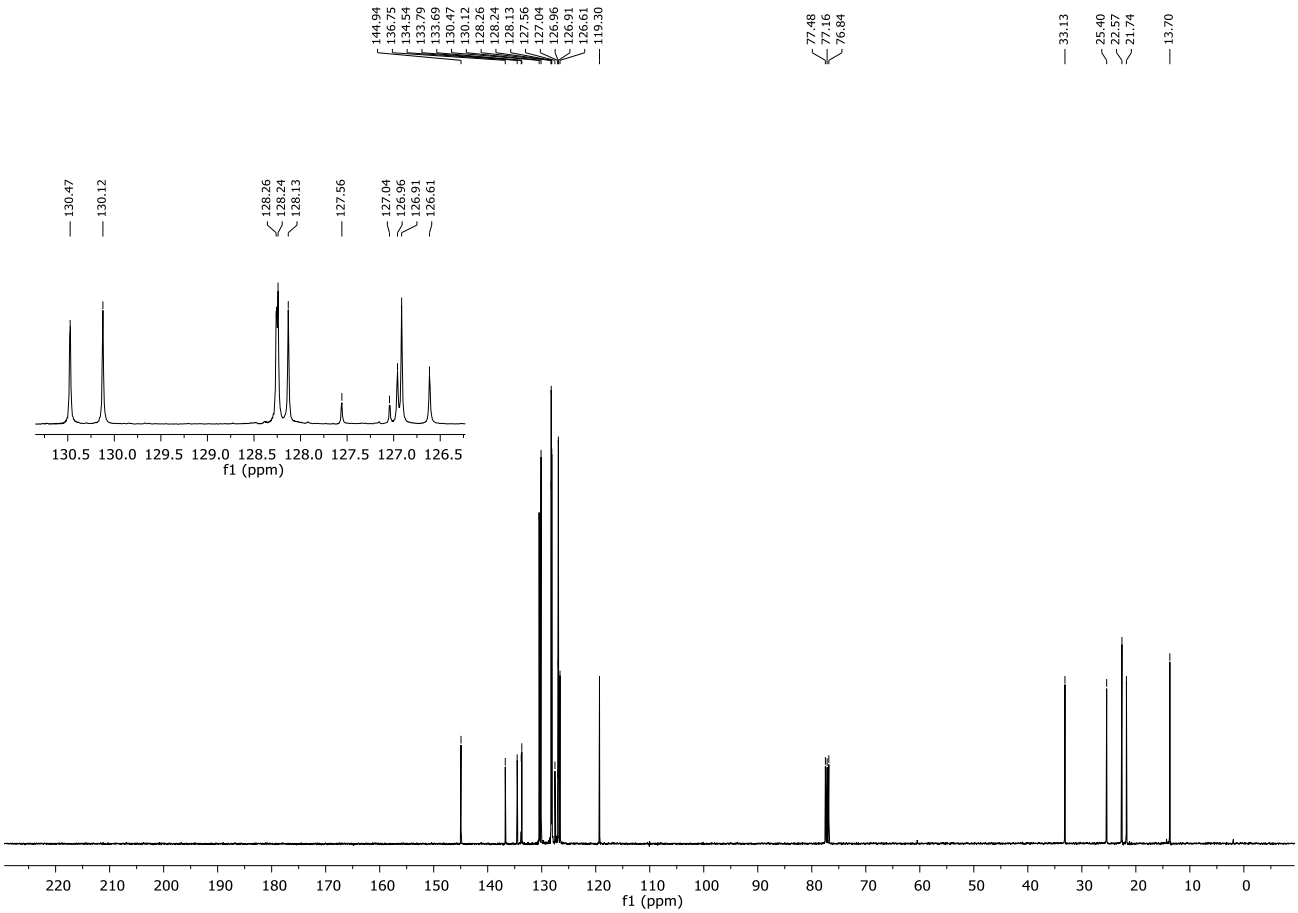

1.99
1.06
4.97
3.04
3.99
2.91
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

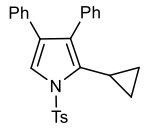

145.11
136.32
134.21
133.84
130.60
130.23
128.28
128.24
128.06
127.27
127.16
126.89
126.66
126.50
118.78
77.48
77.16
76.84
21.79
11.88
130.60
130.23
128.28
128.24
128.06
127.27
127.16
126.89
126.66
126.50
131 130 129 128 127 126
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
n-Bu
N
Ts

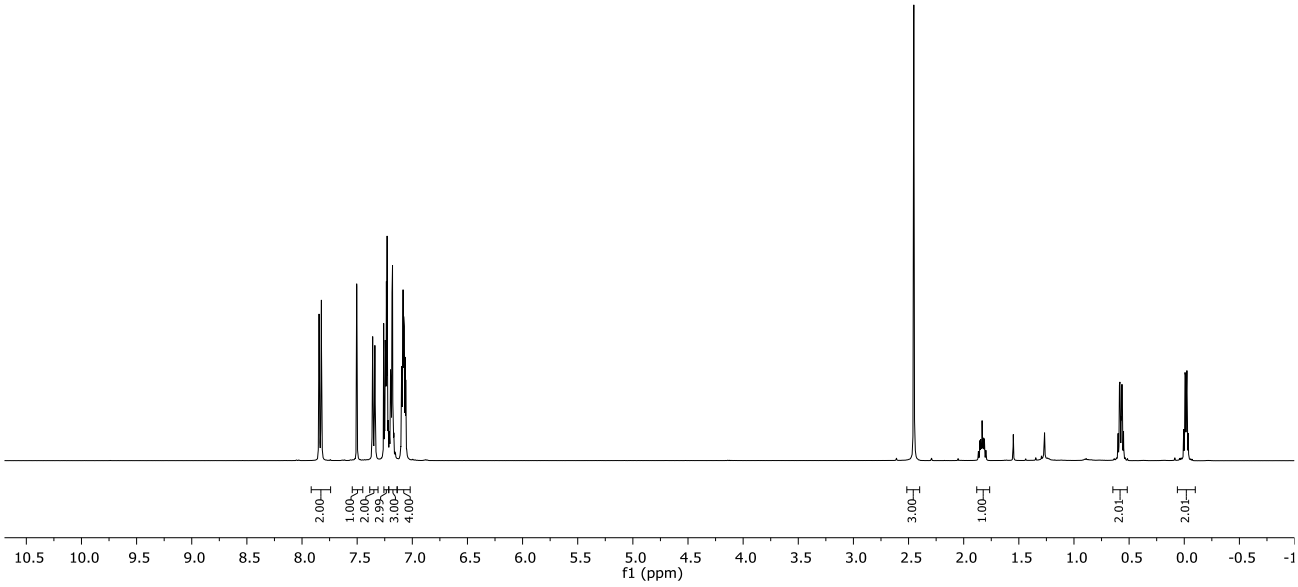
**3ja**

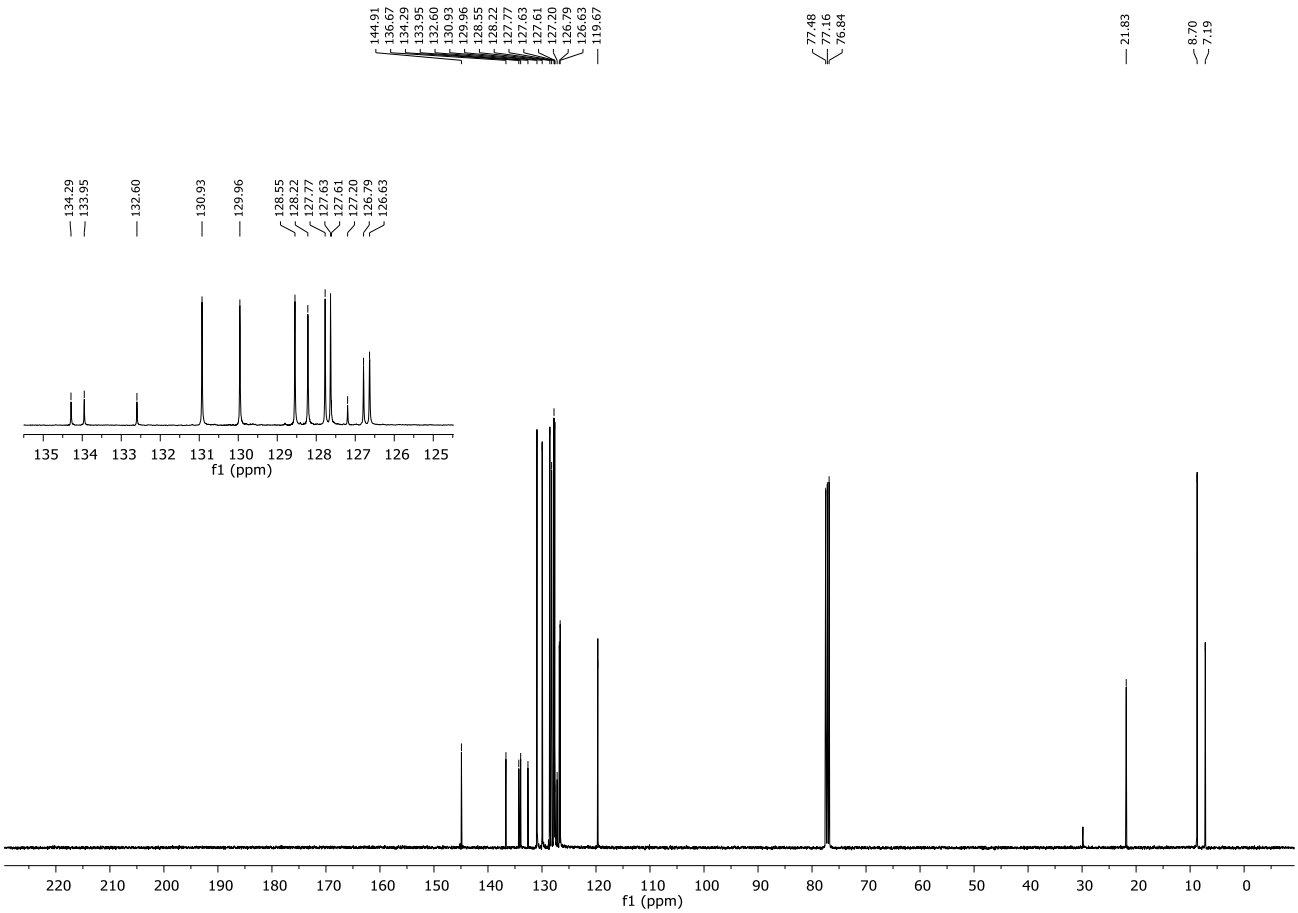

1.99
0.99
2.02
2.99
3.00
4.01
2.02
3.00
2.03
2.03
3.00
f1 (ppm)

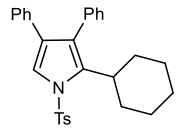

144.94
136.75
134.54
133.79
133.69
130.47
130.12
128.26
128.24
128.13
127.56
127.04
126.96
126.91
126.61
119.30
77.48
77.16
76.84
33.13
25.40
22.57
21.74
13.70
130.47
130.12
128.26
128.24
128.13
127.56
127.04
126.96
126.91
126.61
f1 (ppm)
f1 (ppm)


Ph
Ph
N
Ts

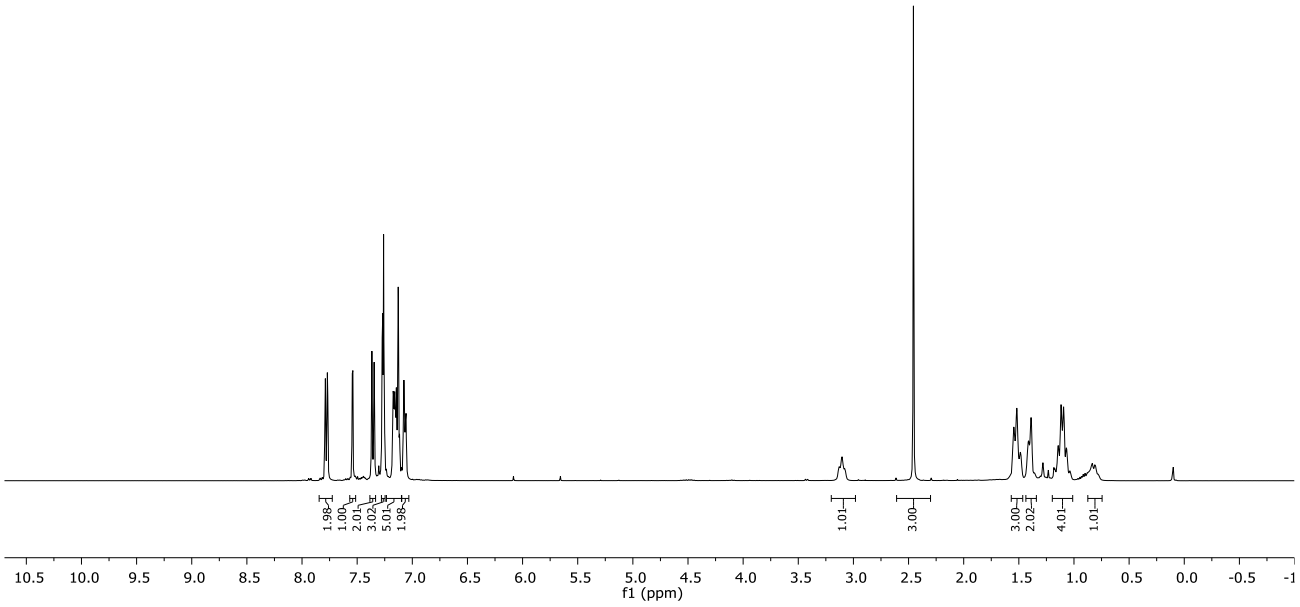
**3ka**


2.00
1.00
2.00
2.99
3.00
4.00
3.00
1.00
2.01
2.01
f1 (ppm)

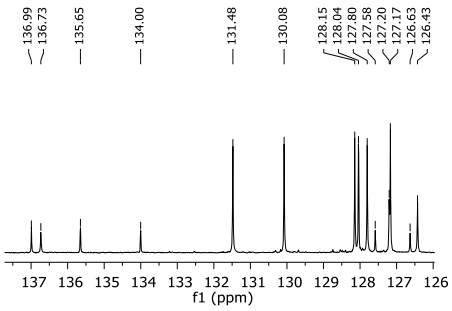

144.91
136.67
134.29
133.95
132.60
130.93
129.96
128.55
128.22
127.77
127.63
127.61
127.20
126.79
126.63
119.67
77.48
77.16
76.84
21.83
8.70
7.19
f1 (ppm)


Ph
Ph
N
Ts

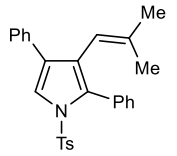
**3la**


1.98
1.00
2.01
3.02
5.01
1.98
1.01
3.00
3.00
2.02
4.01
1.01
f1 (ppm)

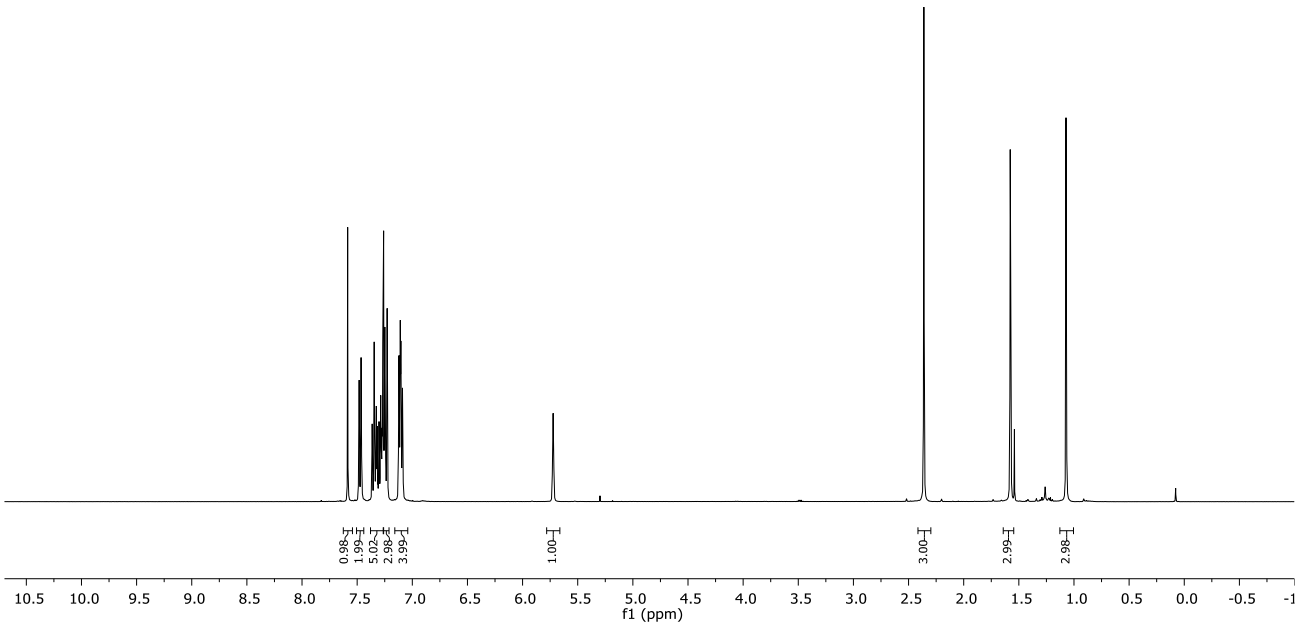

144.99
136.99
136.73
135.65
134.00
131.48
130.08
128.15
128.04
127.80
127.58
127.20
127.17
126.63
126.43
118.22
77.48
77.16
76.84
37.46
32.93
27.27
25.83
21.81

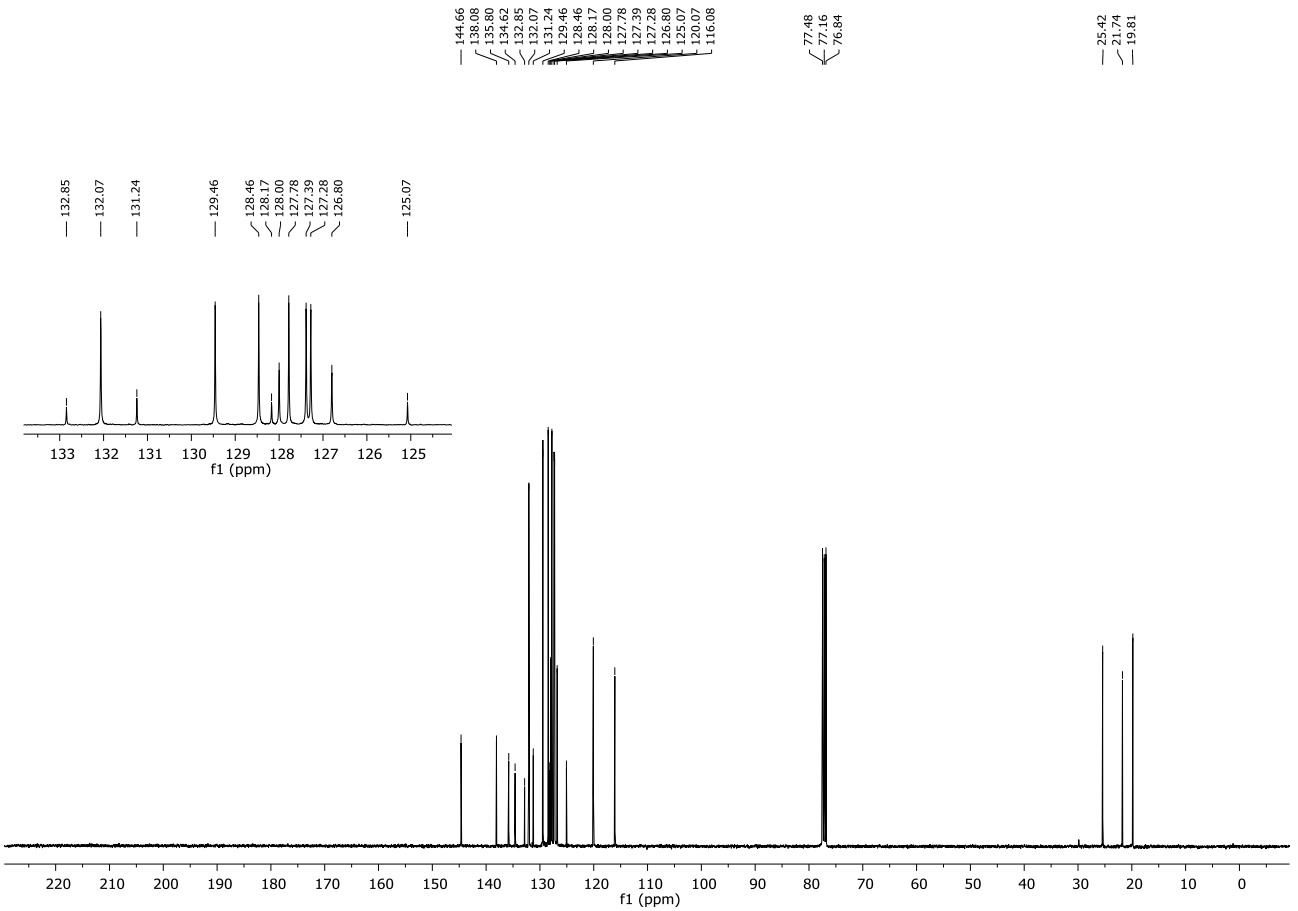

136.99
136.73
135.65
134.00
131.48
130.08
128.15
128.04
127.80
127.58
127.20
127.17
126.63
126.43
f1 (ppm)

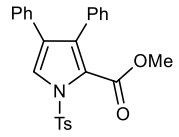

f1 (ppm)


Me
Ph
Me
Ph
N
Ts

**3ma**

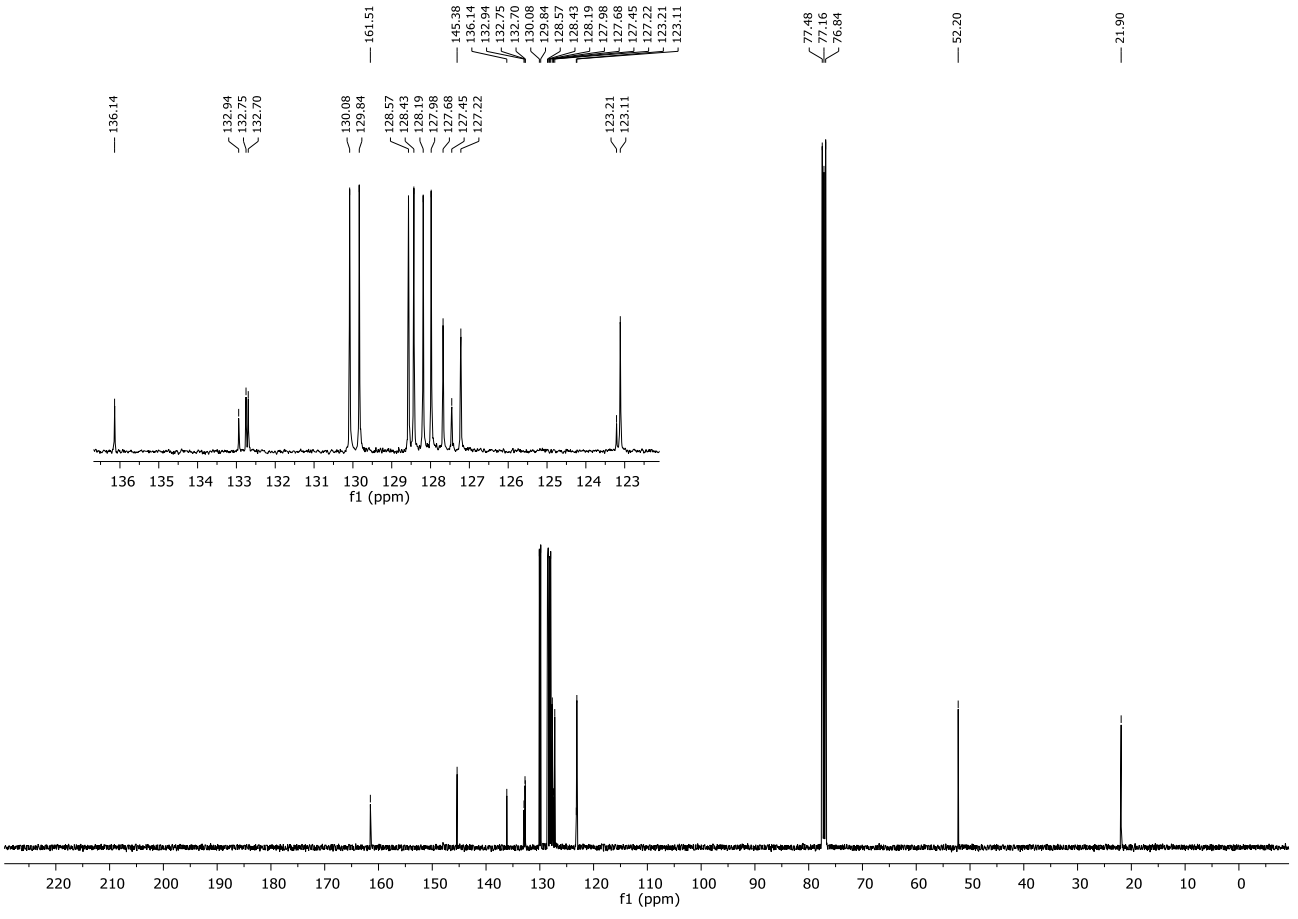

0.98
1.99
5.02
2.98
3.99
1.00
3.00
2.99
2.98
f1 (ppm)

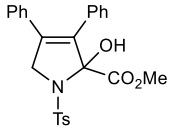

144.66
138.08
135.80
134.62
132.85
132.07
131.24
129.46
128.46
128.17
128.00
127.78
127.39
127.28
126.80
125.07
120.07
116.08
77.48
77.16
76.84
25.42
21.74
19.81
f1 (ppm)


Ph
Ph
OMe
N
Ts
O

**3na**

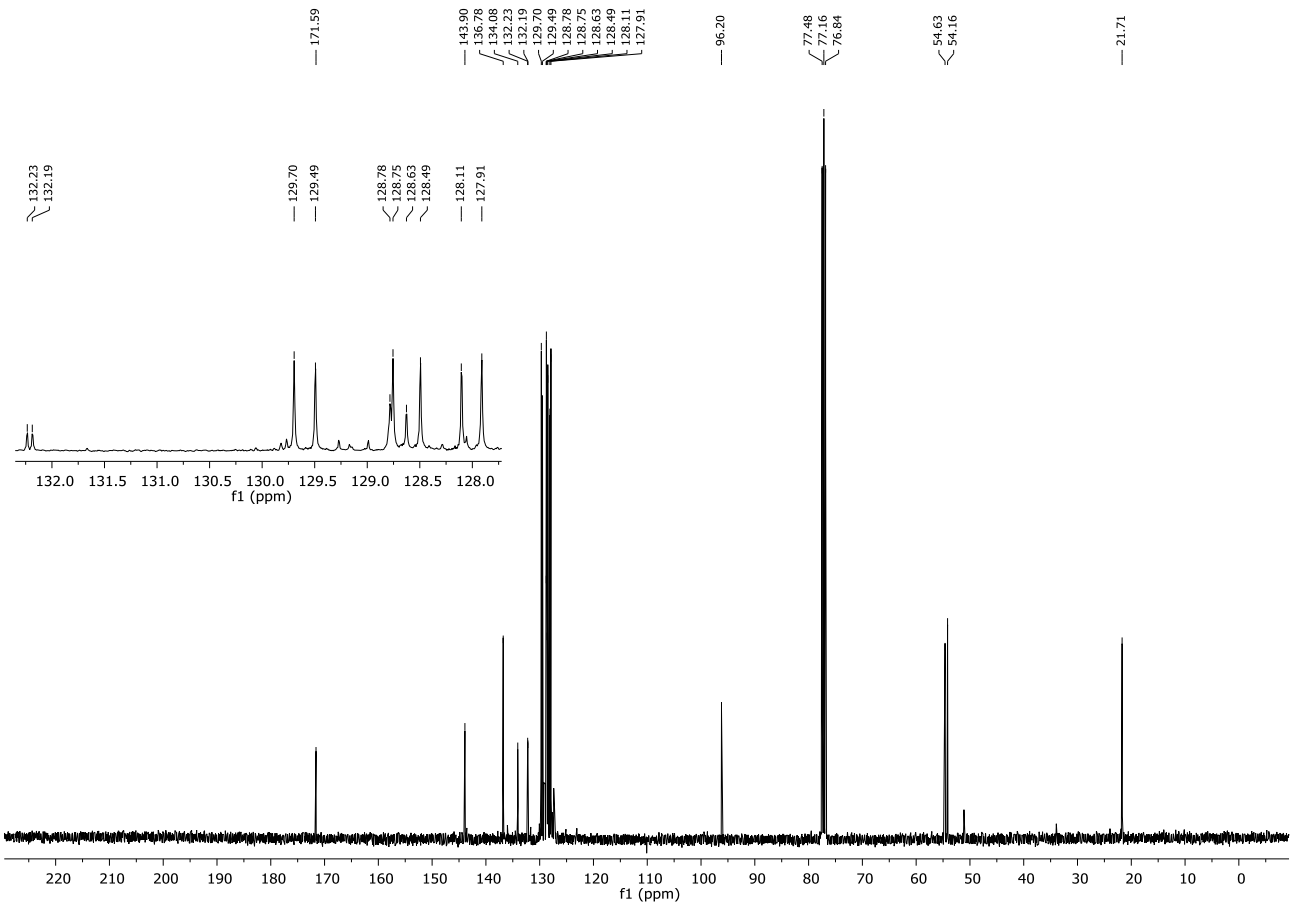

1.99
0.99
2.01
2.01
4.00
4.01
3.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

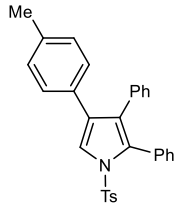

161.51
145.38
136.14
132.94
132.75
132.70
130.08
129.84
128.57
128.43
128.19
127.98
127.68
127.45
127.22
123.21
123.11
77.48
77.16
76.84
52.20
21.90
136 135 134 133 132 131 130 129 128 127 126 125 124 123
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



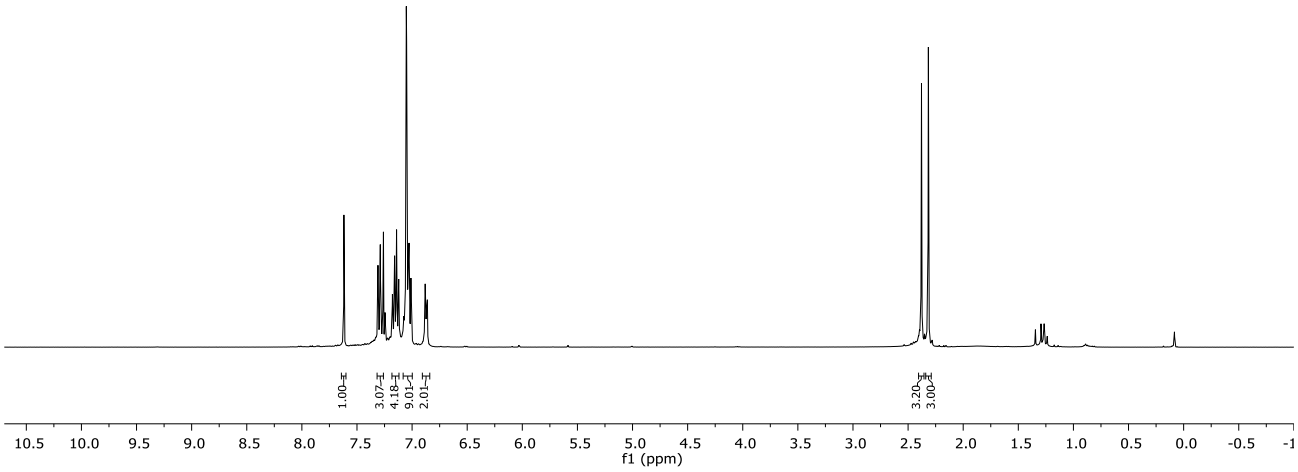

**5na**
(contains trace impurities)

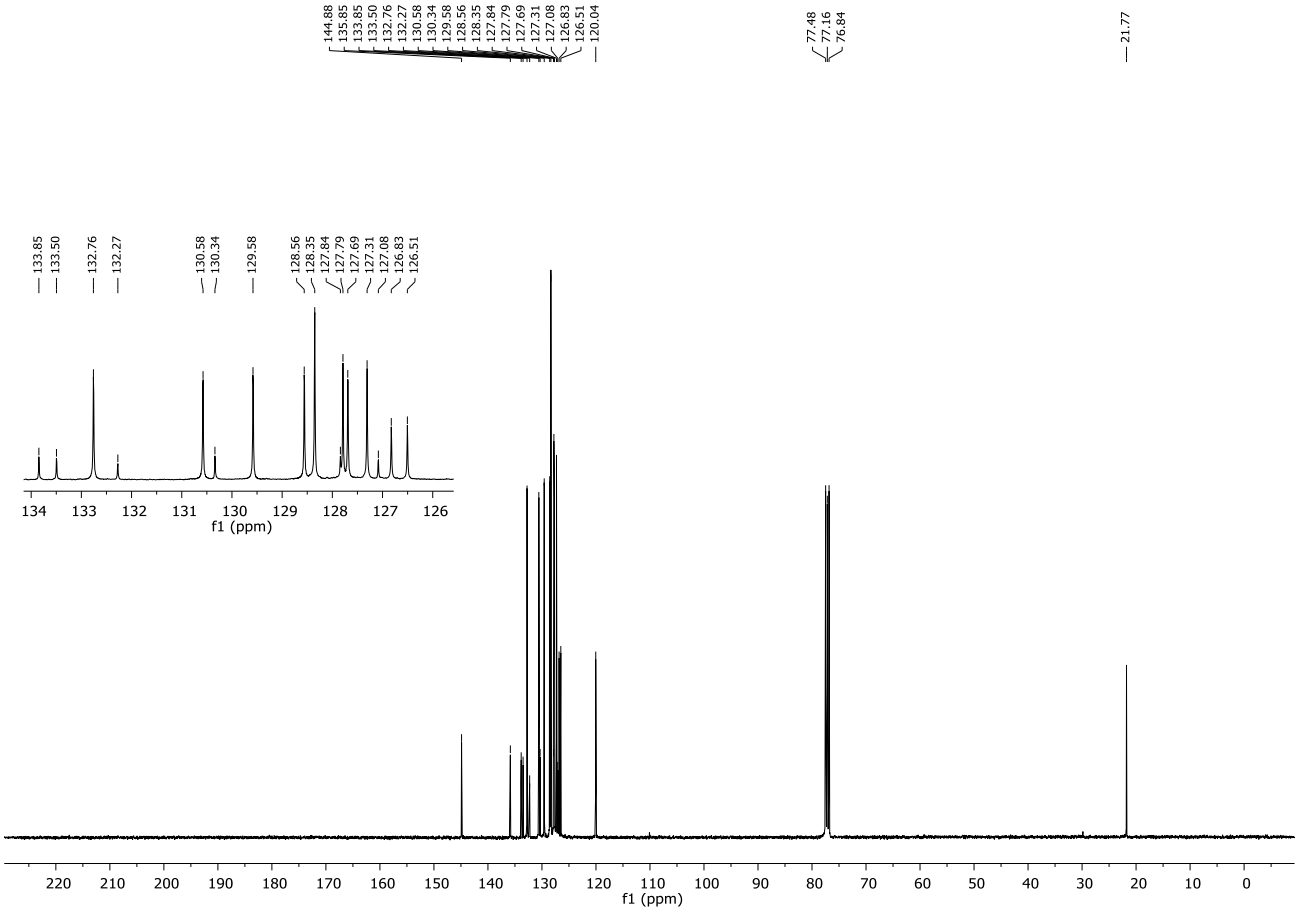


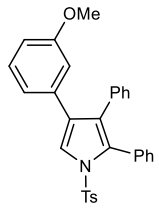




Me
Ph
Ph
N
Ts

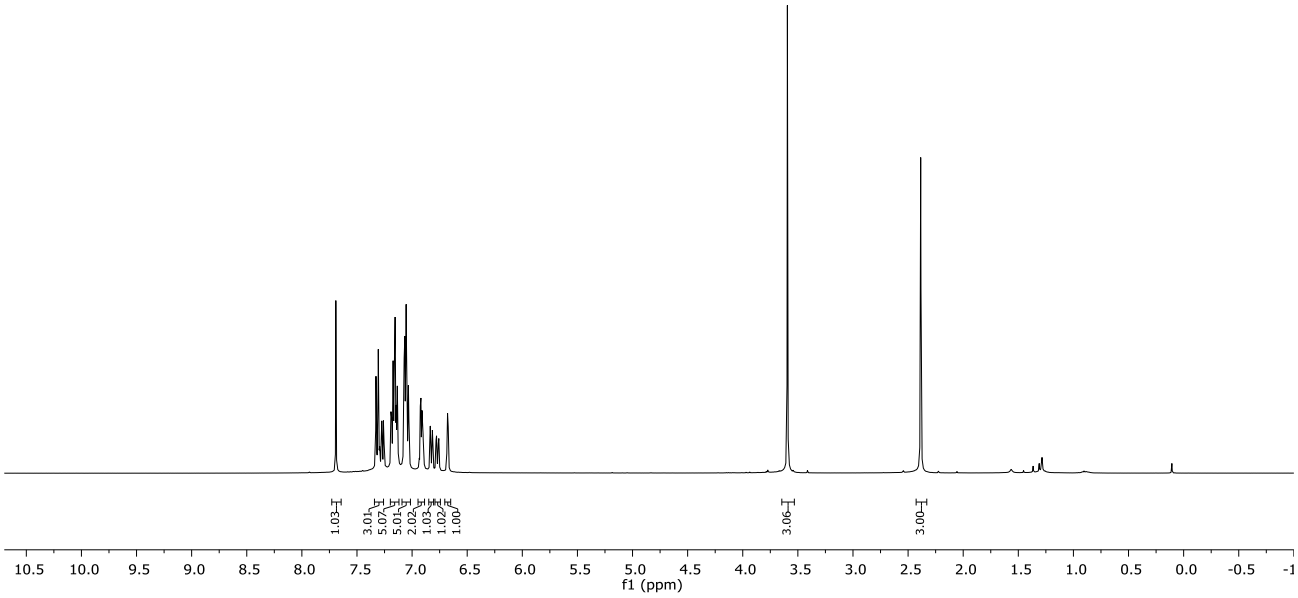
**3ab**


1.00
3.07
4.18
9.01
2.01
3.20
3.00
f1 (ppm)

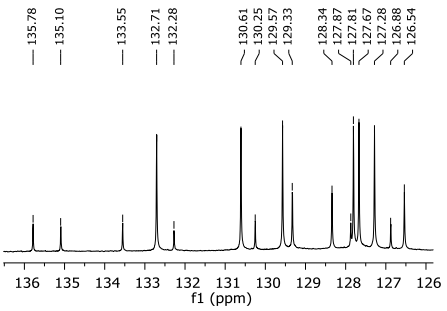

144.88
135.85
133.85
133.50
132.76
132.27
130.58
130.34
129.58
128.56
128.35
127.84
127.79
127.69
127.31
127.08
126.83
126.51
120.04
77.48
77.16
76.84
21.77
f1 (ppm)


OMe
Ph
Ph
N
Ts

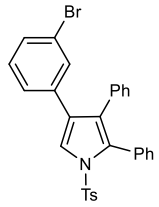
**3ac**


1.03
3.01
5.07
5.01
2.02
1.03
1.02
1.00
3.06
3.00
f1 (ppm)

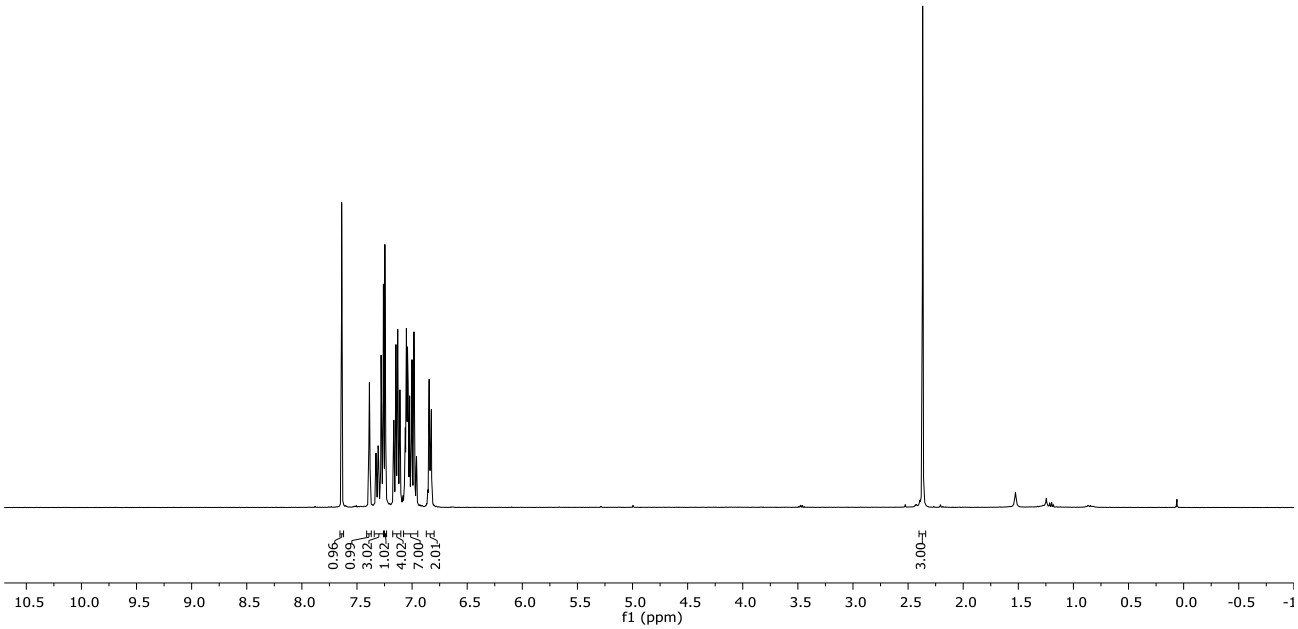

159.42
144.91
135.78
135.10
133.55
132.71
132.28
130.61
130.25
129.57
129.33
128.34
127.87
127.81
127.67
127.28
126.88
126.54
120.82
119.99
113.56
113.02
77.48
77.16
76.84
55.06
21.74

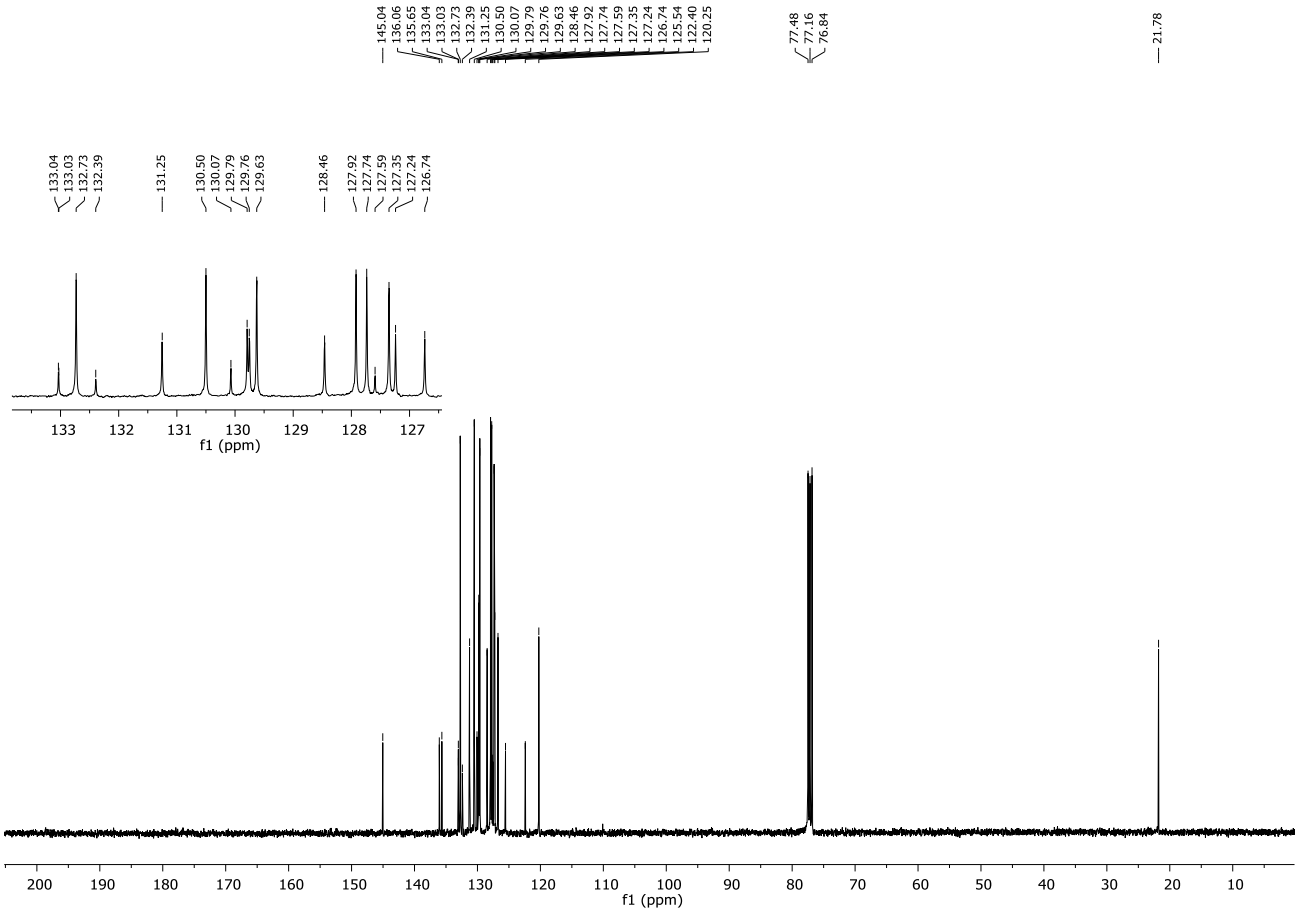

135.78
135.10
133.55
132.71
132.28
130.61
130.25
129.57
129.33
128.34
127.87
127.81
127.67
127.28
126.88
126.54
136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)

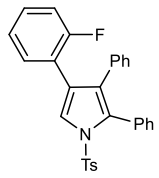

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
Ph
Ph
N
Ts

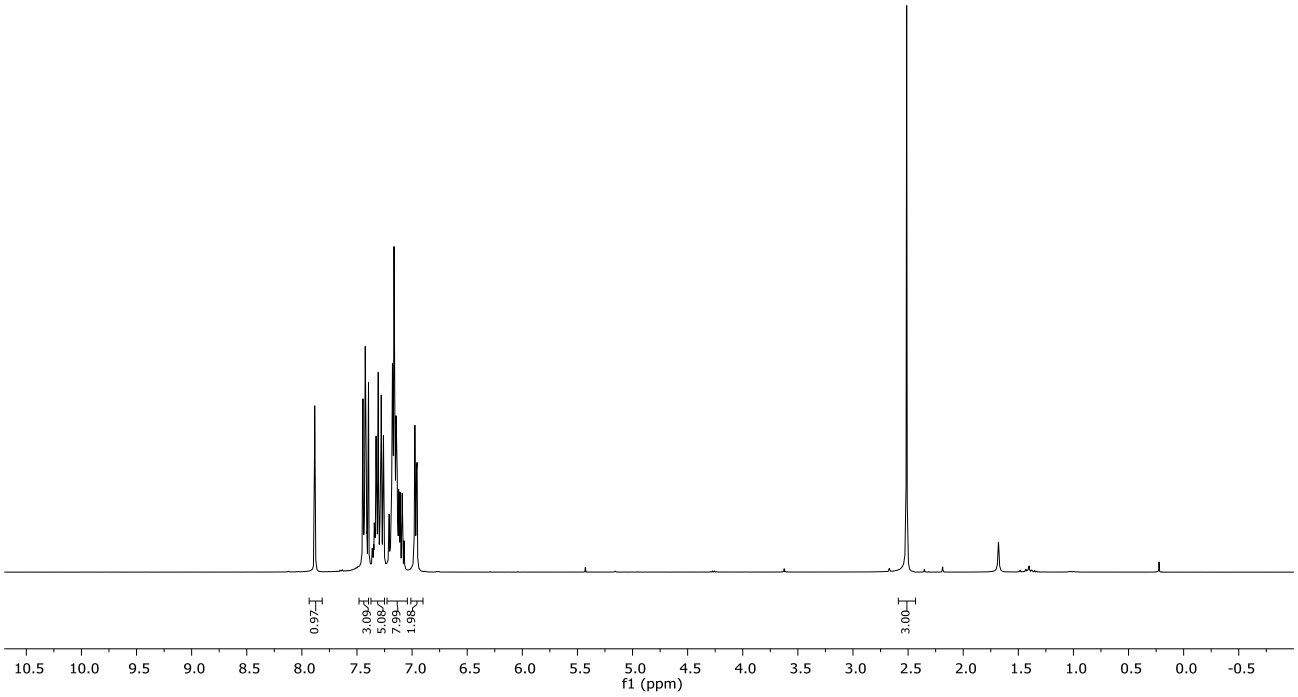
**3ad**

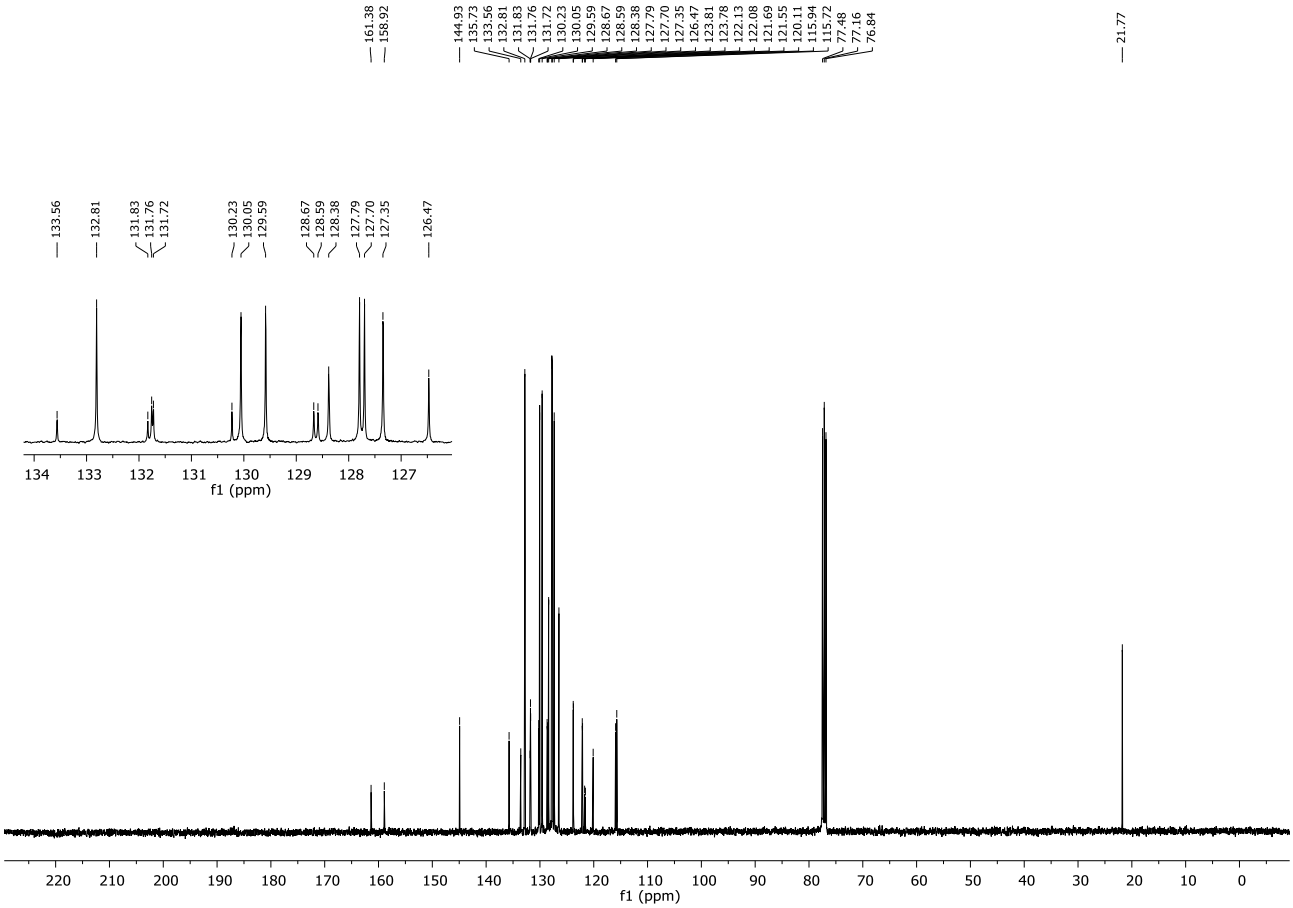

0.96
0.99
3.02
1.02
4.02
7.00
2.01
3.00
f1 (ppm)

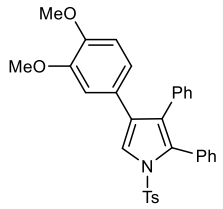

145.04
136.06
135.65
133.04
133.03
132.73
132.39
131.25
130.50
130.07
129.79
129.76
129.63
128.46
127.92
127.74
127.59
127.35
127.24
126.74
125.54
122.40
120.25
77.48
77.16
76.84
21.78
f1 (ppm)


F
Ph
Ph
N
Ts

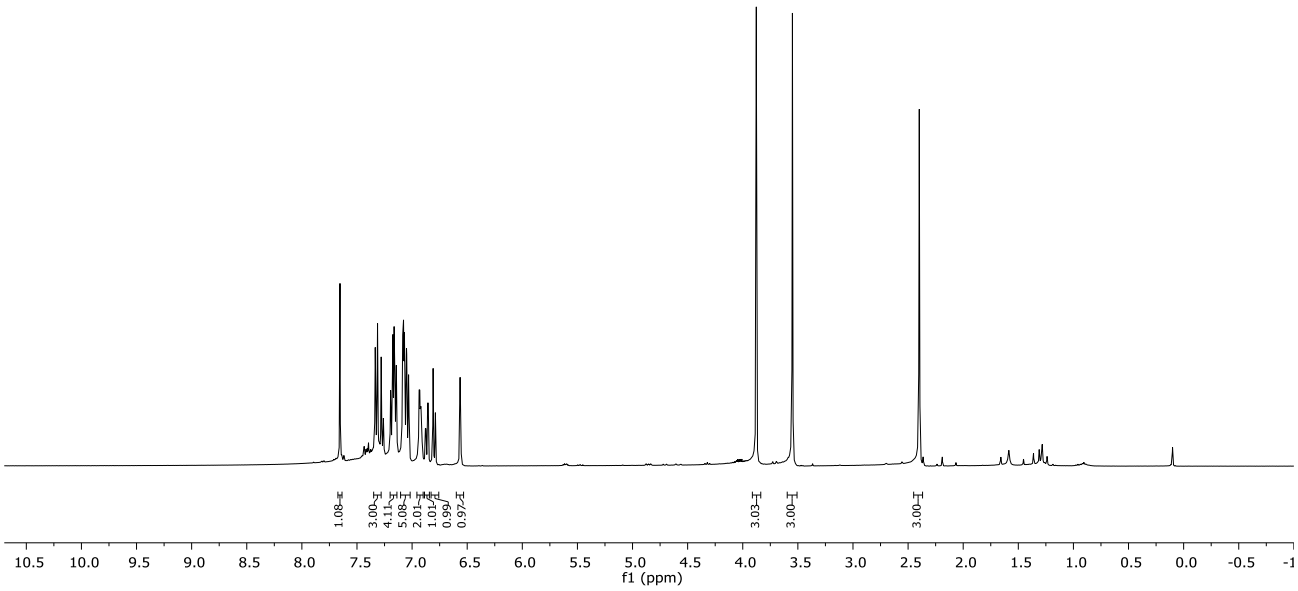
**3ae**


0.97
3.09
5.08
7.99
1.98
3.00
f1 (ppm)

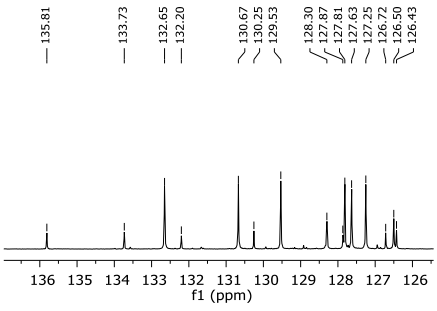

161.38
158.92
144.93
135.73
133.56
132.81
131.83
131.76
131.72
130.23
130.05
129.59
128.67
128.59
128.38
127.79
127.70
127.35
126.47
123.81
123.78
122.13
122.08
121.69
121.55
120.11
115.94
115.72
77.48
77.16
76.84
21.77
f1 (ppm)

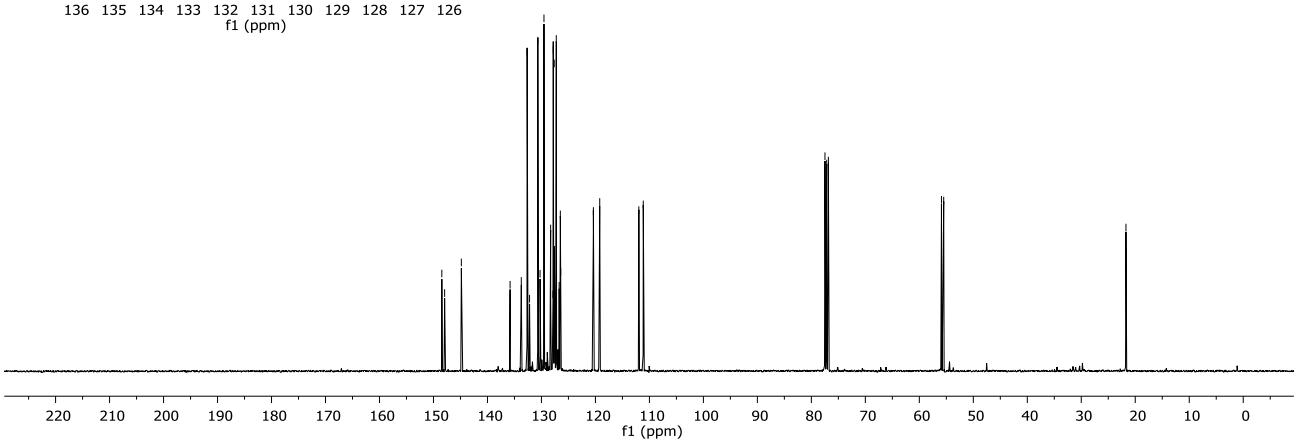

MeO
MeO
Ph
Ph
N
Ts

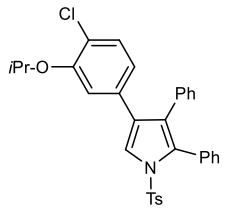
**3af**


1.08
3.00
4.11
5.08
2.01
1.01
0.99
0.97
3.03
3.00
3.00
f1 (ppm)

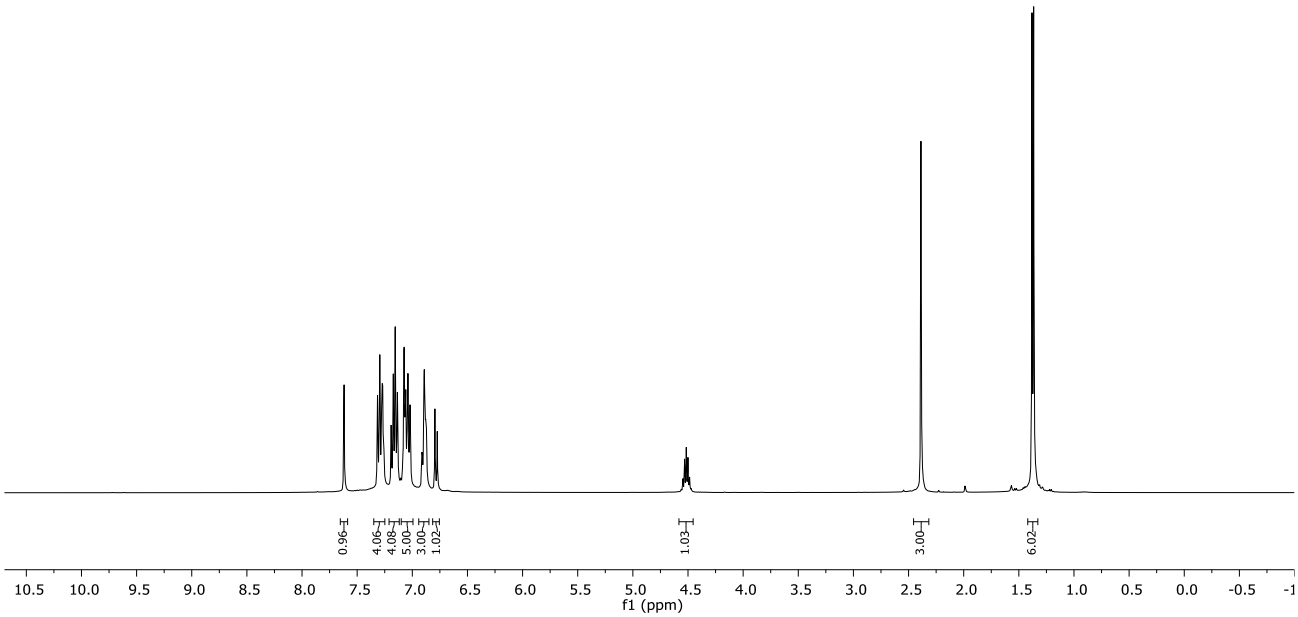

148.45
147.93
144.84
135.81
133.73
132.65
132.20
130.67
130.25
129.53
128.30
127.87
127.81
127.63
127.25
126.72
126.50
126.43
120.38
119.20
111.96
111.14
77.48
77.16
76.84
55.90
55.49
21.72

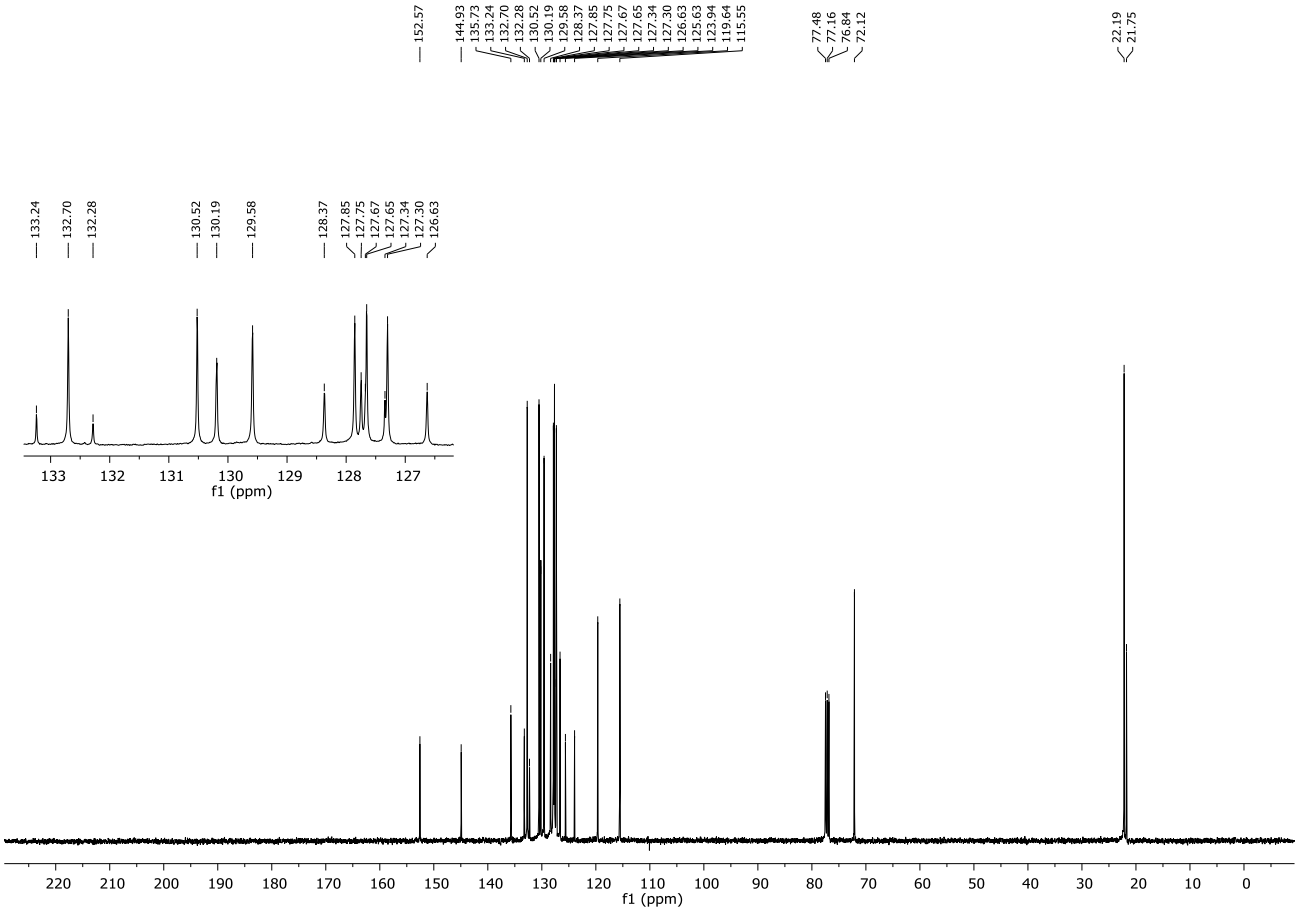

135.81
133.73
132.65
132.20
130.67
130.25
129.53
128.30
127.87
127.81
127.63
127.25
126.72
126.50
126.43
f1 (ppm)

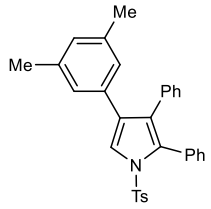

f1 (ppm)


Cl
iPr-O
Ph
Ph
N
Ts

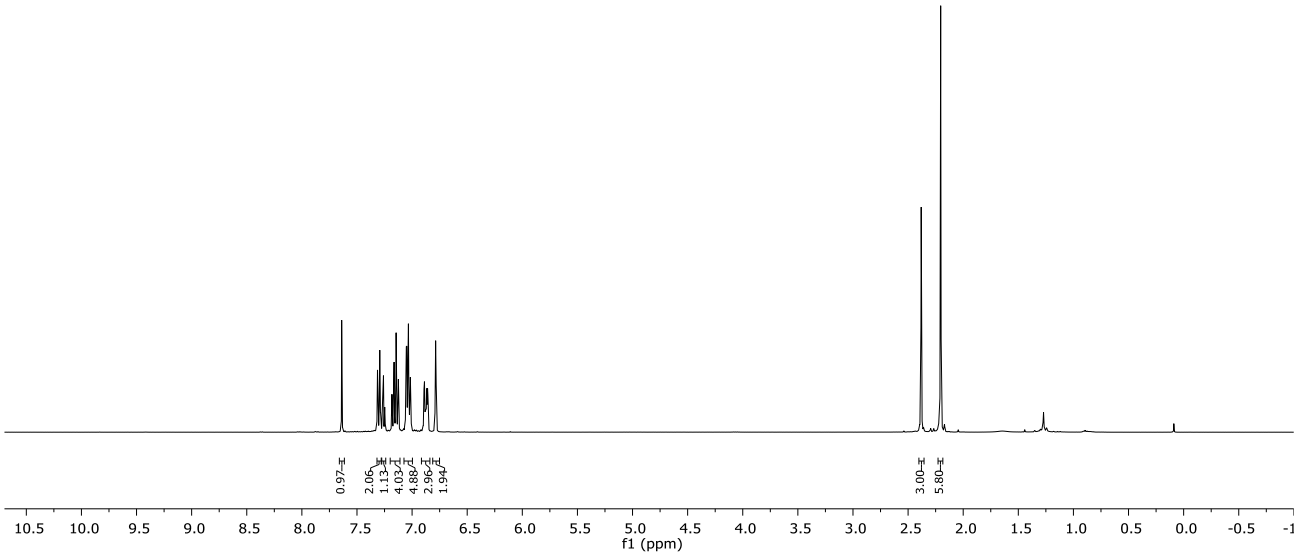
**3ag**

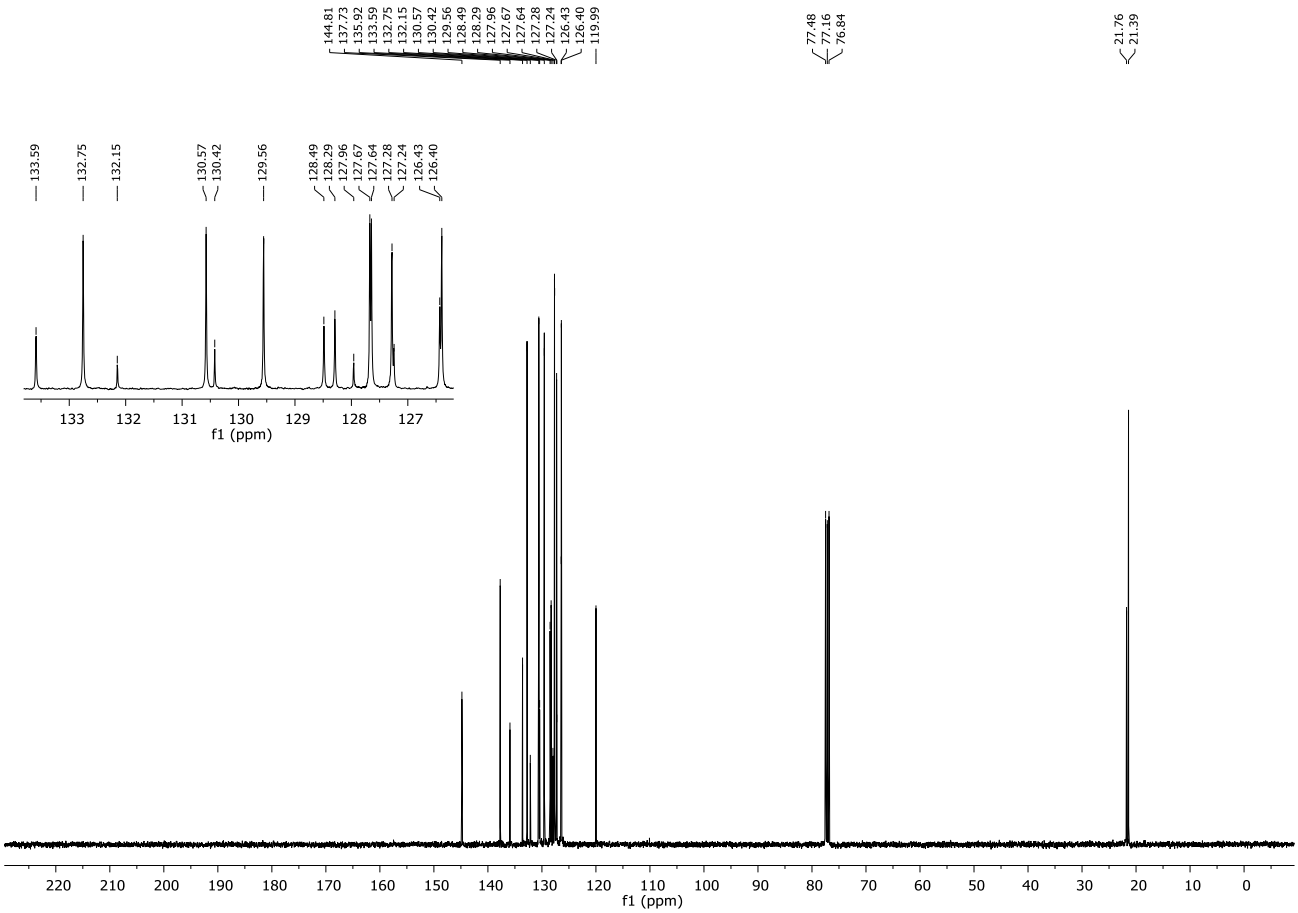

0.96
4.06
4.08
5.00
3.00
1.02
1.03
3.00
6.02
f1 (ppm)

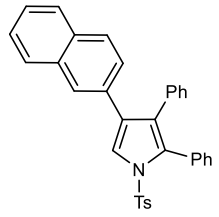

152.57
144.93
135.73
133.24
132.70
132.28
130.52
130.19
129.58
128.37
127.85
127.75
127.67
127.65
127.34
127.30
126.63
125.63
123.94
119.64
115.55
77.48
77.16
76.84
72.12
22.19
21.75
f1 (ppm)


Me
Me
Ph
Ph
N
Ts

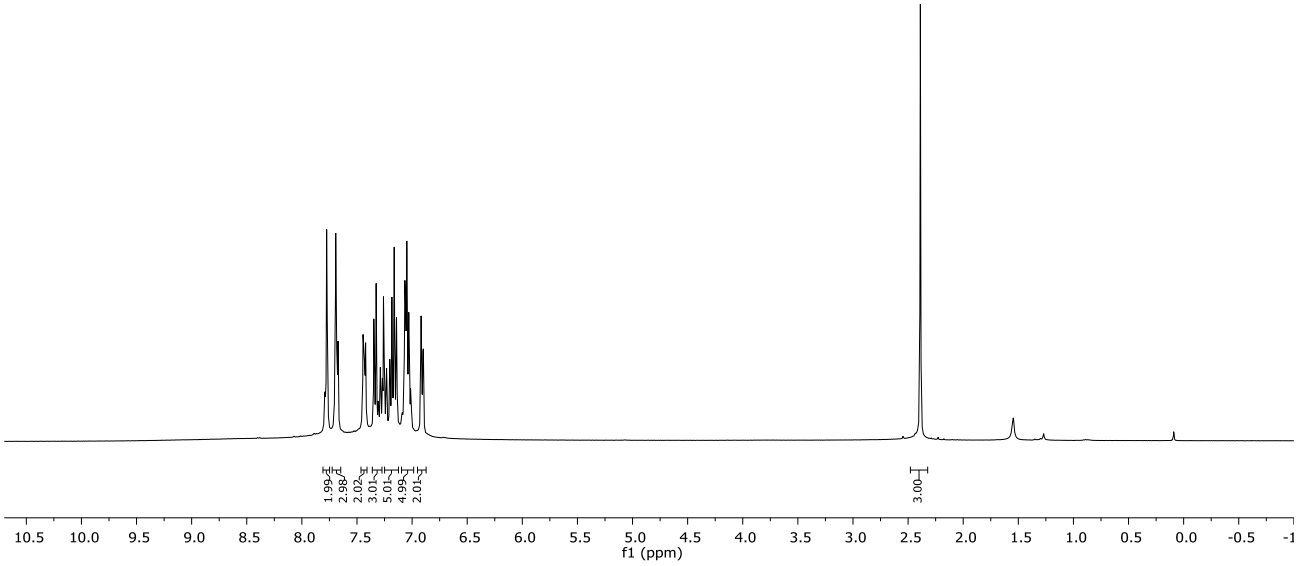
**3ah**

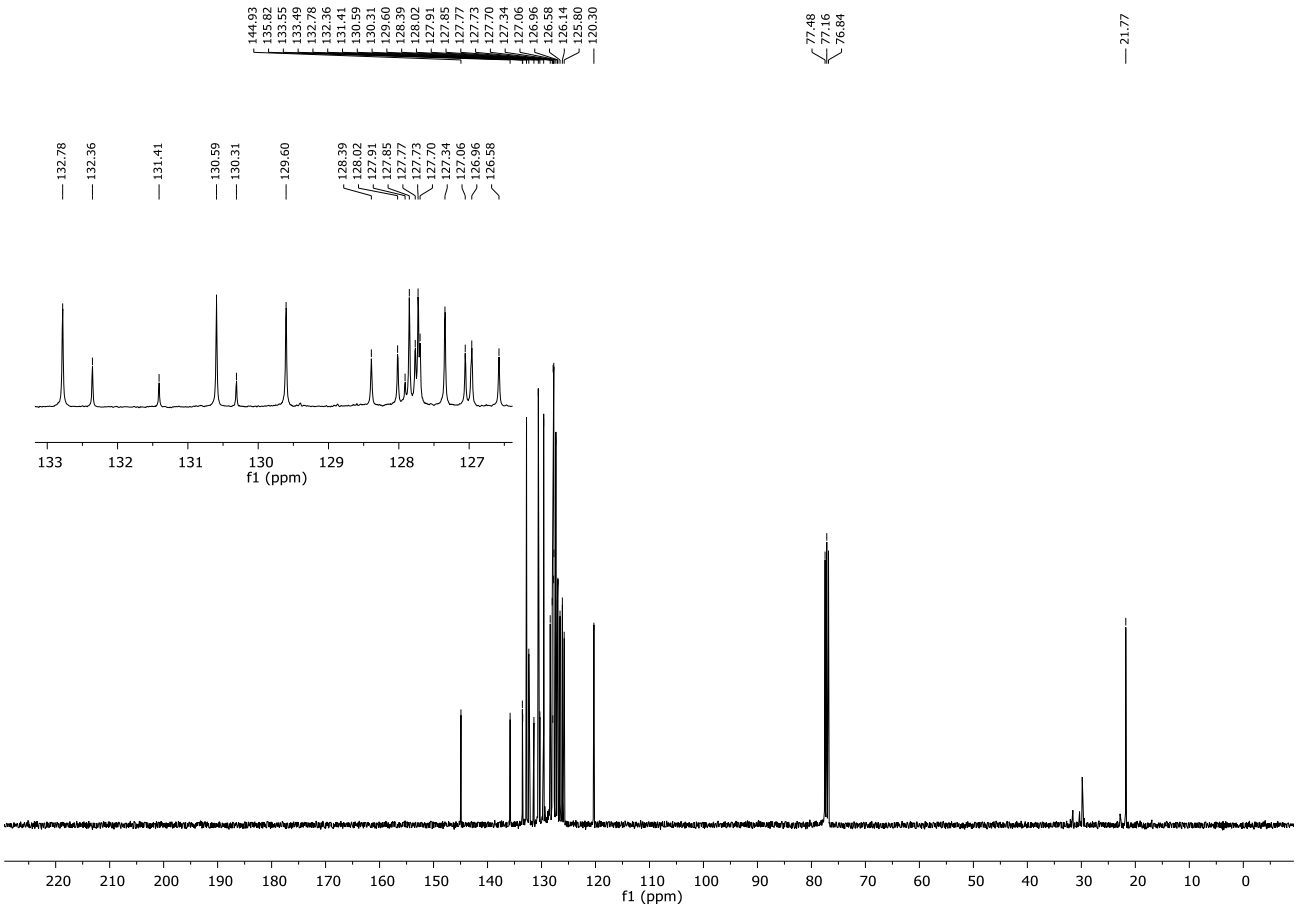

0.97
2.05
1.13
4.03
4.88
2.96
1.94
3.00
5.80
f1 (ppm)

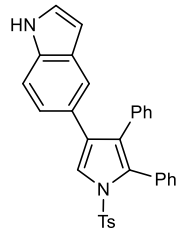

144.81
137.73
135.92
133.59
132.75
132.15
130.57
130.42
129.56
128.49
128.29
127.96
127.67
127.64
127.28
127.24
126.43
126.40
119.99
77.48
77.16
76.84
21.76
21.39
133.59
132.75
132.15
130.57
130.42
129.56
128.49
128.29
127.96
127.67
127.64
127.28
127.24
126.43
126.40
f1 (ppm)
f1 (ppm)


Ph
Ph
N
Ts

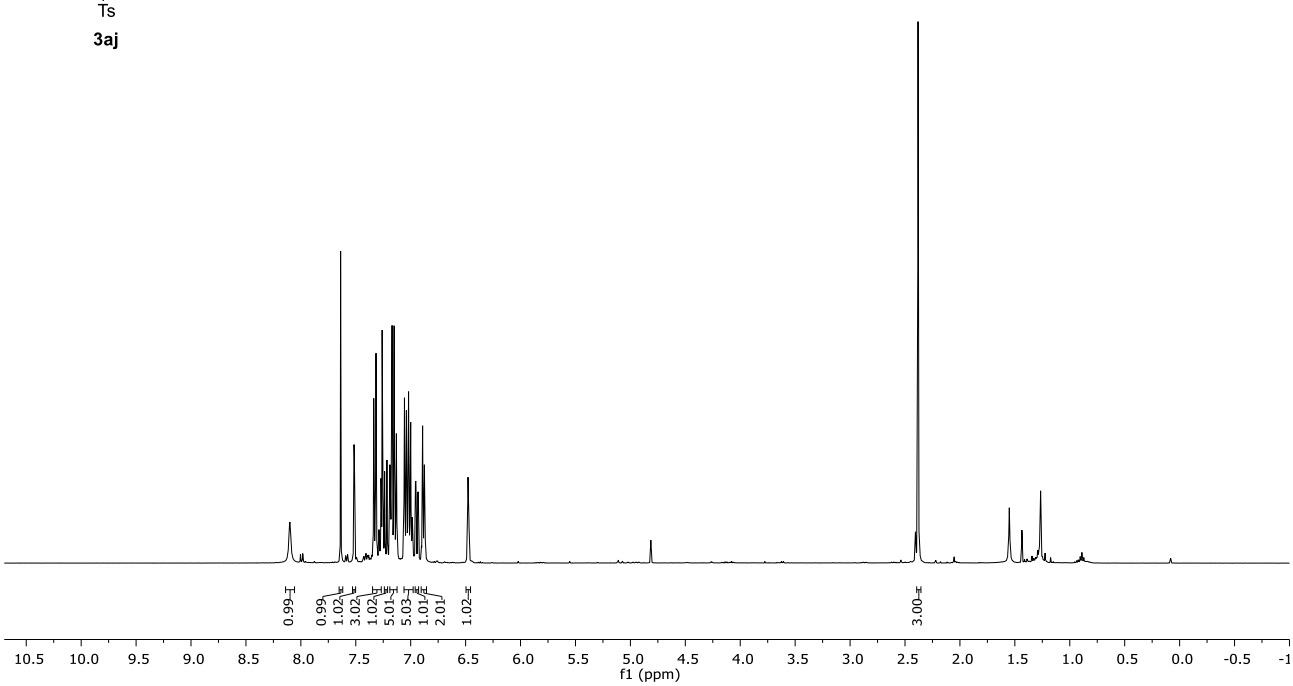
**3ai**

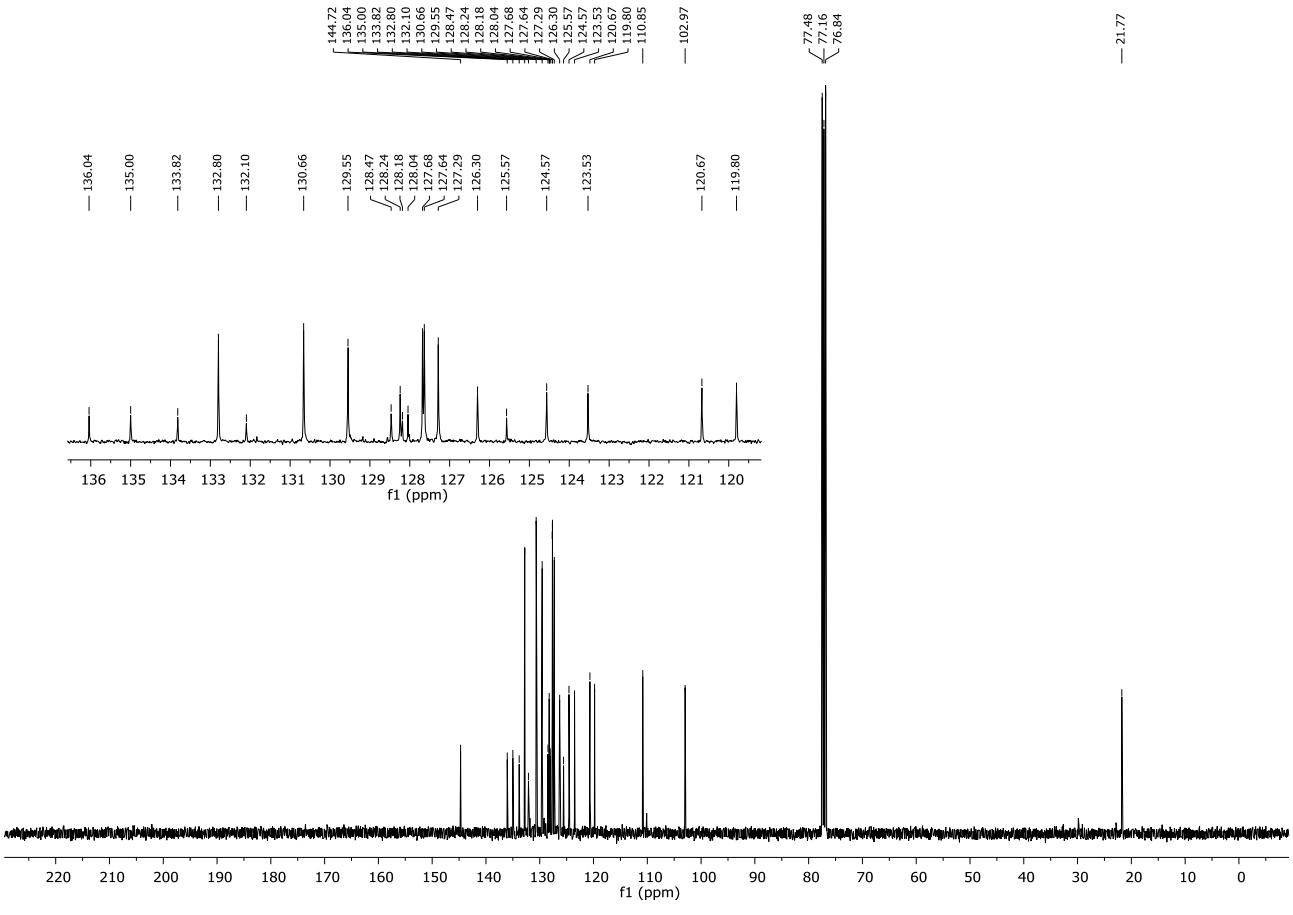

1.99
2.98
2.02
3.01
5.01
4.99
2.01
3.00
f1 (ppm)

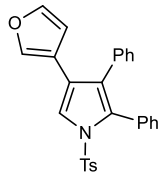

144.93
135.82
133.55
133.49
132.78
132.36
131.41
130.59
130.31
129.60
128.39
128.02
127.91
127.85
127.77
127.73
127.70
127.34
127.06
126.96
126.58
126.14
125.80
120.30
77.48
77.16
76.84
21.77
f1 (ppm)


HN
Ph
Ph
N
Ts

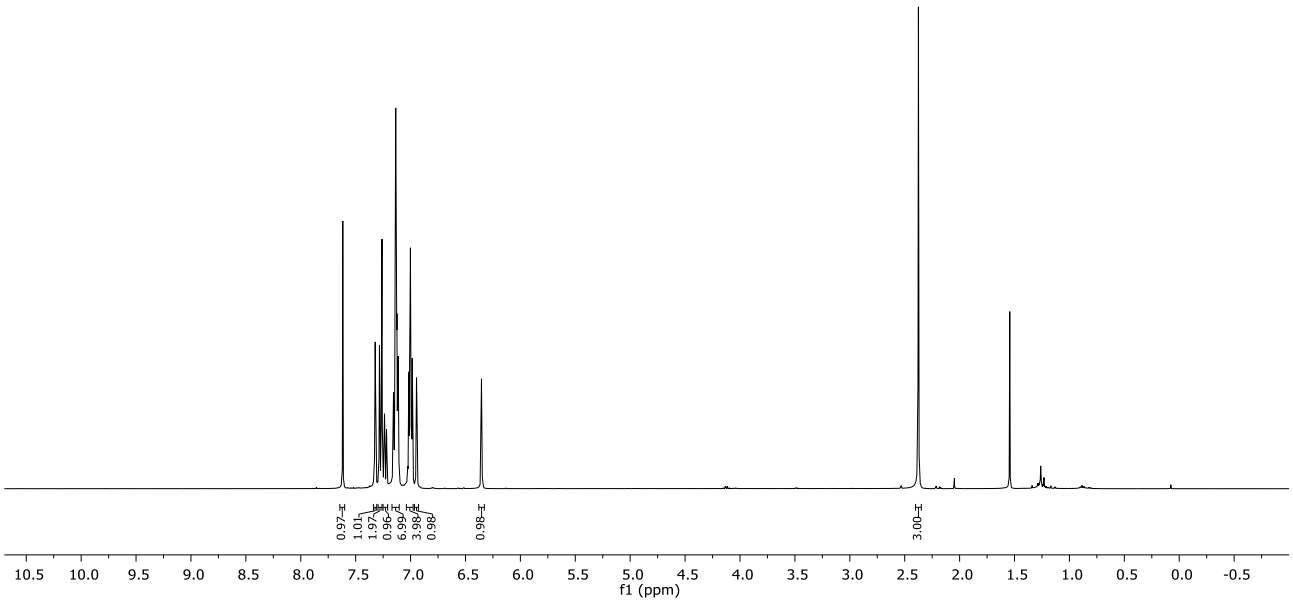
**3aj**

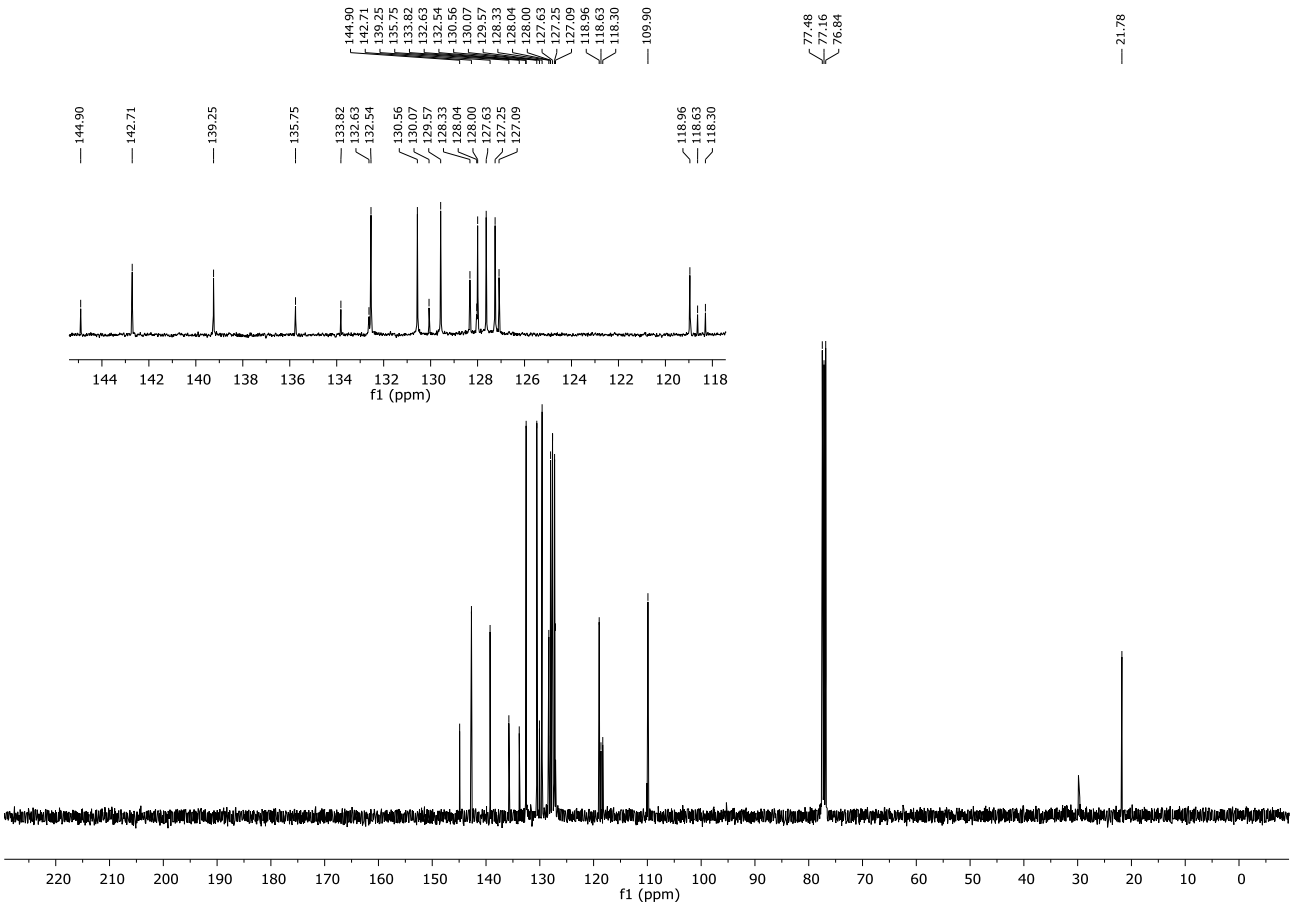

0.99
0.99
1.02
3.02
1.02
5.01
5.03
1.01
2.01
1.02
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

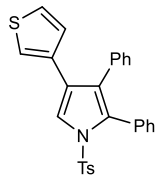

144.72
136.04
135.00
133.82
132.80
132.10
130.66
129.55
128.47
128.24
128.18
128.04
127.68
127.64
127.29
126.30
125.57
124.57
123.53
120.67
119.80
110.85
102.97
77.48
77.16
76.84
21.77
136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Ph
Ph
N
Ts

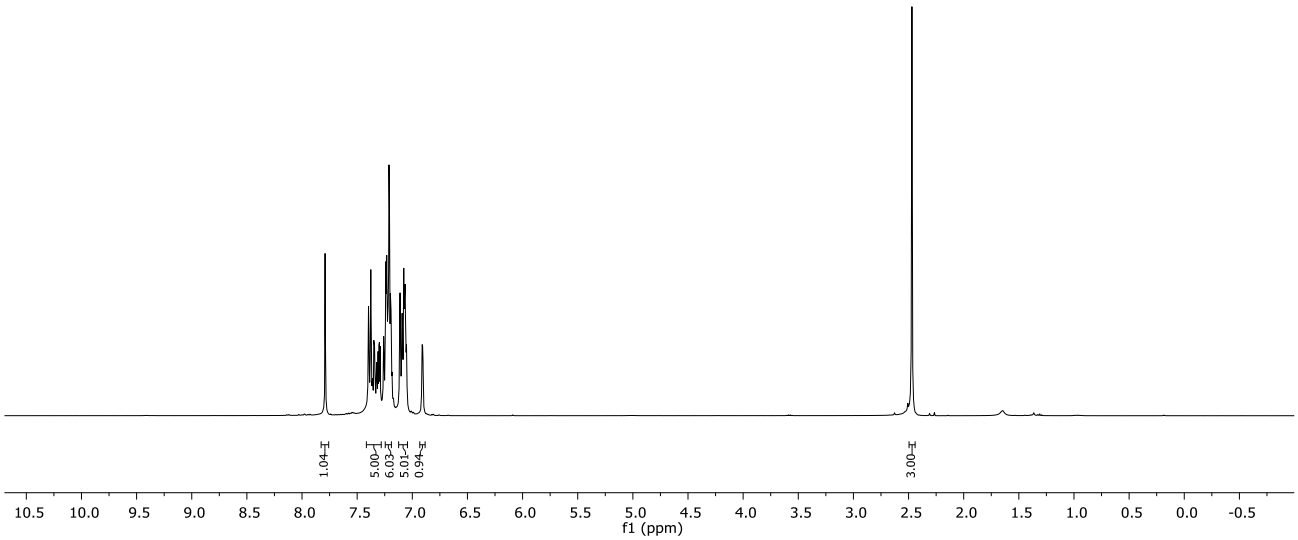
**3ak**

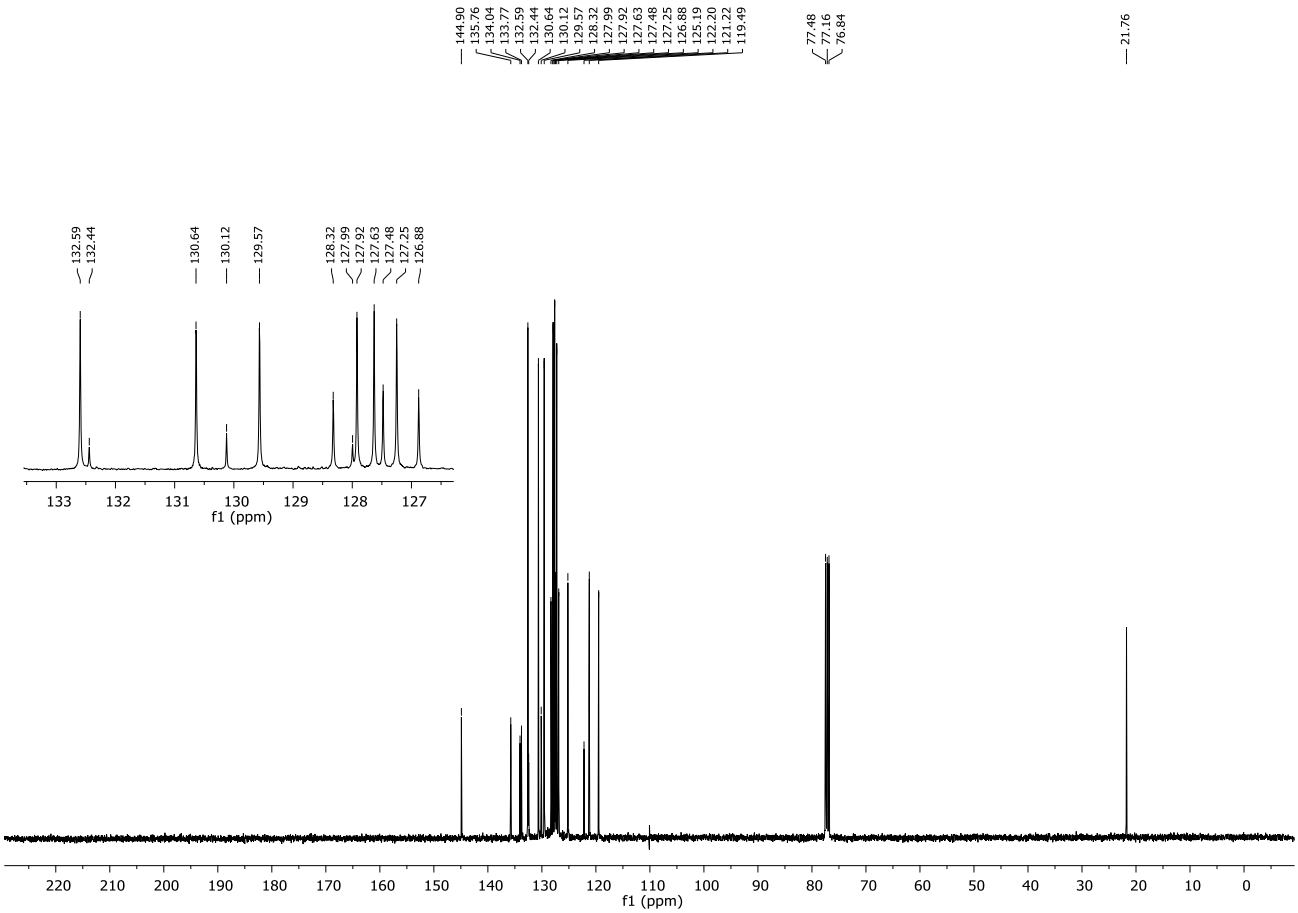

0.97
1.01
1.97
0.96
6.99
3.98
0.98
0.98
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

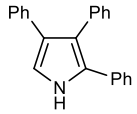

144.90
142.71
139.25
135.75
133.82
132.63
132.54
130.56
130.07
129.57
128.33
128.04
128.00
127.63
127.25
127.09
118.96
118.63
118.30
109.90
77.48
77.16
76.84
21.78
144 142 140 138 136 134 132 130 128 126 124 122 120 118
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


S
Ph
Ph
N
Ts

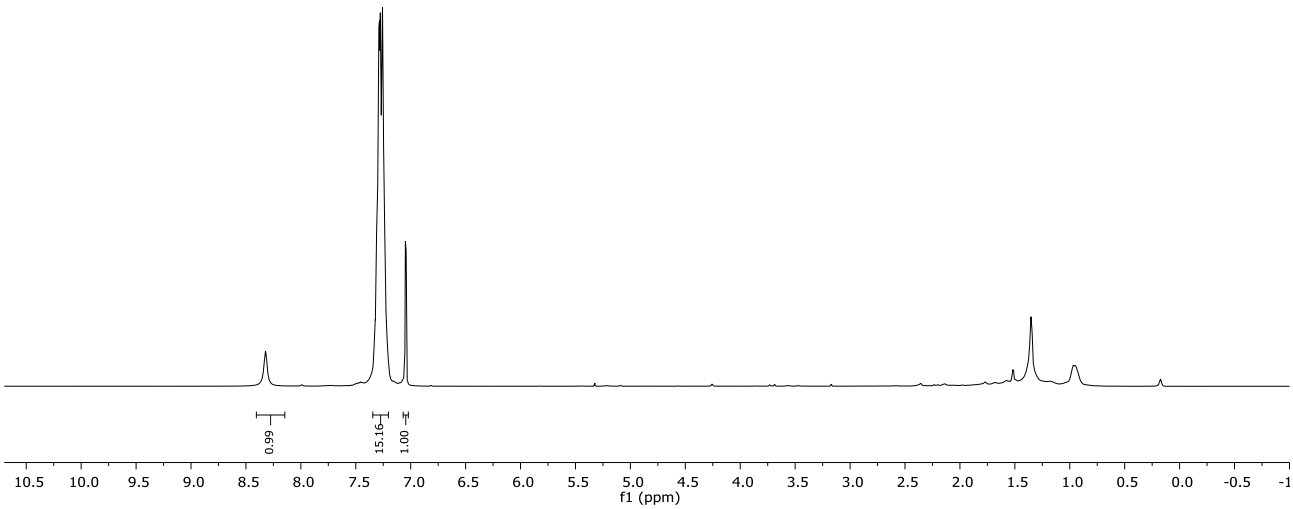
**3al**

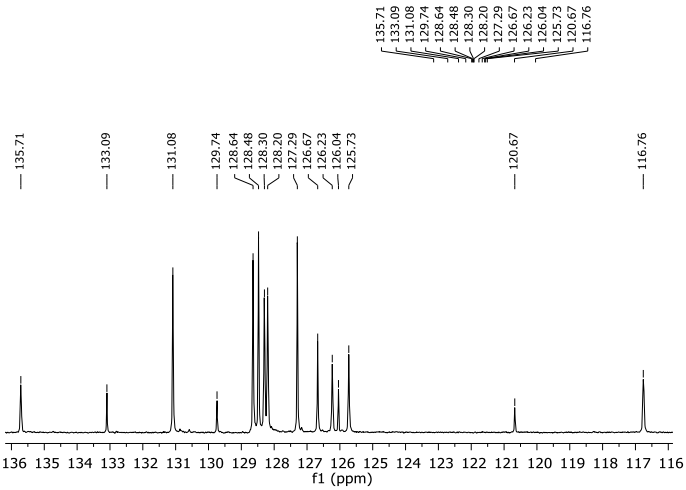

1.04
5.00
6.03
5.01
0.94
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


144.90
135.76
134.04
133.77
132.59
132.44
130.64
130.12
129.57
128.32
127.99
127.92
127.63
127.48
127.25
126.88
125.19
122.20
121.22
119.49
77.48
77.16
76.84
21.76
132.59
132.44
130.64
130.12
129.57
128.32
127.99
127.92
127.63
127.48
127.25
126.88
133 132 131 130 129 128 127
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

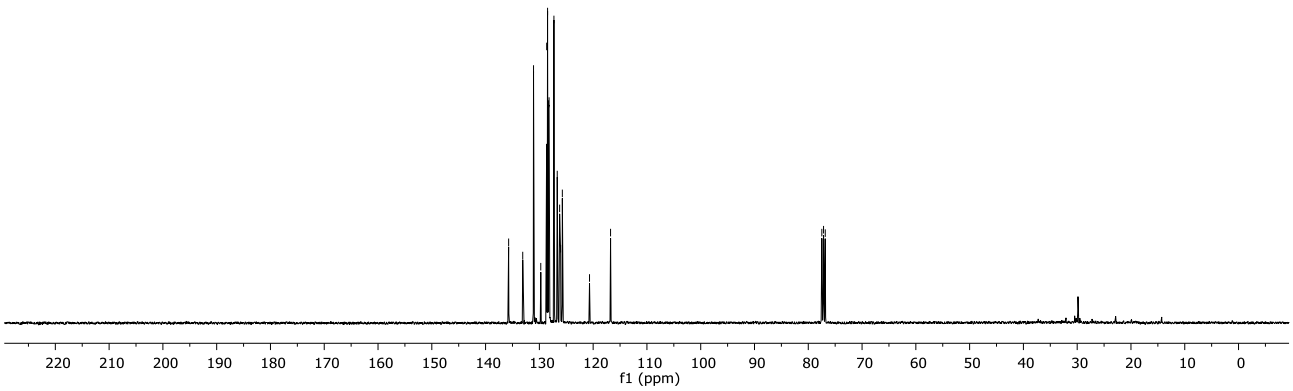

Ph
Ph
Ph
N
H

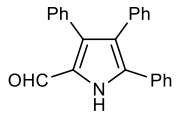
**6**


0.99
15.16
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

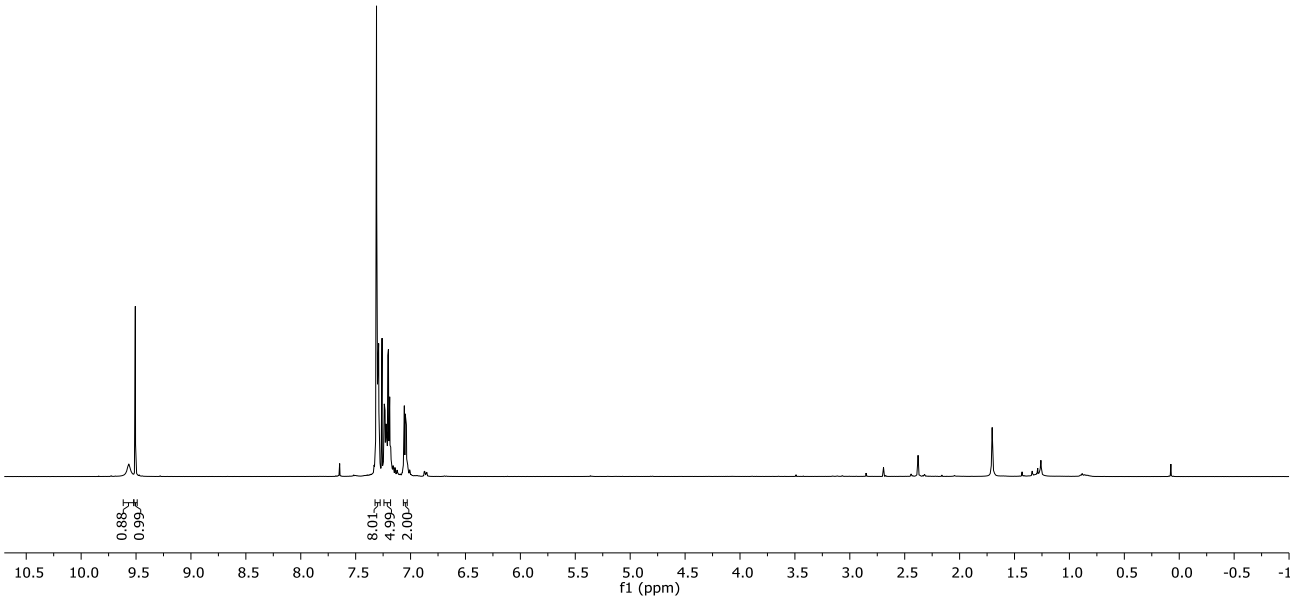

135.71
133.09
131.08
129.74
128.64
128.48
128.30
128.20
127.29
126.67
126.23
126.04
125.73
120.67
116.76
136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116
f1 (ppm)

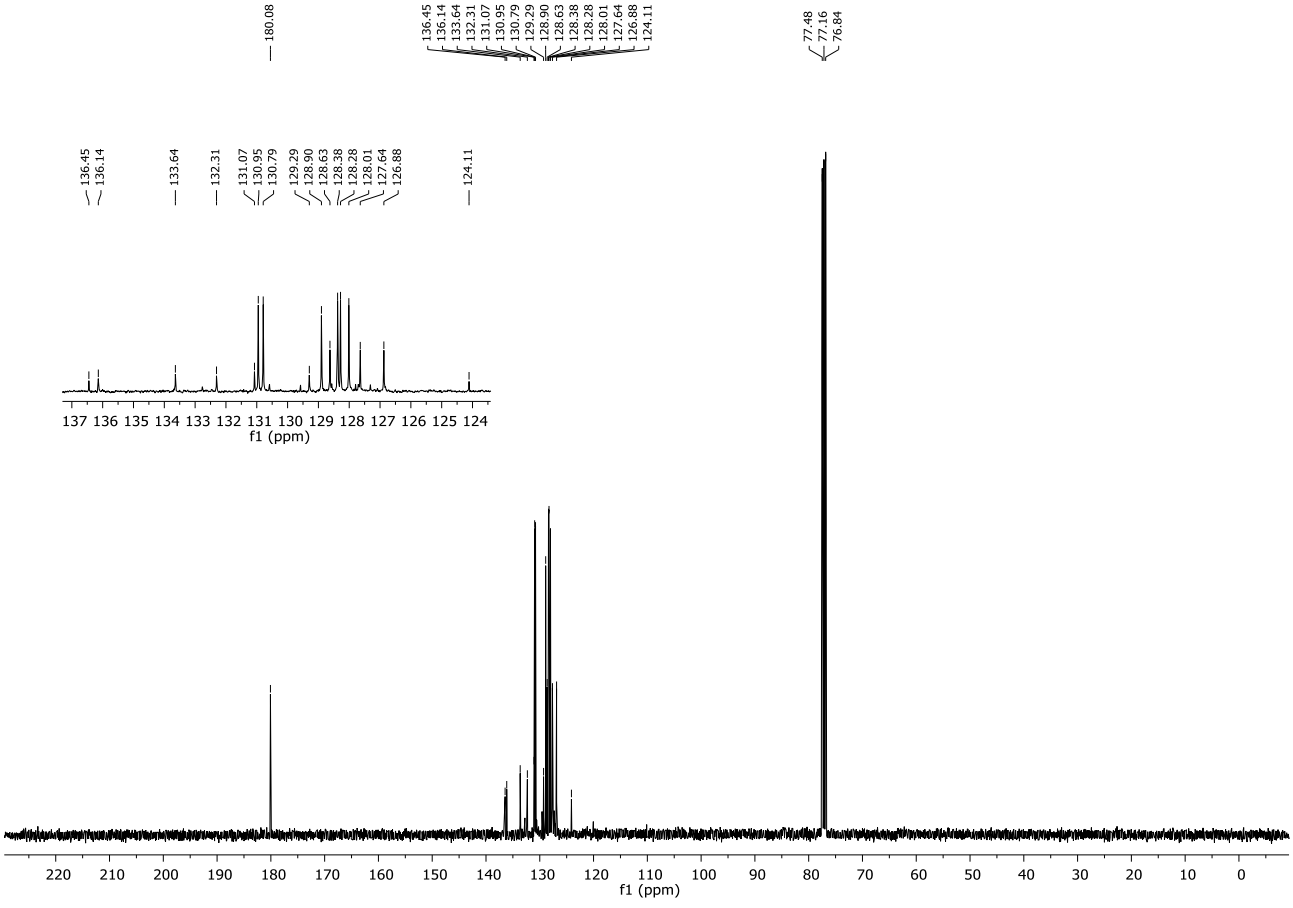

77.48
77.16
76.84

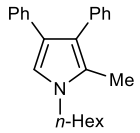

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
OHC
N
H
Ph

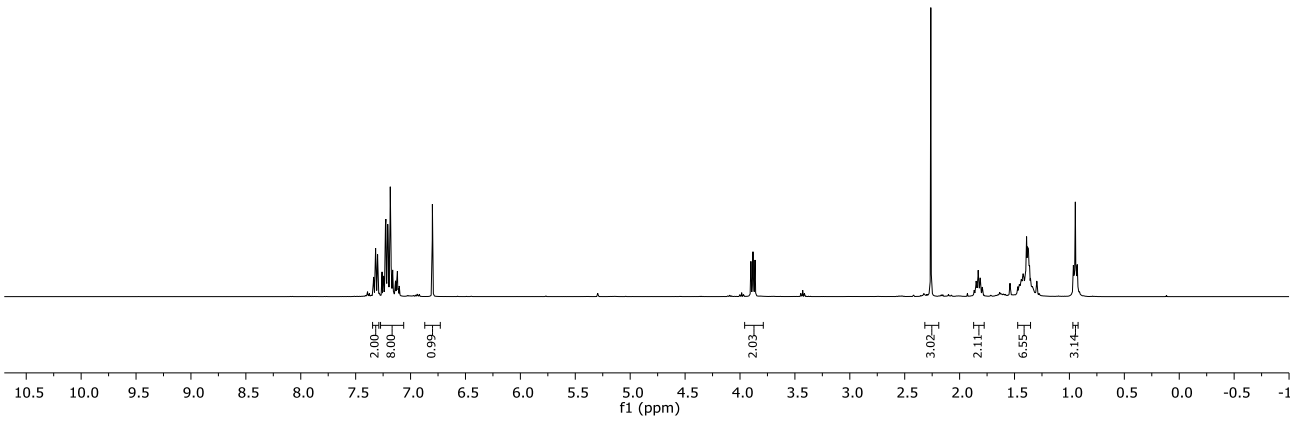
**8**

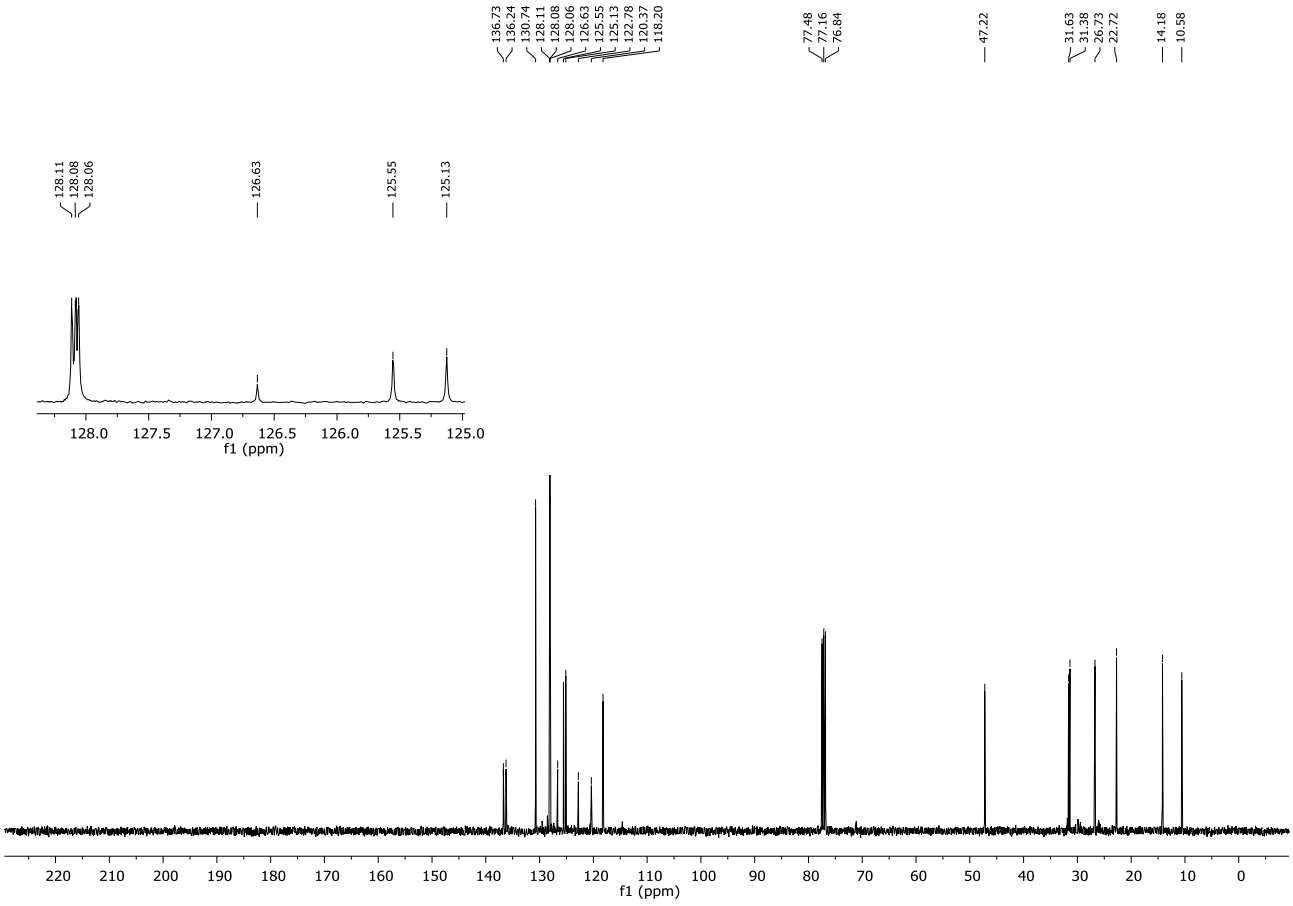

0.88
0.99
8.01
4.99
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


180.08
136.45
136.14
133.64
132.31
131.07
130.95
130.79
129.29
128.90
128.63
128.38
128.28
128.01
127.64
126.88
124.11
77.48
77.16
76.84
137 136 135 134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
Me
N
*n*-Hex

**10**


2.00
8.00
0.99
2.03
3.02
2.11
6.55
3.14
f1 (ppm)


136.73
136.24
130.74
128.11
128.08
128.06
126.63
125.55
125.13
122.78
120.37
118.20
77.48
77.16
76.84
47.22
31.63
31.38
26.73
22.72
14.18
10.58
f1 (ppm)

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