Development of an Amine Catalyzed Regioselective Synthesis of Pyrroles

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General Considerations

All reactions were conducted in flame-dried glassware under ambient conditions unless otherwise stated.

Infrared (IR) spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, ν_{max} in cm^{-1}. Samples were recorded on neat samples or as thin films using sodium chloride plates as a dichloromethane solution. Bands are characterised as broad (br), strong (s), medium (m), or weak (w).

^{1}H NMR spectra were recorded on a Bruker AVIII HD 400 (400 MHz), Bruker AVI 400 (400 MHz), Bruker AMX-400 (400 MHz) or DPX-400 (400 MHz) supported by an Aspect 3000 data system. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane with the residual protic solvent resonance as the internal standard ($CHCl_3$: δ 7.26) unless otherwise stated. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), assignments).

^{13}C NMR spectra were recorded on a Bruker AVIII HD 400 (100.6 MHz), Bruker AVI 400 (100.6 MHz), Bruker AMX-400 (100.6 MHz) or DPX-400 (100.6 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CHCl_3$: δ 77.16) unless otherwise stated.

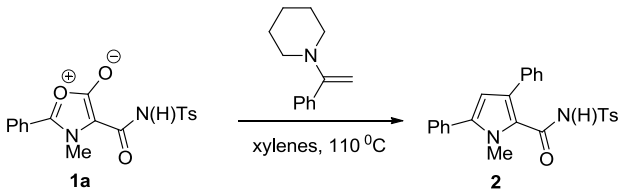
^{19}F NMR spectra were recorded on a Bruker AVIII HD 400 (235.1 MHz) or Bruker AMX-400 (235.1 MHz).

High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a MicroMass LCT operating in Electrospray mode (TOF ES+) or a MicroMass Prospec operating in FAB (FAB+), EI (EI+) or CI (CI+) mode.

Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with silica (0.2 mm, Merck DC-alufolien Kieselgel 60 F254) which were developed using standard visualizing agents: UV light or potassium permanganate. Flash chromatography was performed on silica-gel (BDH Silica Gel 60 43-60). Melting points, performed on recrystallised solids, were recorded on a Gallenkamp melting point apparatus and are uncorrected. All solvents and reagents were purified using standard laboratory techniques according to methods published in "Purification of Laboratory Chemicals" by Perrin, Armarego and Perrin (Pergamon Press, 1966).

Münchnones **1-e** were prepared according to procedures described previously.[1] Acetophenone and phenylacetaldehyde enamines were synthesized according to a reported method.[2,3]

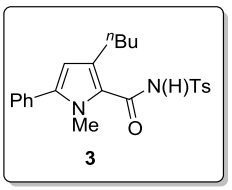
Representative Procedure for 1-substituted enamine-münchnone [3+2] Cycloadditions: synthesis of 5-tosylcarbamoyl-1-methyl-2,4 diphenyl-1*H*-pyrrole (2).



To a flame-dried two neck round bottom flask equipped with a stirrer bar and reflux condenser was added a solution of 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol, 1.0 eq.) and *N*-(1-phenylvinyl)piperidine (101 mg, 0.54 mmol, 2.0 eq.) in xylenes (2 mL) under N_2 at room temperature. The mixture was left to stir at room temperature for 10-15 minutes and afterwards, heated at 110 °C for 1-4 h. After cooling, the crude materials were purified by flash chromatography on silica gel (eluting with 5 % EtOAc in petroleum ether) to afford the title compound as a yellow solid (84 mg, 72%).

Melting point: 80-83 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.89-7.87 (m, 2H, ArH), 7.52-7.34 (m, 12H, ArH), 6.19 (s, 1H, pyrlH), 3.81 (s, 3H, NCH_3), 2.45 (s, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 158.2, 144.8, 141.7, 136.0, 134.5, 131.8, 131.3, 129.6, 129.4 (x3C), 128.7 (x2C), 128.6, 128.5, 120.8, 111.5, 35.3, 21.7; **FTIR:** ν_{max}: 3323 (w), 1674 (s), 1416 (s), 1164 (s), 1063 (s), 699 (s), 657 (s) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{25}H_{22}N_2O_3S$: 431.1424, found: 431.1422.

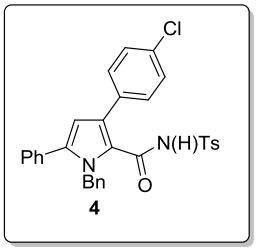
Synthesis of 5-tosylcarbamoyl-1-methyl-2-phenyl-4-*n*-butyl-1*H*-pyrrole (3).



Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-phenyl -1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol) and *N*-1-hexenylpiperidine (90 mg, 0.54 mmol), the title compound was isolated as a yellow oil (64 mg, 58%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 – 8.03 (m, 2H, ArH), 7.46 – 7.36 (m, 5H, ArH), 7.36 – 7.33 (m, 2H, ArH), 6.08 (s, 1H, pyrlH), 3.69 (s, 3H, NCH_3), 2.77 – 2.72 (m, 2H, CH_2), 2.46 (s, 3H, CH_3), 1.69 – 1.61 (m, 2H, CH_2), 1.51 – 1.42 (m, 2H, CH_2), 0.99 (t, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 161.3, 144.3, 136.3, 135.8, 130.7, 130.5, 130.2, 129.7, 129.3, 128.3, 127.6, 121.0, 113.3, 34.5, 32.1, 25.8, 22.7, 21.7, 14.1; **FTIR:** ν_{max}: 3063 (w), 2956 (m), 1672 (s), 1450 (s), 1161 (s), 1070 (m), 763 (s) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{23}H_{26}N_2O_3S$: 411.1737, found: 411.1746

Synthesis of 5-tosylcarbamoyl-1-benzyl-2-phenyl-4-chlorophenyl-1*H*-pyrrole (4).



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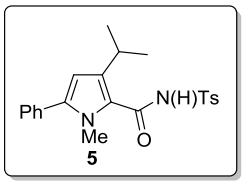
Following the general procedure using 3-benzyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1b** (100 mg, 0.22 mmol) and *N*-(1-(4-chlorophenyl)vinyl)piperidine (99 mg, 0.44 mmol), the title compound was isolated as a colorless oil (105 mg, 88%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 8.0 Hz, 2H, ArH), 7.42 -7.38 (m, 5H, ArH), 7.35-7.31 (m, 3H, ArH), 7.30-7.27 (m, 3H, ArH), 7.12-7.05 (m, 3H, ArH), 6.74-6.66 (m, 2H, ArH), 6.23 (s, 1H, PyrH), 5.46 (s, 2H, CH_2), 2.46 (s, 3H, CH_3). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 158.1, 144.7, 141.9, 138.1, 135.8, 134.4, 132.4, 131.3, 130.5, 130.6 (x2C), 129.5, 129.4, 128.8, 128.7, 128.4, 128.3, 127.2, 126.3, 120.6, 111.7, 49.2, 21.7; **FTIR:** ν_{max}: 3321 (w), 1683 (s), 1454 (m), 1167 (s), 1086 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{31}H_{25}{}^{35}ClN_2O_3S$: 541.1347, found: 541.1359.

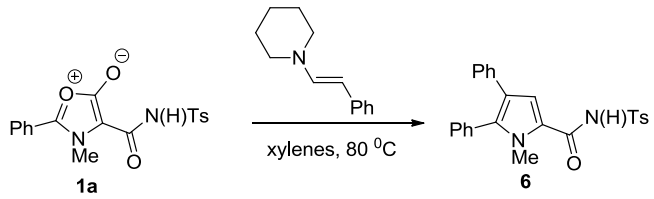
Synthesis of 5-tosylcarbamoyl-1-methyl-2-phenyl-4-isopropyl-1*H*-pyrrole (5).



Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol) and 1-(2-methyl-1-methylenepropyl) piperidine (82 mg, 0.54 mmol), the title compound was isolated as a yellow oil (65 mg, 61%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16 (br, 1H, NHTs), 8.08 – 8.04 (m, 2H, ArH), 7.49 – 7.32 (m, 7H, ArH), 6.14 (s, 1H, pyrlH), 3.66 (s, 3H, NCH_3), 3.25 – 3.14 (m, 1H, CH), 2.46 (s, 3H, CH_3), 1.31 (d, *J* = 6.0 Hz, 6H, CH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 165.0, 158.4, 144.9, 138.1, 136.0, 131.6, 129.6, 129.3, 128.6, 128.5, 128.3, 126.2, 107.7, 34.9, 26.9, 24.4, 21.7; **FTIR:** ν_{max}: 3066 (w), 2961 (m), 1676 (s), 1453 (s), 1165 (s), 1079 (m) cm^{-1}**; HRMS:** m/z [MH^+] calc. for $C_{22}H_{24}N_2O_3S$: 397.1585, found: 397.1585.

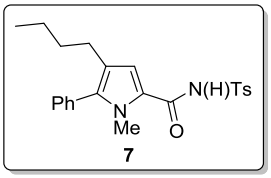
Representative Procedure for isomeric 2-substituted enamine-münchnone [3+2] Cycloadditions: synthesis of 5-tosylcarbamoyl-1-methyl-2,3-diphenyl-1*H*-pyrrole (6).



To a flame-dried two neck round bottom flask equipped with a stirrer bar and reflux condenser was added a solution of 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol, 1.0 eq.) and 1-(2-phenylethenyl)piperidine (101 mg, 0.54 mmol, 2.0 eq.) in xylenes (2 mL) under N_2 at room temperature. The mixture was left to stir at room temperature for 10-15 minutes and afterwards, heated at 80 °C for 1-4 h. After cooling, the crude materials were purified by flash chromatography on silica gel (eluting with 5 % EtOAc in petroleum ether) to afford the title compound as a colorless oil (84 mg, 72%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.72 (br, 1H, NHTs), 8.12 – 8.04 (m, 2H, ArH), 7.43 – 7.36 (m, 5H, ArH), 7.24 – 7.13 (m, 5H, ArH), 7.08 – 7.04 (m, 3H, ArH, pyrlH), 3.70 (s, 3H, NCH_3), 2.46 (s, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 157.7, 144.9, 139.6, 136.1, 134.4, 130.9, 130.8, 129.6, 128.8 (x2C), 128.4, 128.3, 127.8, 126.1, 123.6, 122.6, 115.0, 34.5, 21.7; **FTIR:** ν_{max} : 3292 (m), 2919 (s), 1680 (s), 1440 (s), 1330 (s), 1159 (s), 1038 (s), 701 (s) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{25}H_{22}N_2O_3S$: 431.1424, found: 431.1430.

Synthesis of 5-tosylcarbamoyl-1-methyl-2-phenyl-3-*n*-butyl-1*H*-pyrrole (7).

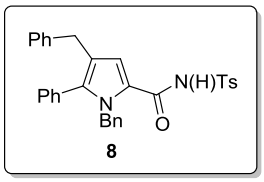


7

Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (400 mg, 1.07 mmol) and 1-(1-hexenyl)piperidine (359 mg, 2.14 mmol), the title compound was isolated as a yellow oil (290 mg, 66%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 – 8.07 (m, 2H, ArH), 7.48 – 7.36 (m, 5H, ArH), 7.25 – 7.21 (m, 2H, ArH), 6.91 (s, 1H, pyrlH), 3.65 (s, 3H, NCH_3), 2.46 (s, 3H, CH_3), 2.38 – 2.19 (m, 2H, CH_2), 1.45 – 1.34 (m, 2H, CH_2), 1.30 – 1.13 (m, 2H, CH_2), 0.78 (t, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 157.9, 144.6, 140.5, 136.5, 130.0, 130.4, 129.6, 128.5, 128.4, 128.3, 123.4, 121.6, 115.8, 34.4, 32.9, 25.4, 22.2, 21.7, 13.8; **FTIR:** ν_{max} : 3271 (m), 2955 (m), 1679 (s), 1430 (s), 1164 (s), 703 (s) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{23}H_{26}N_2O_3S$: 411.1737, found: 411.1742.

Synthesis of 5-tosylcarbamoyl-1,3-dibenzyl-2-phenyl-1*H*-pyrrole (8).

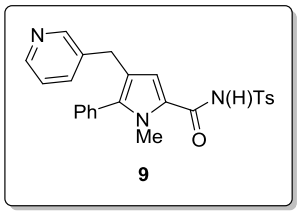


8

Following the general procedure using 3-benzyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1b** (100 mg, 0.22 mmol) and 1-(3-phenyl-1-propenyl)piperidine (90 mg, 0.44 mmol), the title compound was isolated as a colorless oil (78 mg, 68%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (br, 1H, NHTs), 7.93 – 7.90 (m, 2H, ArH), 7.46 – 7.33 (m, 4H, ArH), 7.30 – 7.05 (m, 11H, ArH), 6.69 – 6.58 (m, 3H, ArH, pyrlH), 5.38 (s, 2H, CH_2), 3.66 (s, 2H, CH_2), 2.45 (s, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 157.2, 144.5, 141.0, 140.9, 138.4, 136.0, 130.6, 130.4, 129.4, 128.8, 128.6, 128.5 (x2C), 128.3, 128.2, 126.9, 126.3, 126.1, 122.5, 121.8, 116.4, 49.0, 32.1, 21.7; **FTIR:** ν_{max}: 3027 (w), 2924 (m), 1679 (s), 1453 (s), 1166 (s), 700 (s) cm^{-1}**;** **HRMS:** m/z [MH^+] calc. for $C_{32}H_{28}N_2O_3S$: 521.1893, found: 521.1904.

Synthesis of 5-tosylcarbamoyl-1-methyl-2-phenyl-3-(pyridine-3-ylmethyl)-1*H*-pyrrole (9).

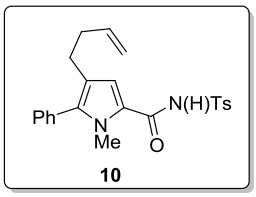


9

Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol) and 3-(3-piperidin-1-yl)ally)pyridine (108 mg, 0.54 mmol), the title compound was isolated as a yellow oil (84 mg, 70%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 – 8.31 (m, 2H, ArH), 8.03 – 7.96 (m, 2H, ArH), 7.48 – 7.32 (m, 6H, ArH), 7.26 – 7.11 (m, 3H, ArH), 6.65 (s, 1H, pyrH), 3.68 (m, 5H, NCH_3, CH_2), 2.45 (s, 3H, CH_3). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 158.2, 149.4, 147.1, 144.4, 140.2, 136.8, 136.7, 136.5, 130.4, 129.5, 128.9, 128.8, 128.7, 128.3, 123.5, 122.6, 120.4, 116.0, 34.5, 29.6, 21.7. **FTIR:** ν_{max}: 3055 (w), 2962 (m), 2920 (m), 1675 (s), 1455 (s), 1163 (s), 1075 (s), 813 (s) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{25}H_{23}N_3O_3S$: 446.1533, found: 446.1540.

Synthesis of 5-tosylcarbamoyl-1-methyl-2-phenyl-3-(but-3-en-1-yl)-1*H*-pyrrole (10).

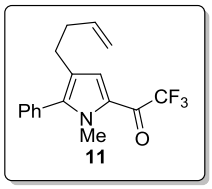


10

Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol) and 1-(hexa-1,5-dien-1-yl)piperidine (89 mg, 0.54 mmol), the title compound was isolated as a yellow oil (65 mg, 59%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (br, 1H, NHTs), 8.12 – 7.98 (m, 2H, ArH), 7.50 – 7.35 (m, 5H, ArH), 7.26 – 7.18 (m, 2H, ArH), 6.77 (s, 1H, pyrH), 5.86 – 5.61 (m, 1H, CH), 5.00 – 4.80 (m, 2H, CH_2), 3.64 (s, 3H, NCH_3), 2.46 (s, 3H, CH_3), 2.44 – 2.39 (m, 2H, CH_2), 2.22 – 2.16 (m, 2H, CH_2). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 157.5, 144.7, 140.6, 137.0, 136.3, 130.8, 130.4, 129.6, 128.6 (x2C), 128.4, 122.4, 121.6, 115.2, 115.0, 34.7, 34.4, 25.3, 21.7; **FTIR:** ν_{max}: 3436 (w), 2919 (m), 1676 (s), 1454 (s), 919 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{23}H_{25}N_2O_3S$: 409.1580, found: 409.1582.

Synthesis of 5-trifluoroacetyl -1-methyl-2-phenyl-3-(but-3-en-1-yl)-1*H*-pyrrole (11).

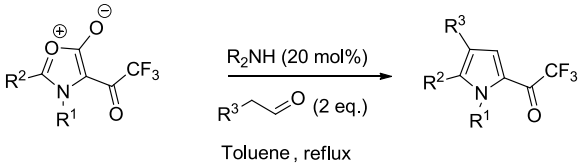


11

Following the general procedure using 3-methyl-4-trifluoroacetyl-2-phenyl-1,3-oxazolonium-5-olate **1c** (100 mg, 0.37 mmol) and 1-(hexa-1,5-dien-1-yl)piperidine (122 mg, 0.74 mmol), the title compound was isolated as a colorless oil (62 mg, 54%).

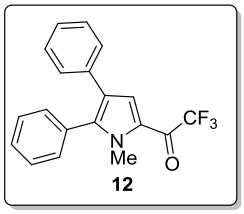
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 – 7.46 (m, 3H, ArH), 7.34 – 7.30 (m, 2H, ArH), 7.20 – 7.17 (m, 1H, pyrH), 5.92 – 5.69 (m, 1H, CH), 5.06 – 4.81 (m, 2H, CH_2), 3.79 (s, 3H, CH_3), 2.52 – 2.44 (m, 2H, CH_2), 2.28 – 2.21 (m, 2H, CH_2). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 169.0 (q, *J* = 58.0 Hz), 144.7, 137.7, 129.0 (x2C), 129.2, 128.8, 124.6, 124.2, 122.9 (q, *J* = 4.0 Hz), 118.8, 115.2, 35.2, 34.5, 25.4; **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ -71.0; **FTIR:** ν_{max}: 3429 (w), 2925 (w), 1662 (s), 1450 (m), 1441 (m), 940 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{17}H_{16}F_3NO$: 308.1257, found: 308.1257.

Representative Procedure for Amine Catalyzed Münchnone Cycloadditions



To a flame-dried three neck round bottom flask equipped with a stirrer bar, condenser and Dean-Stark trap was added a solution of aldehyde (2 eq.) and amine (20 mol%) in toluene (15 mL) under N_2 at room temperature. The mixture was stirred at room temperature for 10-15 minutes. Münchnone (1.0 eq.) was then added and the mixture heated at reflux for 24 h. After cooling, the crude materials were purified by flash chromatography on silica gel (eluting with 5% EtOAc in petroleum ether) to afford the pyrrole products.

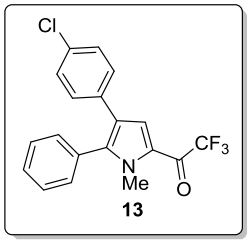
Synthesis of 5-trifluoroacetyl-1-methyl-2,3-diphenyl-1*H*-pyrrole (12).



Following the general procedure using 3-methyl-4-trifluoroacetyl-2-phenyl-1,3-oxazolonium-5-olate **1c** (100 mg, 0.37 mmol), phenylacetaldehyde (89 mg, 0.74 mmol) and dibenzylamine (14 µL, 0.074 mmol) the title compound was isolated as yellow solid (87 mg, 71%).

Melting point: 89-92 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.50 – 7.46 (m, 4H, ArH), 7.34 – 7.30 (m, 2H, ArH), 7.27 – 7.18 (m, 3H, ArH), 7.17 – 7.13 (m, 2H, ArH, PyrlH), 3.88 (s, 3H, NCH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 170.0 (q, *J* = 35.0 Hz), 143.5, 134.0, 130.6, 130.0, 129.4, 128.9, 128.4, 128.1, 126.6, 125.8, 124.9, 122.6 (q, *J* = 4.0 Hz), 117.3 (q, *J* = 291.0 Hz), 35.3; **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ -71.0; **FTIR:** ν_{max}: 3061 (w), 1667 (s), 1442 (m), 1301 (m), 1174 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{19}H_{14}NOF_3$: 330.1107, found: 330.1107.

Synthesis of 5-trifluoroacetyl-1-methyl-2-phenyl-3- (4-chlorophenyl) 1*H*-pyrrole (13).

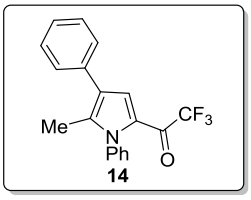


13

Following the general procedure using 3-methyl-4-trifluoroacetyl-2-phenyl-1,3-oxazolonium-5-olate **1c** (100 mg, 0.37 mmol), (4-chlorophenyl)acetaldehyde (114 mg, 0.74 mmol) and dibenzylamine (14 µL, 0.074 mmol) the title compound was isolated as a yellow oil (78 mg, 58%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 – 7.46 (m, 3H, ArH), 7.43 – 7.41 (m, 1H, ArH), 7.31 – 7.27 (m, 2H, ArH), 7.22 – 7.17 (m, 2H, ArH), 7.07 – 7.03 (m, 2H, ArH, PyrlH), 3.86 (s, 3H, NCH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 170.1 (q, *J* = 35.0 Hz), 143.4, 132.5 (x2C), 130.5, 129.7, 129.6, 129.3, 129.1, 128.6, 124.9, 124.5, 122.3 (q, *J* = 4.0 Hz), 117.2 (q, *J* = 291.0 Hz), 35.3; **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ -71.0; **FTIR:** ν_{max}: 3424 (w), 1666 (s), 1513 (m), 1434 (m), 1450 (m), 1173 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{19}H_{13}{}^{35}$[Cl]NOF_3: 364.0711, found: 364.0718.

Synthesis of 5-trifluoroacetyl-1,3-diphenyl-2-methyl-1*H*-pyrrole (14).



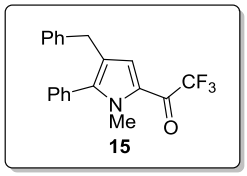
14

Following the general procedure using 3-phenyl-4-trifluoroacetyl-2-methyl-1,3-oxazolonium-5-olate **1d** (100 mg, 0.37 mmol), phenylacetaldehyde (89 mg, 0.74 mmol) and dibenzylamine (14 µL, 0.074 mmol) the title compound was isolated as a yellow solid (67 mg, 55%).

Melting point: 123-126 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57 – 7.52 (m, 3H, ArH), 7.48 – 7.46 (m, 4H, ArH), 7.45 – 7.43 (m, 1H, ArH), 7.39 – 7.35 (m, 1H, ArH), 7.31 – 7.28 (m, 2H, ArH, PyrlH), 2.20 (s, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 168.3 (q, *J* = 47.0 Hz), 140.6, 138.5, 134.4, 129.4,

128.9, 128.7, 128.3, 127.4, 127.0, 125.8, 124.9, 123.1 (q, *J* = 4.0 Hz), 117.2 (q, *J* = 291.0 Hz), 12.1; **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ -71.0; **FTIR:** ν_{max}: 3061 (w), 1674 (s), 1497 (m), 1409 (m), 1293 (m), 1151 (s) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{19}H_{14}NOF_3$: 330.1108, found: 330.1108.

Synthesis of 5-trifluoroacetyl-1-methyl-2-phenyl-3-benzyl-1*H*-pyrrole (15).

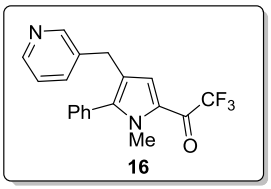


15

Following the general procedure using 3-methyl-4-trifluoroacetyl-2-phenyl-1,3-oxazolonium-5-olate **1c** (100 mg, 0.37 mmol), 3-phenylpropionaldehyde (99 mg, 0.74 mmol) and dibenzylamine (14 µL, 0.074 mmol) the title compound was isolated as an orange oil (85 mg, 67%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 – 7.48 (m, 3H, ArH), 7.30 – 7.24 (m, 4H, ArH), 7.22 – 7.18 (m, 1H, ArH), 7.17 – 7.13 (m, 1H, ArH), 7.09 – 7.06 (m, 2H, ArH, PyrlH), 3.81 (s, 3H, NCH_3), 3.75 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 169.7 (q, *J* = 35.0 Hz), 145.0, 140.7, 130.2, 129.8, 129.3, 128.8, 128.5, 128.3, 126.1, 124.4, 123.9, 123.7 (q, *J* = 4.0 Hz), 117.3 (q, *J* = 291.0 Hz), 35.3, 32.2; **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ -71.0; **FTIR:** ν_{max}: 3064 (w), 1663 (s), 1451 (m), 1296 (m), 1174 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{20}H_{16}NOF_3$: 344.1257, found: 344.1259.

Synthesis of-5-trifluoroacetyl-1-methyl-2-phenyl-3-(pyridine-3-ylmethyl)-1*H*-pyrrole (16).

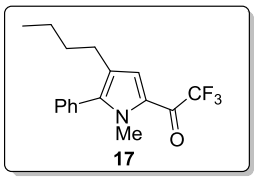


16

Following the general procedure using 3-methyl-4-trifluoroacetyl-2-phenyl-1,3-oxazolonium-5-olate **1c** (100 mg, 0.37 mmol), 3-(3-pyridinyl)propanal (50 mg, 0.74 mmol) and dibenzylamine (14 µL, 0.074 mmol) the title compound was isolated as a brown oil (78 mg, 61%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 – 8.29 (m, 2H, ArH), 7.52 – 7.48 (m, 3H, ArH), 7.38 – 7.35 (m, 1H, ArH), 7.26 – 7.23 (m, 2H, ArH), 7.19–7.11 (m, 2H, ArH, PyrlH), 3.80 (s, 3H, NCH_3), 3.74 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 169.7 (q, *J* = 35.0 Hz), 149.7, 147.6, 144.8, 136.1, 135.8, 130.0, 129.5 (x2C), 129.0, 124.4, 123.4, 123.2 (q, *J* = 4.0 Hz), 122.6, 117.2 (q, *J* = 291.0 Hz), 35.3, 29.6; **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ -71.0; **FTIR:** ν_{max}: 3063 (w), 2925 (w), 1664 (s), 1450 (m), 1295 (m), 1175 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{19}H_{15}N_2OF_3$: 345.1209, found: 345.1209.

Synthesis of 5-trifluoroacetyl -1-methyl-2-phenyl-3-*n*-butyl-1*H*-pyrrole (17).

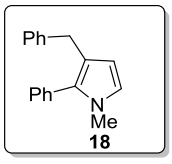


17

Following the general procedure using 3-methyl-4-trifluoroacetyl-2-phenyl-1,3-oxazolonium-5-olate **1c** (100 mg, 0.37 mmol), hexanal (74 mg, 0.74 mmol) and dibenzylamine (14 µL, 0.074 mmol) the title compound was isolated as yellow oil (59 mg, 52%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 – 7.49 (m, 3H, ArH), 7.34 – 7.31 (m, 2H, ArH), 7.15 (s, 1H, pyrlH), 3.79 (s, 3H, NCH_3), 2.42 – 2.34 (m, 2H, CH_2), 1.53 – 1.44 (m, 2H, CH_2), 1.34 – 1.22 (m, 2H, CH_2), 0.86 (t, *J* = 7.0 Hz, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 169.4 (q, *J* = 35.0 Hz), 144.7, 130.1, 129.1, 128.8, 125.7 (x2C), 124.2, 122.9 (q, *J* = 4.0 Hz), 117.4 (q, *J* = 291.0 Hz), 35.0, 32.8, 25.5, 22.3, 13.8; **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ -71.0; **FTIR:** ν_{max}: 2932 (w), 1663 (s), 1451 (m), 1297 (m), 1174 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{17}H_{18}NOF_3$: 310.1446, found: 310.1451.

Synthesis of 1-methyl-2-phenyl-3-benzyl-1*H*-pyrrole (18).

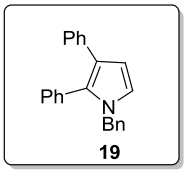


18

Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol), 3-phenylpropionaldehyde (72 mg, 0.54 mmol) and piperidine (5 µL, 0.054 mmol) the title compound was isolated as a yellow oil (35 mg, 52%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 – 7.40 (m, 2H, ArH), 7.38 – 7.30 (m, 3H, ArH), 7.27 – 7.14 (m, 5H, ArH), 6.67 (d, *J* = 3.0 Hz, 1H, PyrlH), 6.05 (d, *J* = 3.0 Hz, 1H, PyrlH), 3.79 (s, 2H, CH_2), 3.54 (s, 3H, NCH_3); **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 142.8, 132.5, 131.5, 130.5, 128.5, 128.3, 128.2, 127.2, 125.5, 121.9, 120.6, 108.5, 34.8, 32.7; **FTIR:** ν_{max}: 3061 (w), 1678 (s), 1494 (m), 1451 (m), 701 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{18}H_{17}N$: 248.1434, found: 248.1434.

Synthesis of *N*-benzyl-2,3-diphenyl pyrrole (19).

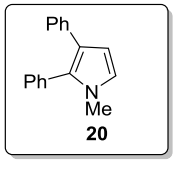


19

Following the general procedure using 3-benzyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1b** (100 mg, 0.22 mmol), phenylacetaldehyde (54 mg, 0.45 mmol) and piperidine (4 µL, 0.045 mmol) the title compound was isolated as a yellow solid (42 mg, 62%).

Melting point: 92-95 ˚C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.36 – 7.18 (m, 12H, ArH), 7.14 – 7.08 (m, 1H, ArH), 7.06 – 7.02 (m, 2H, ArH), 6.82 (d, *J* = 3.0 Hz, 1H, PyrlH), 6.55 (d, *J* = 3.0 Hz, 1H, PyrlH), 5.03 (s, 2H, CH_2). **^{13}C NMR ($CDCl_3$, 101 MHz):** δ 138.6, 136.5, 132.8, 131.3, 131.0, 128.6, 128.5, 128.1, 127.7 (x2C), 127.4, 126.8, 125.1, 122.8, 121.7, 108.5, 50.7; **FTIR:** ν_{max}: 3061 (w), 1603 (s), 1505 (m), 1344 (m), 1073 (m), 697 (s) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{23}H_{19}N$: 310.1592, found: 310.1592.

Synthesis of 1-methyl-2,3-diphenyl-1*H*-pyrrole (20).

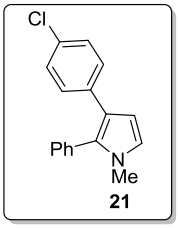


20

Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol), phenylacetaldehyde (65 mg, 0.54 mmol) and piperidine (5 µL, 0.054 mmol) the title compound was isolated as a colorless oil (37 mg, 58%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 – 7.31 (m, 5H, ArH), 7.24 – 7.17 (m, 4H, ArH), 7.15 – 7.09 (m, 1H, ArH), 6.79 (d, *J* = 3.0 Hz, 1H, PyrlH), 6.47 (d, *J* = 3.0 Hz, 1H, PyrlH), 3.56 (s, 3H, NCH_3); **^{13}C NMR, 101 MHz):** δ 136.7, 132.8, 131.1, 130.7, 128.5, 128.1, 127.8, 127.5, 125.1, 122.8, 122.3, 107.9, 34.8; **FTIR:** ν_{max}: 3061 (w), 2923 (w), 1678 (s), 1448 (m), 1394 (m), 699 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{17}H_{15}N$: 234.1277, found: 234.1278.

Synthesis -1-methyl-2-phenyl-3- (4-chlorophenyl) 1*H*-pyrrole (21).

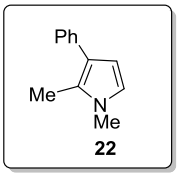


21

Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-phenyl-1,3-oxazolonium-5-olate **1a** (100 mg, 0.27 mmol), (4-chlorophenyl)acetaldehyde (83 mg, 0.54 mmol) and piperidine (5 µL, 0.054 mmol) the title compound was isolated as a colorless oil (46 mg, 64%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 – 7.37 (m, 3H, ArH), 7.32 – 7.28 (m, 2H, ArH), 7.18 – 7.08 (m, 4H, ArH), 6.77 (d, *J* = 3.0 Hz, 1H, PyrlH), 6.41 (d, *J* = 3.0 Hz, 1H, PyrlH), 3.54 (s, 3H, NCH_3); **^{13}C NMR, 101 MHz):** δ 135.2, 132.5, 131.0, 130.8, 130.7, 129.0, 128.6, 128.2, 127.8, 122.5, 121.7, 107.7, 34.8; **FTIR:** ν_{max}: 3052(w), 1600 (m), 1504 (m), 1348 (m), 701 (m) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{17}H_{14}{}^{35}ClN$: 268.0888, found: 268.0891.

Synthesis of 1,2-dimethyl-3-phenyl-1*H*-pyrrole (22).



22

Following the general procedure using 3-methyl-4-tosylcarbamoyl-2-methyl-1,3-oxazolonium-5-olate **1e** (100 mg, 0.32 mmol), phenylacetaldehyde (77 mg, 0.64 mmol) and piperidine (6 µL, 0.064 mmol) the title compound was isolated as a colorless oil (31 mg, 56%).

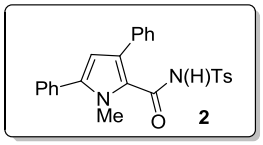
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 – 7.35 (m, 4H, ArH), 7.25 – 7.21 (m, 1H, ArH), 6.64 (d, *J* = 3.0 Hz, 1H, PyrlH), 6.28 (d, *J* = 3.0 Hz, 1H, PyrlH), 3.61 (s, 3H, NCH_3), 2.37 (s, 3H, CH_3); **^{13}C NMR, 101 MHz):** δ 137.6, 128.3, 128.0, 125.4, 125.1, 122.0, 120.6, 107.1, 34.0, 10.7; **FTIR:** ν_{max}: 2966 (w), 1601 (s), 1504 (s), 1443 (m), 1348 (m), 701 (s) cm^{-1}; **HRMS:** m/z [MH^+] calc. for $C_{12}H_{13}N$: 172.1121, found: 172.1123.

References

1. T. K. K. Kakaawla, W. C. Hartley, J. P. A. Harrity, *Eur. J. Org. Chem.* **2016**, 2789.

2. Carlson R., Nilsson Å., *Acta Chemica. Scand. B.* **1984**, *38*, 49.

3. Amat M., Cantó M., Llor N., Escolano C., Molins E., Espinosa E., Bosch J., *J. Org. Chem.* **2002,** *67*, 5343.


Ph
Ph
N
Me
N(H)Ts
O
2

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7.88
7.53
7.52
7.50
7.48
7.47
7.46
7.45
7.42
7.41
7.39
7.38
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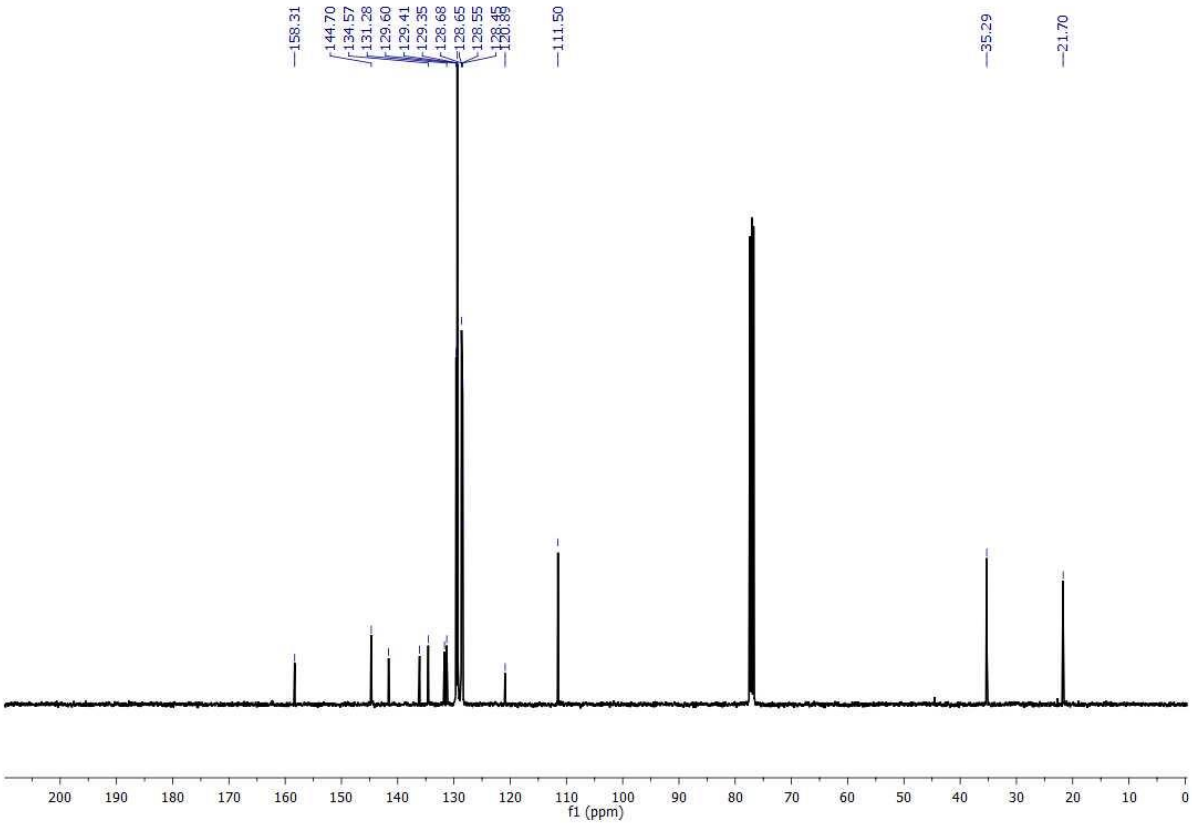
1.99
2.38
1.00
3.11
3.13
f1 (ppm)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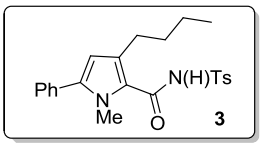
128.68
128.65
128.55
111.50
35.29
21.70
f1 (ppm)


Ph
N
Me
O
N(H)Ts
3

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8.06
8.05
8.05
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7.43
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6.08
3.69
2.75
2.74
2.72
2.46
1.67
1.66
1.64
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1.45
1.00
0.99
0.97
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3.00
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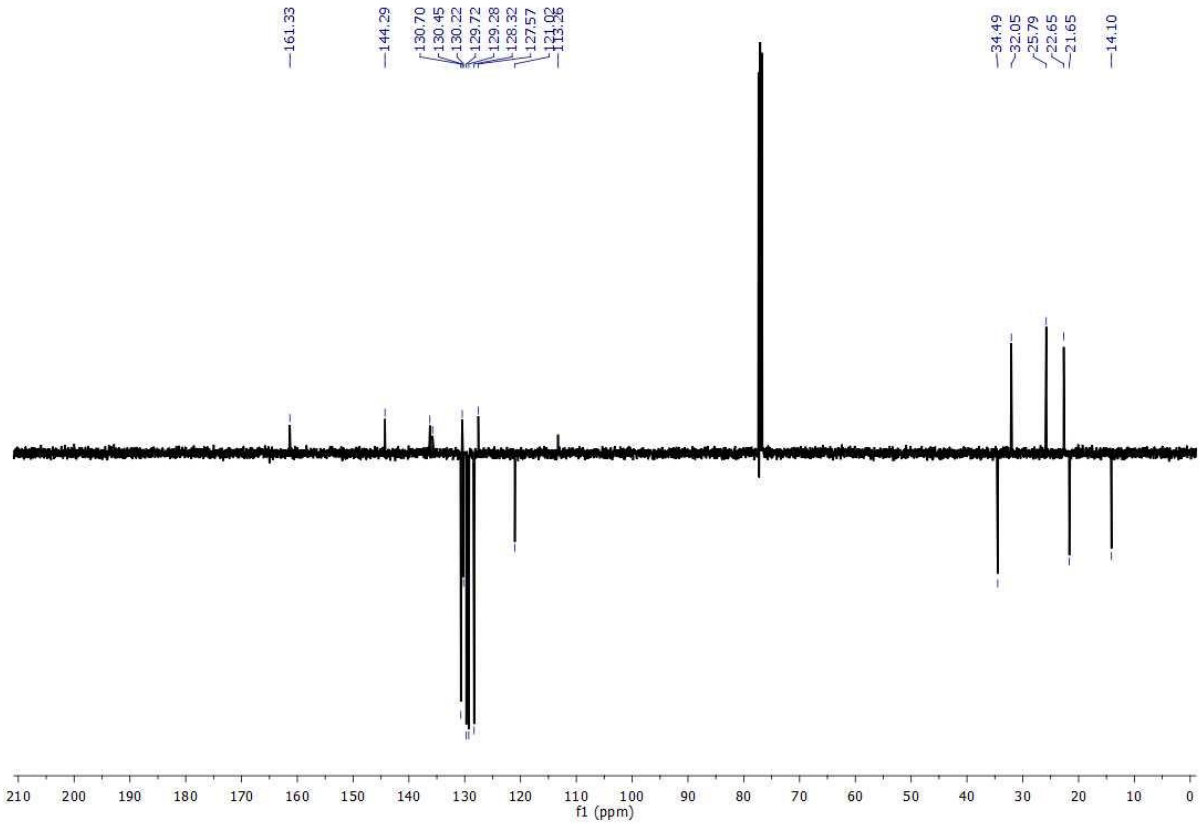
3.31
f1 (ppm)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113.26
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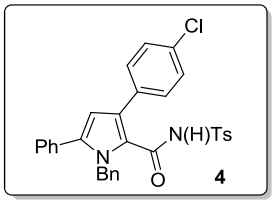
22.65
21.65
14.10
f1 (ppm)


Cl
Ph
N
Bn
O
N(H)Ts
4

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7.40
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7.28
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7.12
7.11
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6.71
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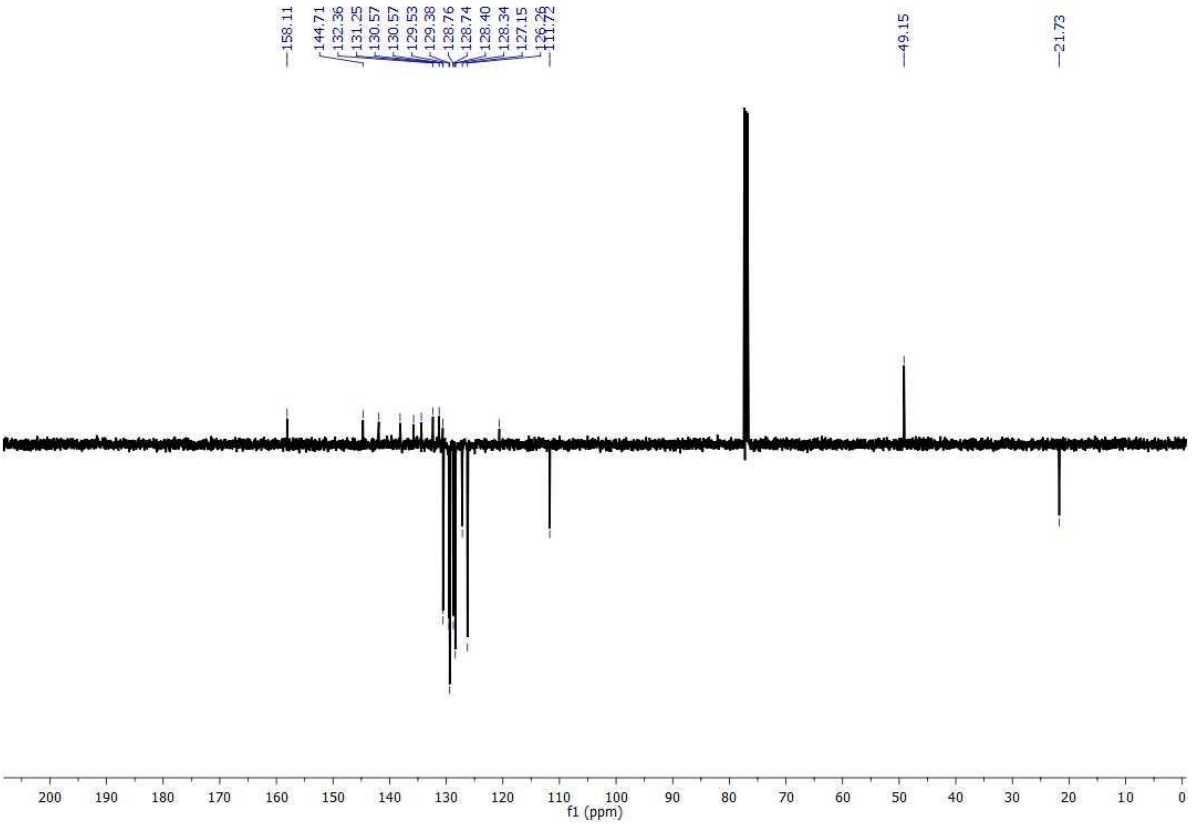
3.28
f1 (ppm)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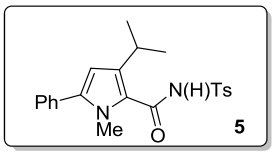
21.73
f1 (ppm)


Ph
N
Me
O
N(H)Ts
5

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8.05
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7.34
7.34
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3.22
3.20
3.18
3.17
3.15
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1.30
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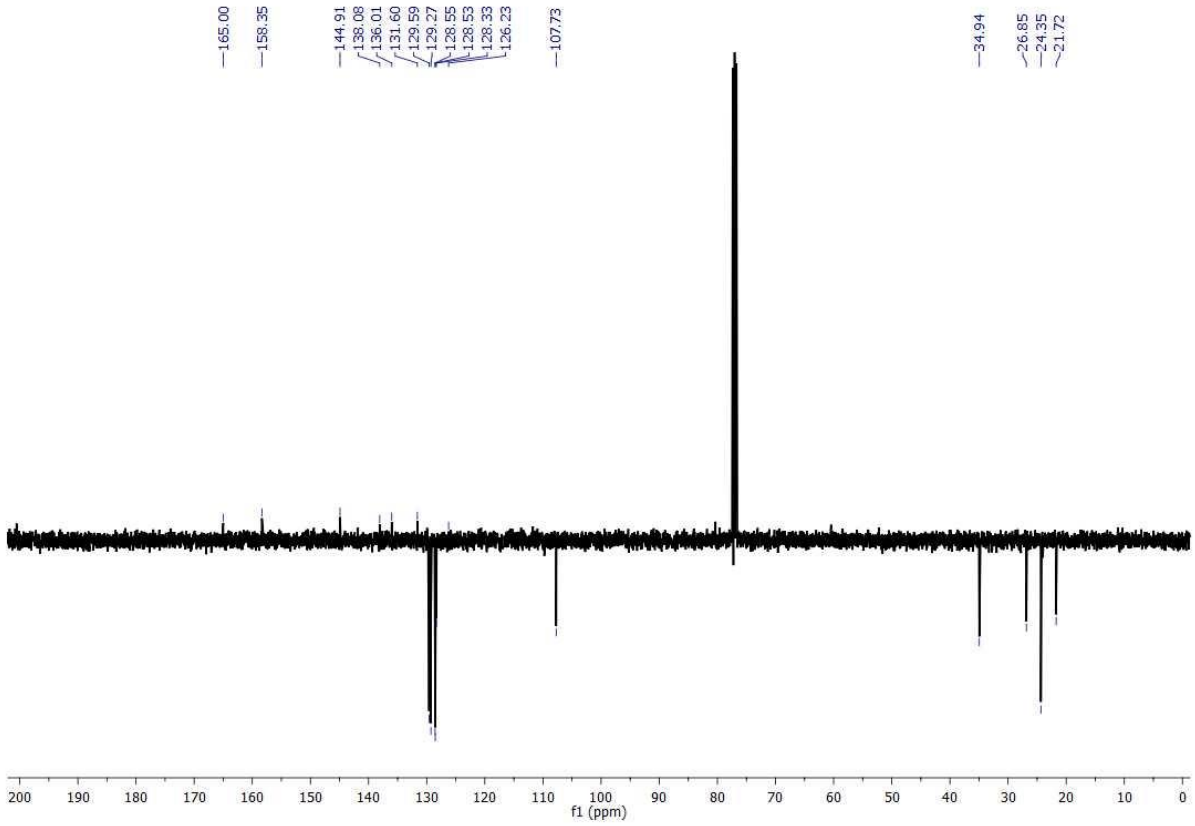
7.46
1.00
2.96
1.04
3.20
2.91
3.04
f1 (ppm)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136.01
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128.33
126.23
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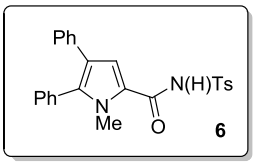
34.94
26.85
24.35
21.72
f1 (ppm)


Ph
Ph
N
Me
N(H)Ts
O
6

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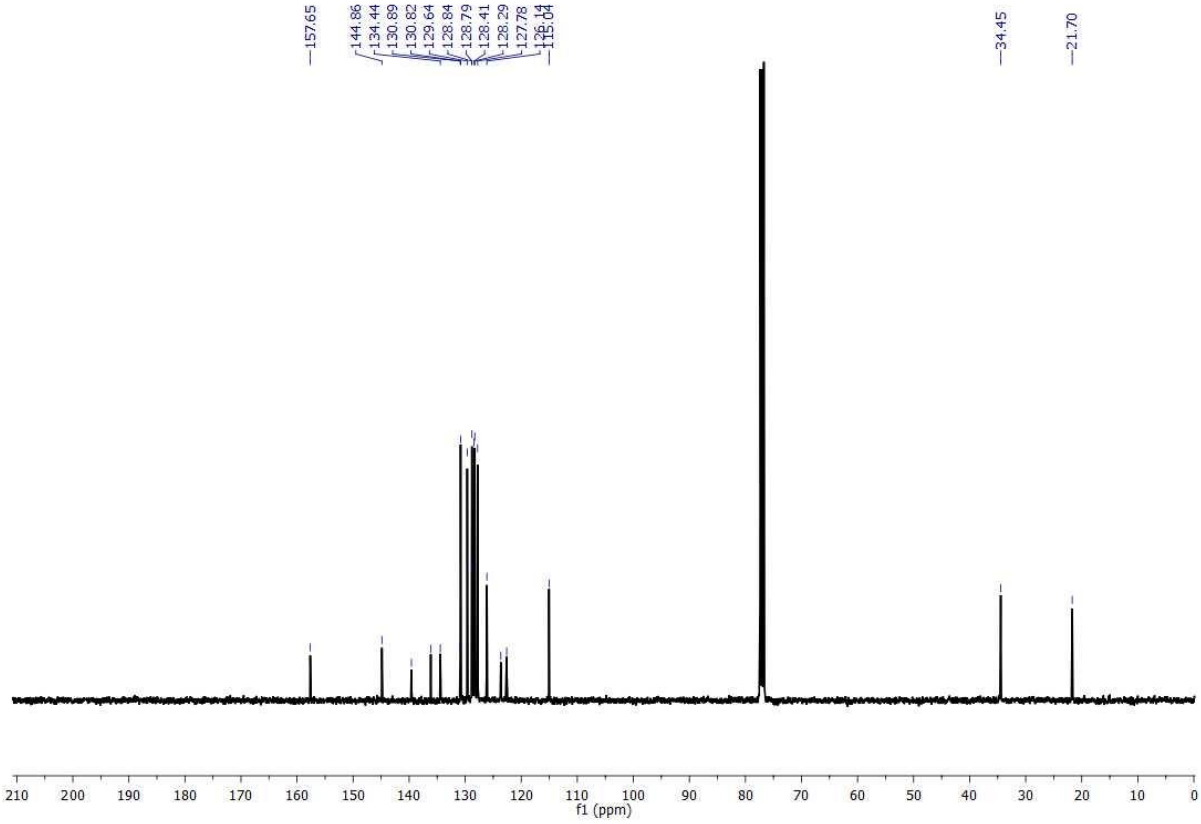
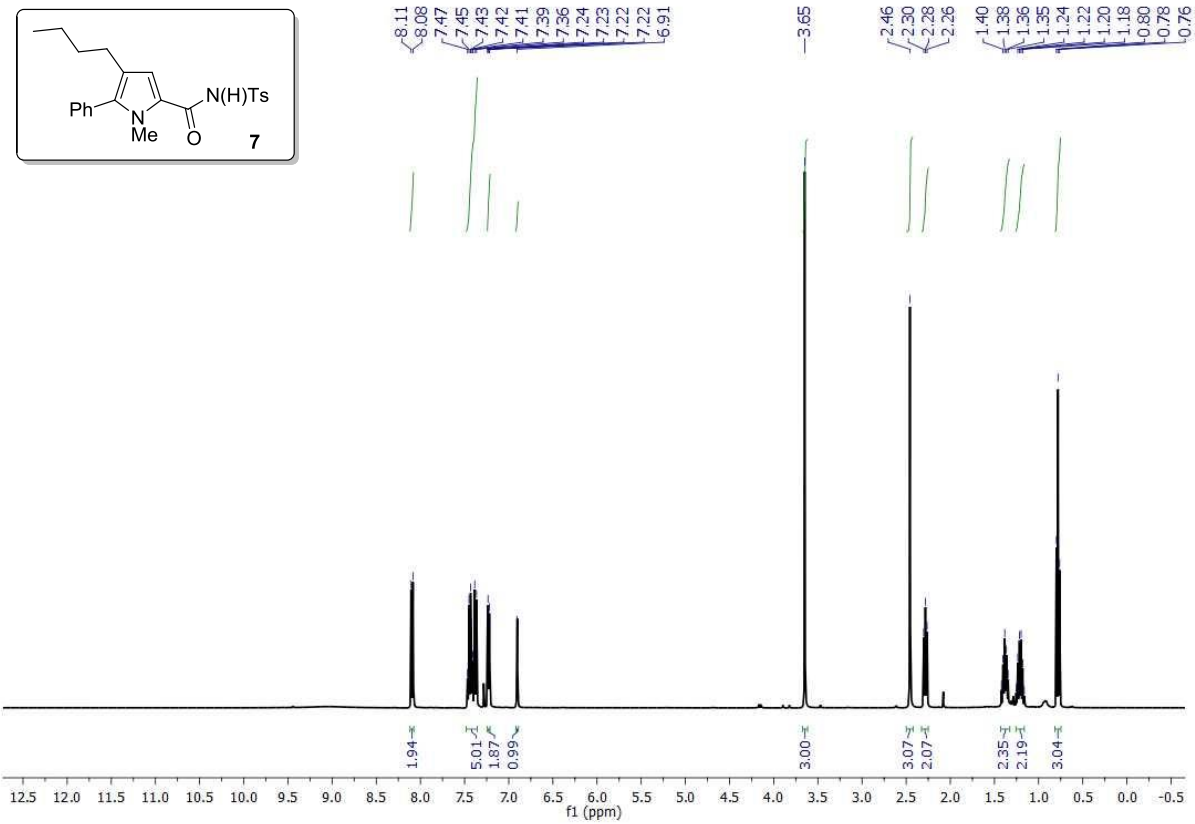
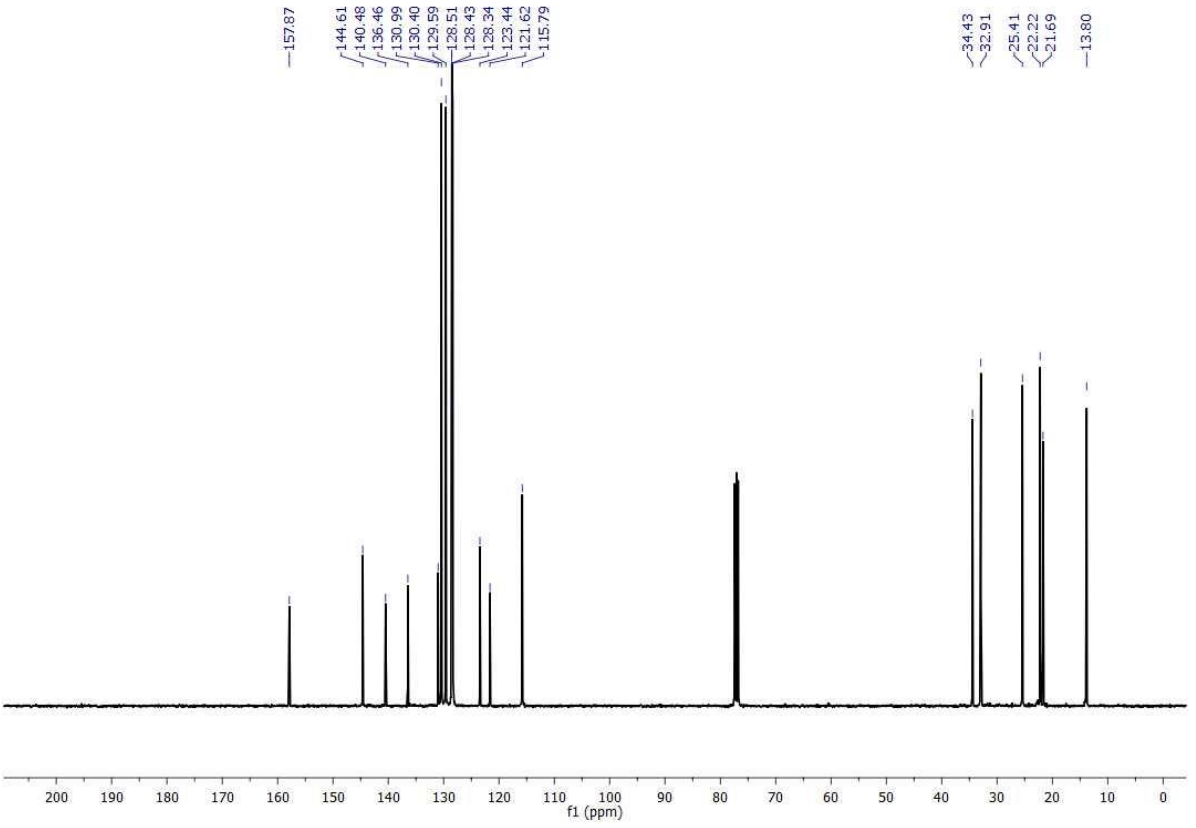
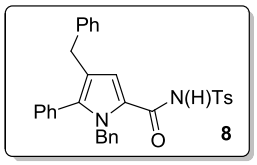
7.21
7.18
7.16
7.15
7.07
7.07
7.06
7.06
7.05
7.05
3.00
2.46
0.77
1.97
5.18
5.19
2.81
3.00
2.97
f1 (ppm)

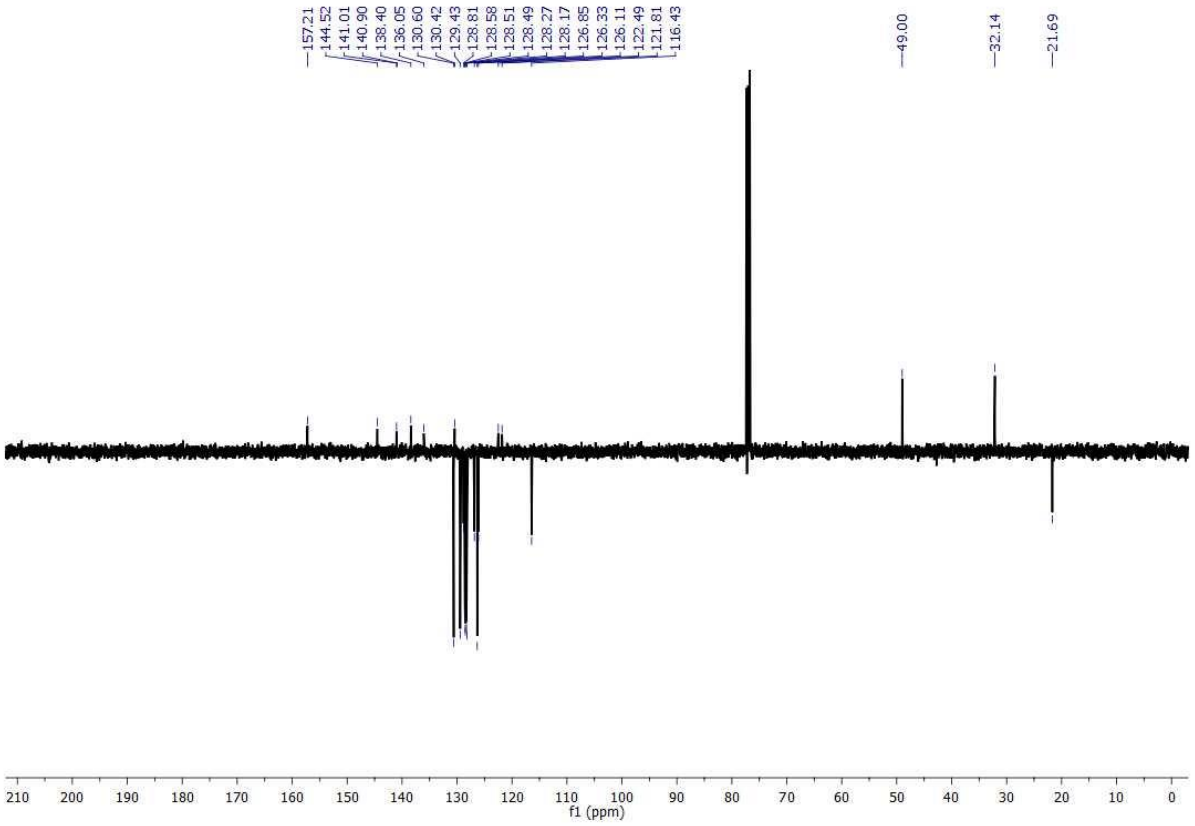

157.65
144.86
134.44
130.89
130.82
129.64
128.84
128.79
128.41
128.29
127.78
126.14
125.04
34.45
21.70
f1 (ppm)

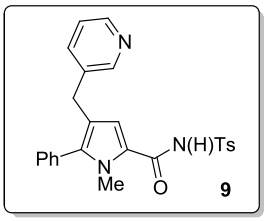

Ph
N
Me
O
N(H)Ts
7
8.11
8.08
7.47
7.45
7.43
7.42
7.41
7.39
7.36
7.24
7.23
7.22
7.22
6.91
3.65
2.46
2.30
2.28
2.26
1.40
1.38
1.36
1.35
1.24
1.22
1.20
1.18
0.80
0.78
0.76
1.94
5.01
1.87
0.99
3.00
3.07
2.07
2.35
2.19
3.04
f1 (ppm)


157.87
144.61
140.48
136.46
130.99
130.40
129.59
128.51
128.43
128.34
123.44
121.62
115.79
34.43
32.91
25.41
22.22
21.69
13.80
f1 (ppm)

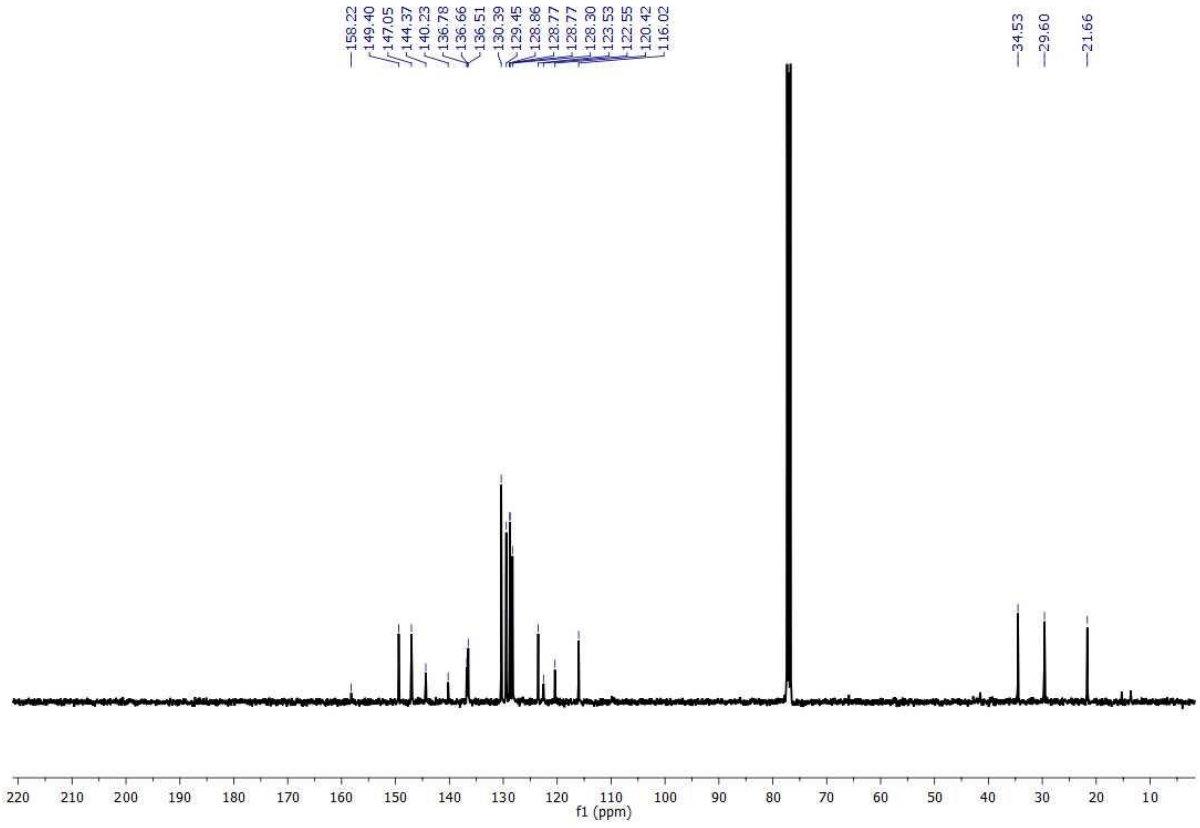

Ph
Ph
N
Bn
N(H)Ts
O
8

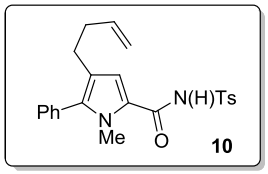
8.21
7.93
7.90
7.39
7.29
7.16
7.09
7.07
6.85
6.63
5.38
3.66
2.45
0.83
1.81
4.26
1.08
2.81
1.76
1.95
3.02
f1 (ppm)


157.21
144.52
141.01
140.90
138.40
136.05
130.60
130.42
129.43
128.81
128.58
128.51
128.49
128.27
128.17
126.85
126.33
126.11
122.49
121.81
116.43
49.00
32.14
21.69
f1 (ppm)

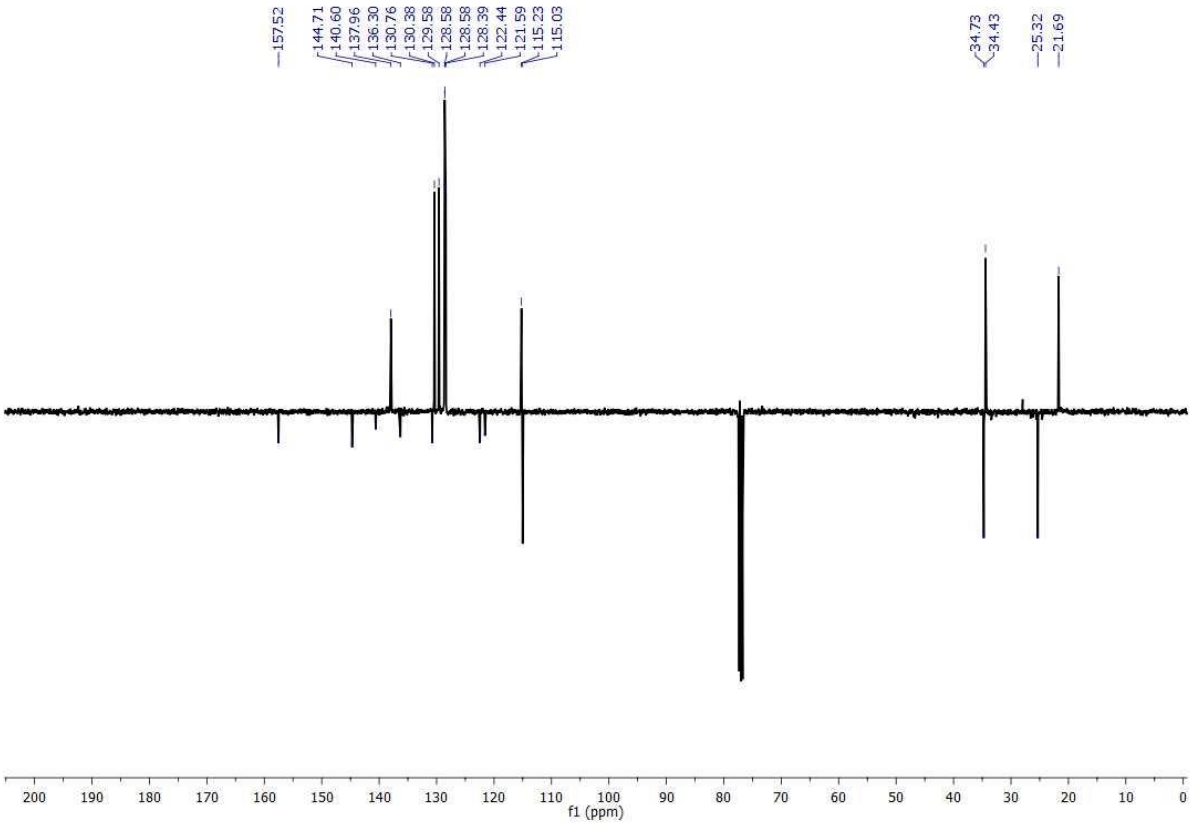

N
Ph
N
Me
O
N(H)Ts
9

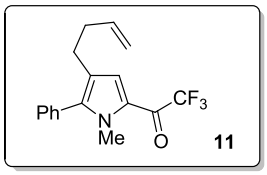
8.40
8.39
8.34
8.01
7.99
7.46
7.35
7.33
7.23
6.65
3.68
2.45
1.81
2.21
6.21
3.03
1.01
5.00
3.33
f1 (ppm)


158.22
149.40
147.05
144.37
140.23
136.78
136.66
136.51
130.39
129.45
128.86
128.77
128.77
128.30
123.53
122.55
120.42
116.02
34.53
29.60
21.66
f1 (ppm)


Ph
N
Me
O
N(H)Ts
10

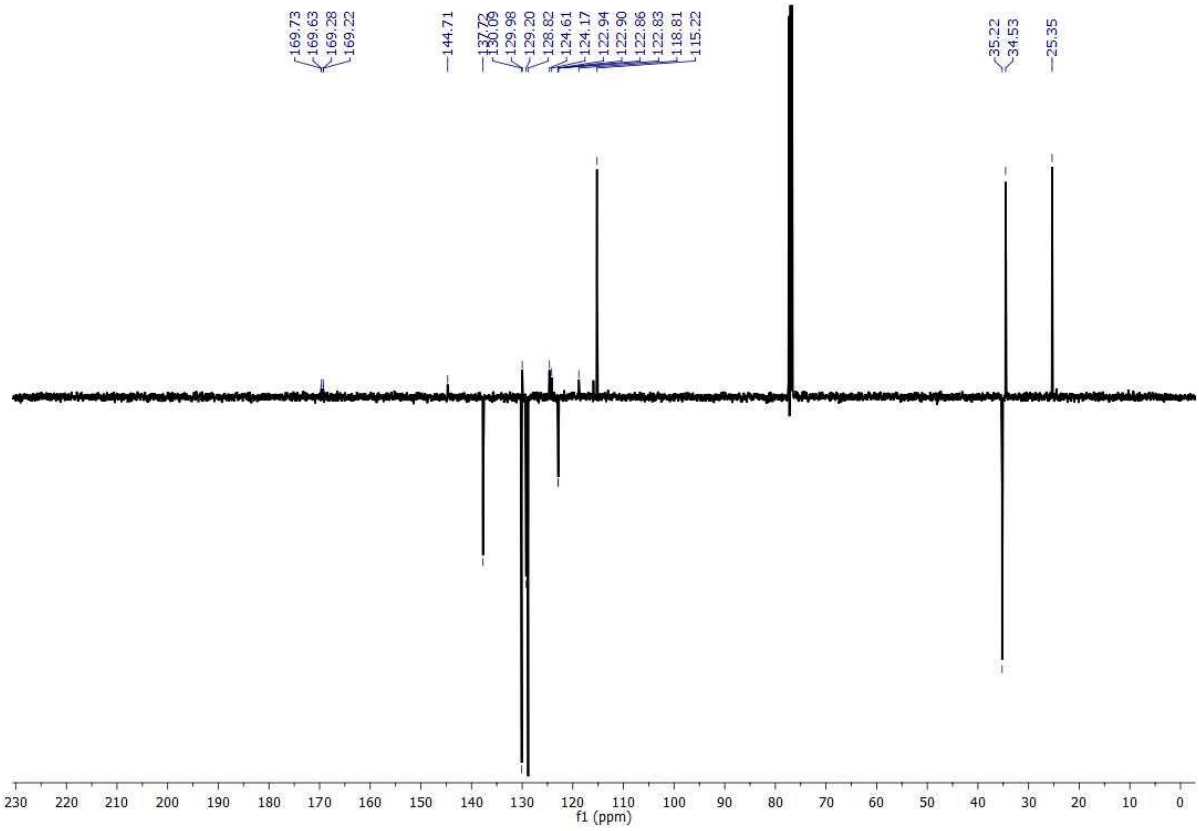
8.63
8.07
8.05
8.05
7.46
7.44
7.38
7.36
6.77
5.77
5.74
5.72
5.71
5.71
5.70
4.97
4.96
4.96
4.94
4.93
4.92
4.91
3.84
2.46
2.43
2.41
2.41
2.39
2.21
2.19
2.17
2.16
0.81
2.07
5.39
2.10
1.04
1.10
2.24
3.00
3.10
2.29
2.20
f1 (ppm)

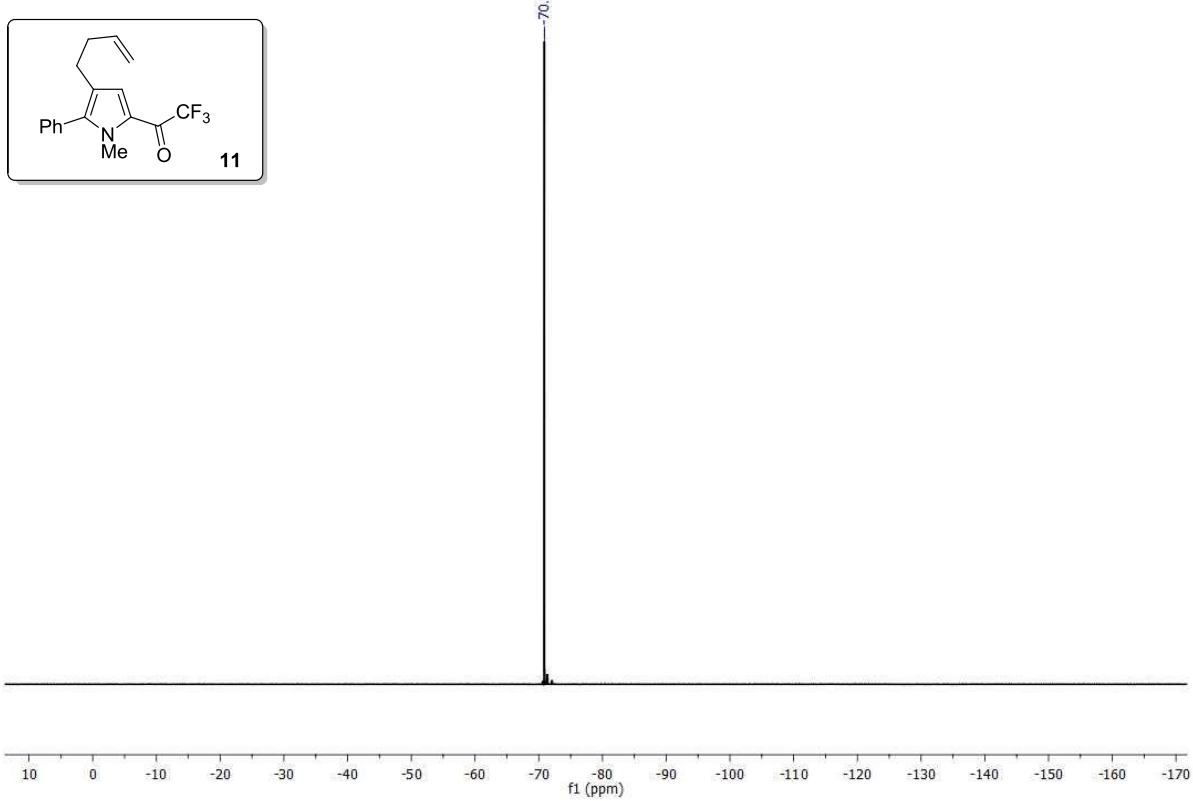

157.52
144.71
140.60
137.96
136.30
130.76
130.38
129.58
128.58
128.58
128.39
122.44
121.59
115.23
115.03
34.73
34.43
25.32
21.69
f1 (ppm)

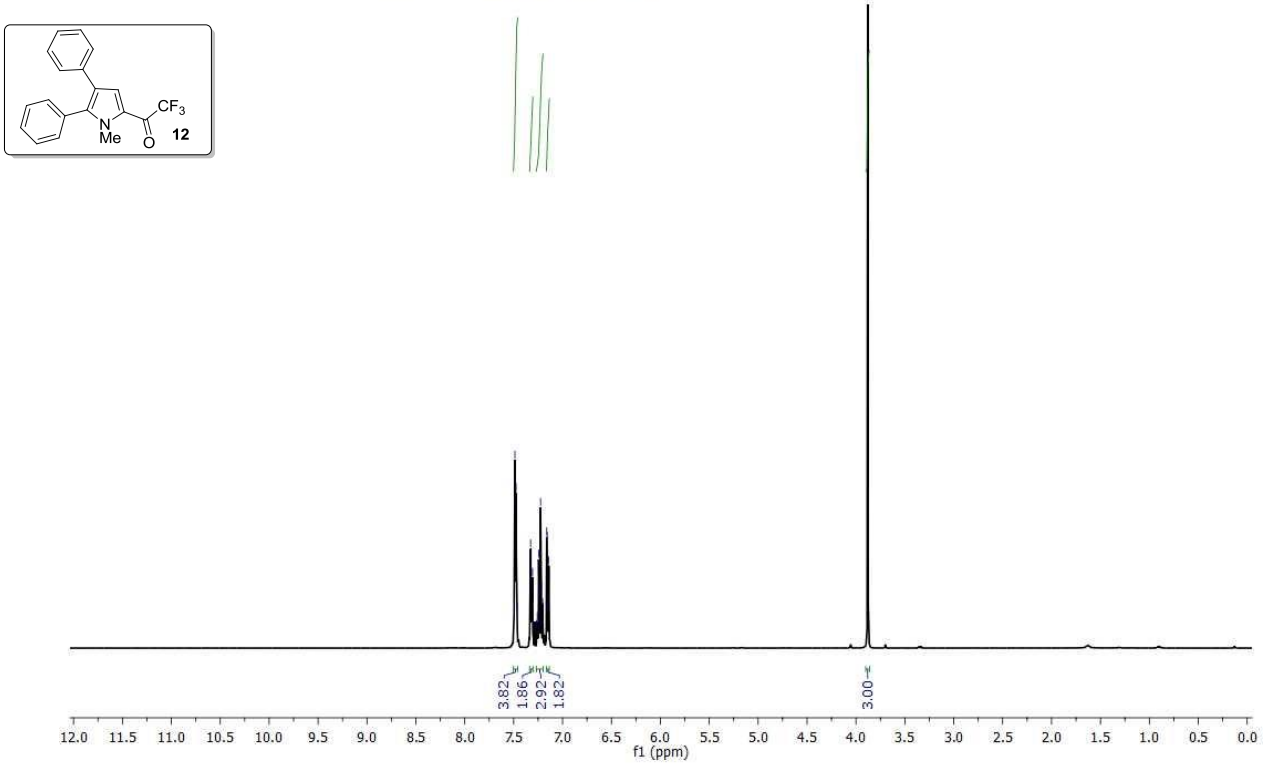

Ph
N
Me
O
CF3

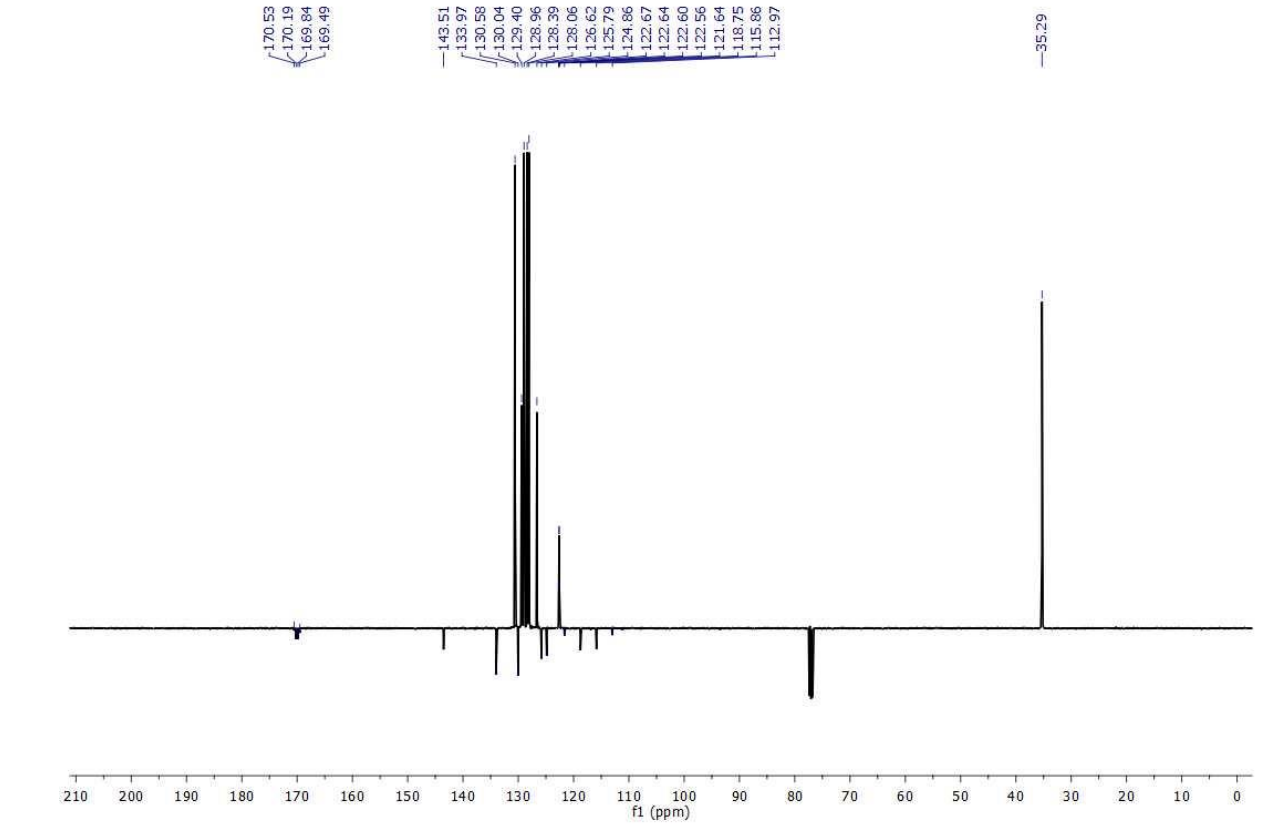
11

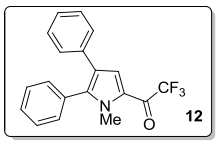
7.55
7.54
7.53
7.51
7.51
7.50
7.48
7.48
7.33
7.31
7.31
7.31
7.19
7.18
5.79
5.77
5.75
5.74
5.72
5.00
5.00
4.97
4.97
4.96
4.96
4.94
4.93
2.50
2.48
2.48
2.46
2.27
2.26
2.24
2.22
3.16
2.00
0.99
1.03
2.04
3.00
2.02
2.12
f1 (ppm)


169.73
169.63
169.28
169.22
144.71
137.72
130.09
129.98
129.20
128.82
124.61
124.17
122.94
122.90
122.86
122.83
118.81
115.22
35.22
34.53
25.35
f1 (ppm)

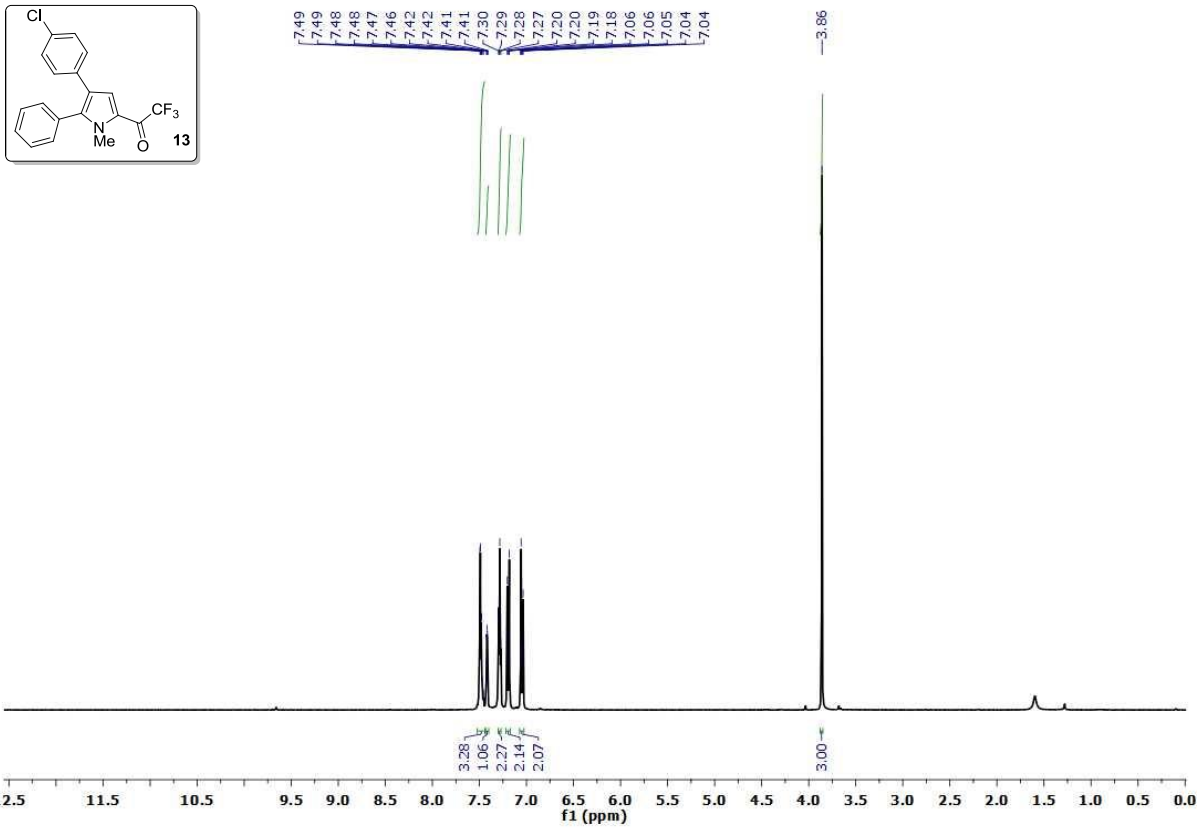

Ph
N
Me
O
CF3
11
-70.88
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

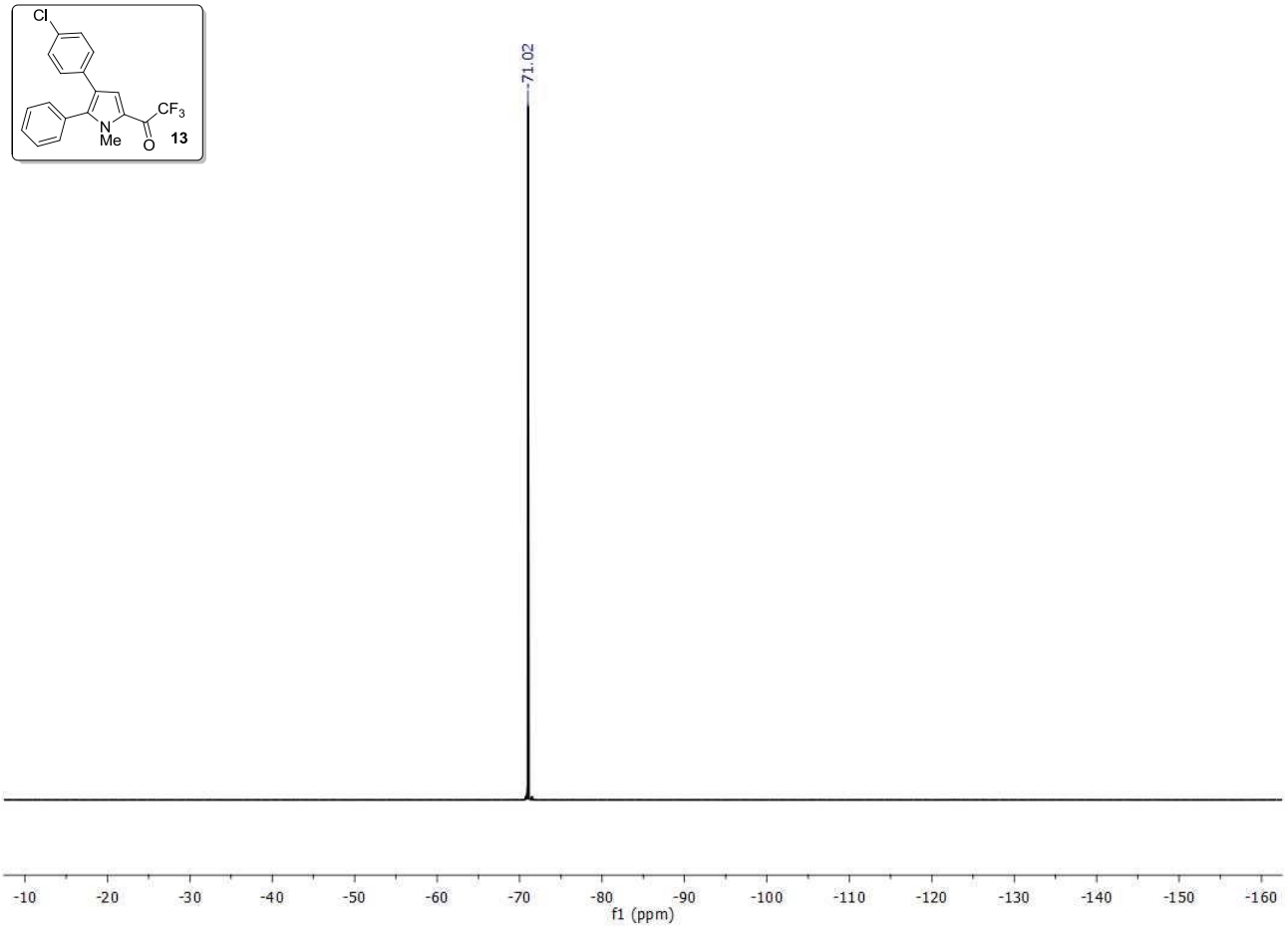

7.49
7.49
7.48
7.48
7.46
7.33
7.33
7.32
7.31
7.31
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.20
7.16
7.16
7.15
7.15
7.14
7.14
3.88
3.82
1.86
2.92
1.82
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
CF3
N
Me
O
12

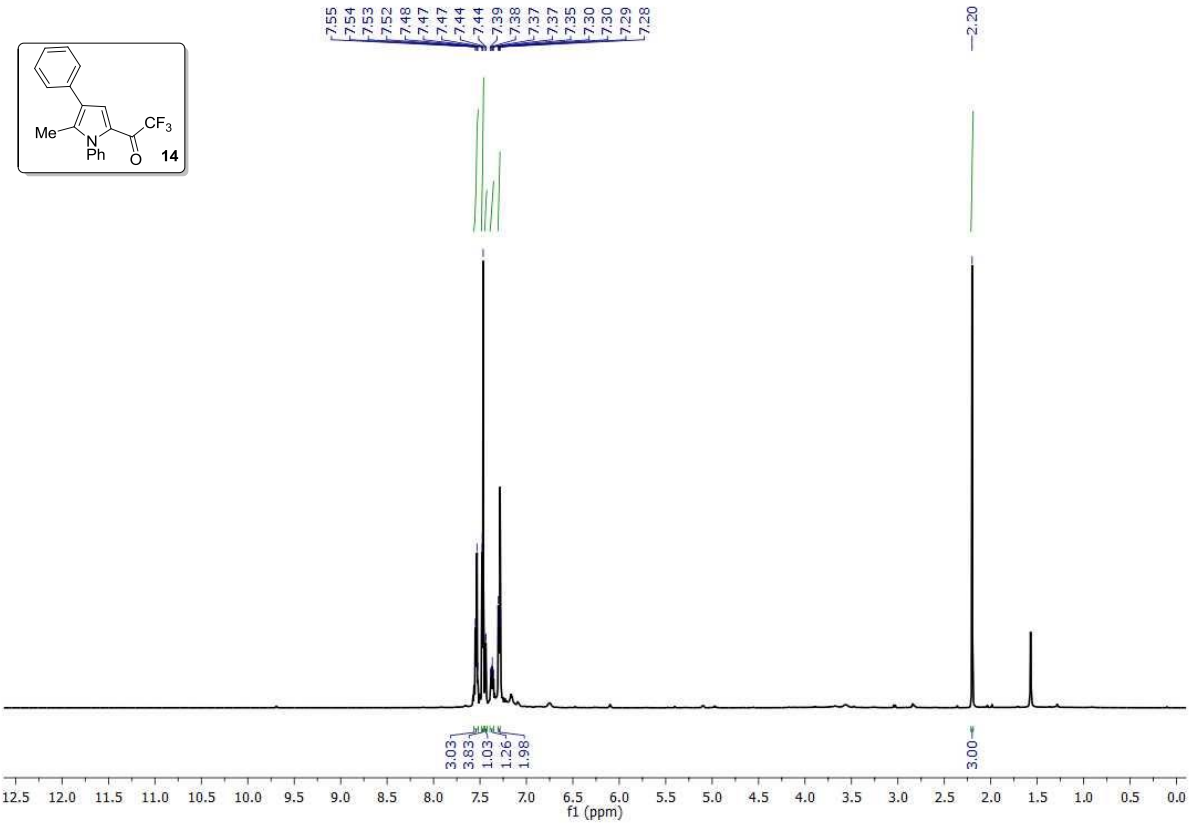

170.53
170.19
169.84
169.49
143.51
133.97
130.58
130.04
129.40
128.96
128.39
128.06
126.62
125.79
124.86
122.67
122.64
122.60
122.56
121.64
118.75
115.86
112.97
35.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

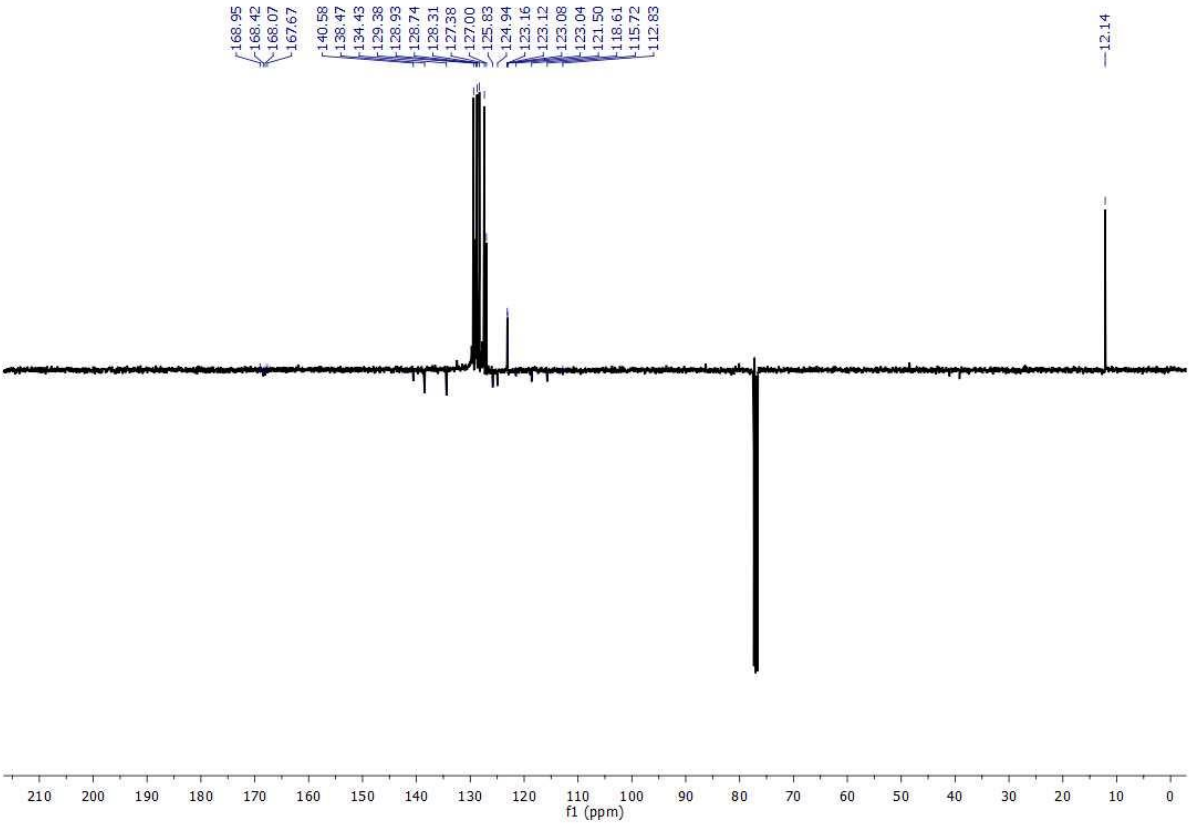

CF3
N
Me
O
12

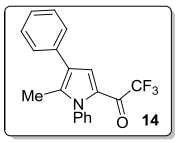
-70.94
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


Cl
CF3
N
Me
O
13
7.49
7.49
7.48
7.48
7.47
7.46
7.42
7.42
7.41
7.41
7.30
7.29
7.28
7.27
7.20
7.20
7.19
7.18
7.06
7.06
7.05
7.04
7.04
3.86
3.28
1.06
2.27
2.14
2.07
3.00
12.5
11.5
10.5
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
f1 (ppm)
170.58
170.23
169.88
169.53
143.39
132.48
130.49
129.74
129.57
129.24
129.09
128.57
124.90
124.52
122.28
122.25
121.55
118.66
115.77
112.88
35.30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

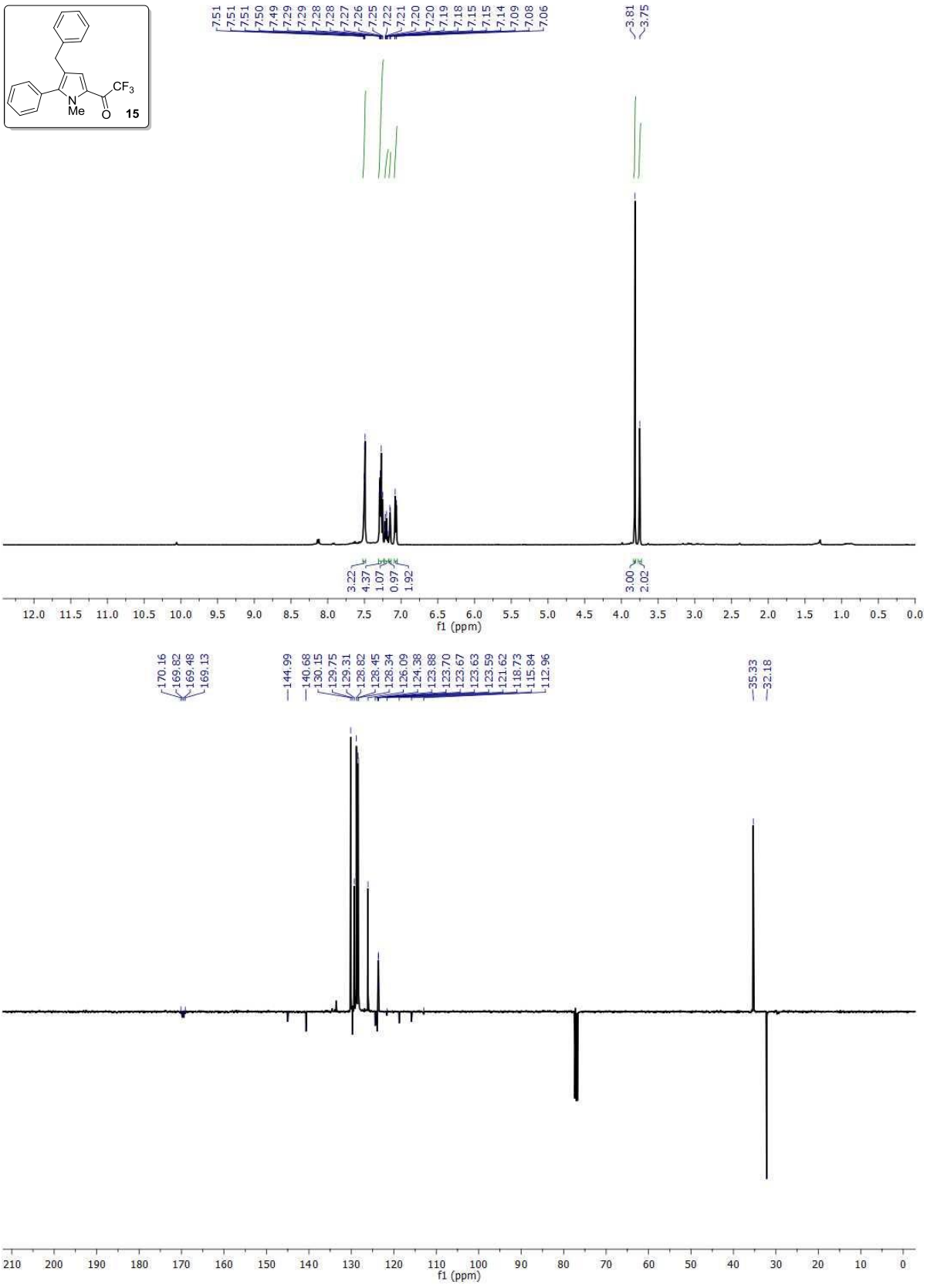

Cl
CF3
N
Me
O
13
-71.02
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

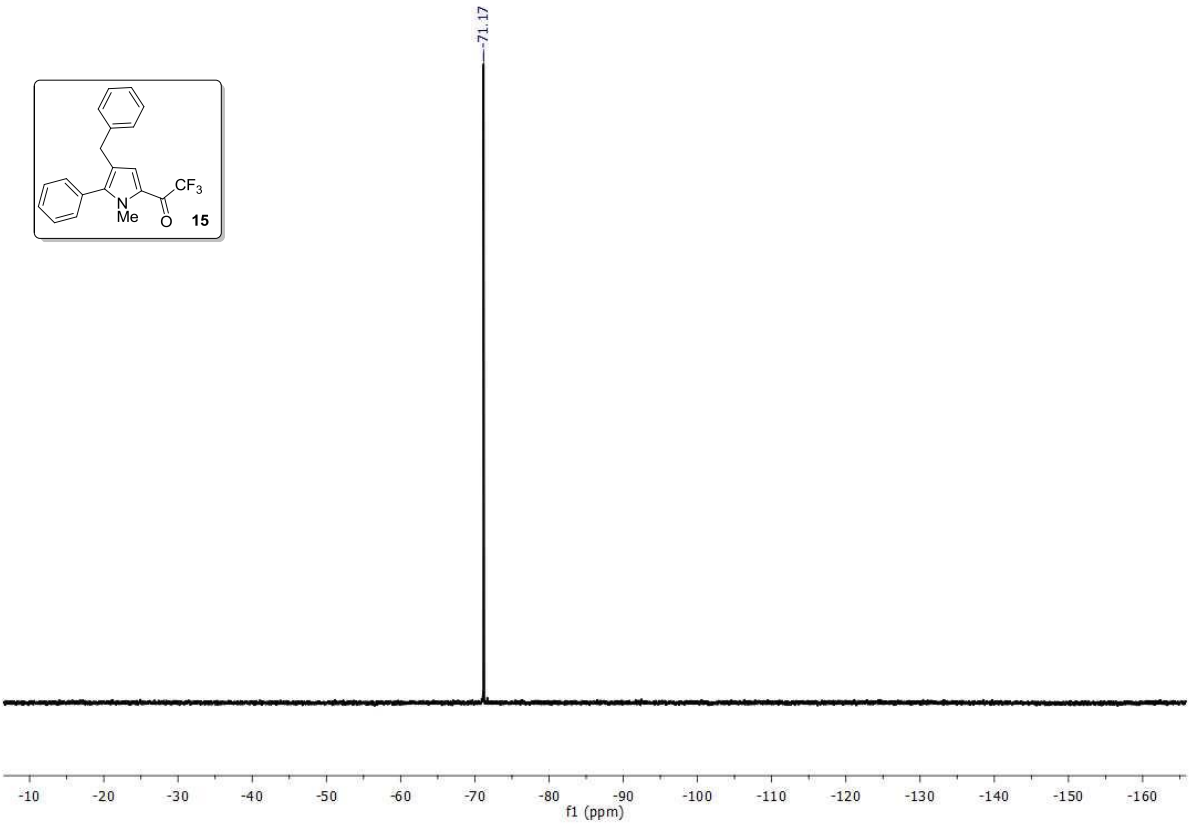

Me
N
Ph
CF3
O
14
7.55
7.54
7.53
7.52
7.48
7.47
7.47
7.44
7.44
7.39
7.38
7.37
7.37
7.35
7.30
7.30
7.29
7.28
2.20
3.03
3.83
1.03
1.26
1.98
3.00
f1 (ppm)

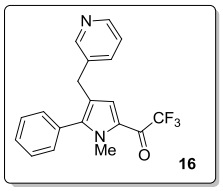

168.95
168.42
168.07
167.67
140.58
138.47
134.43
129.38
128.93
128.74
128.31
127.38
127.00
125.83
124.94
123.16
123.12
123.08
123.04
121.50
118.61
115.72
112.83
12.14
f1 (ppm)


Me
N
Ph
CF3
O
14

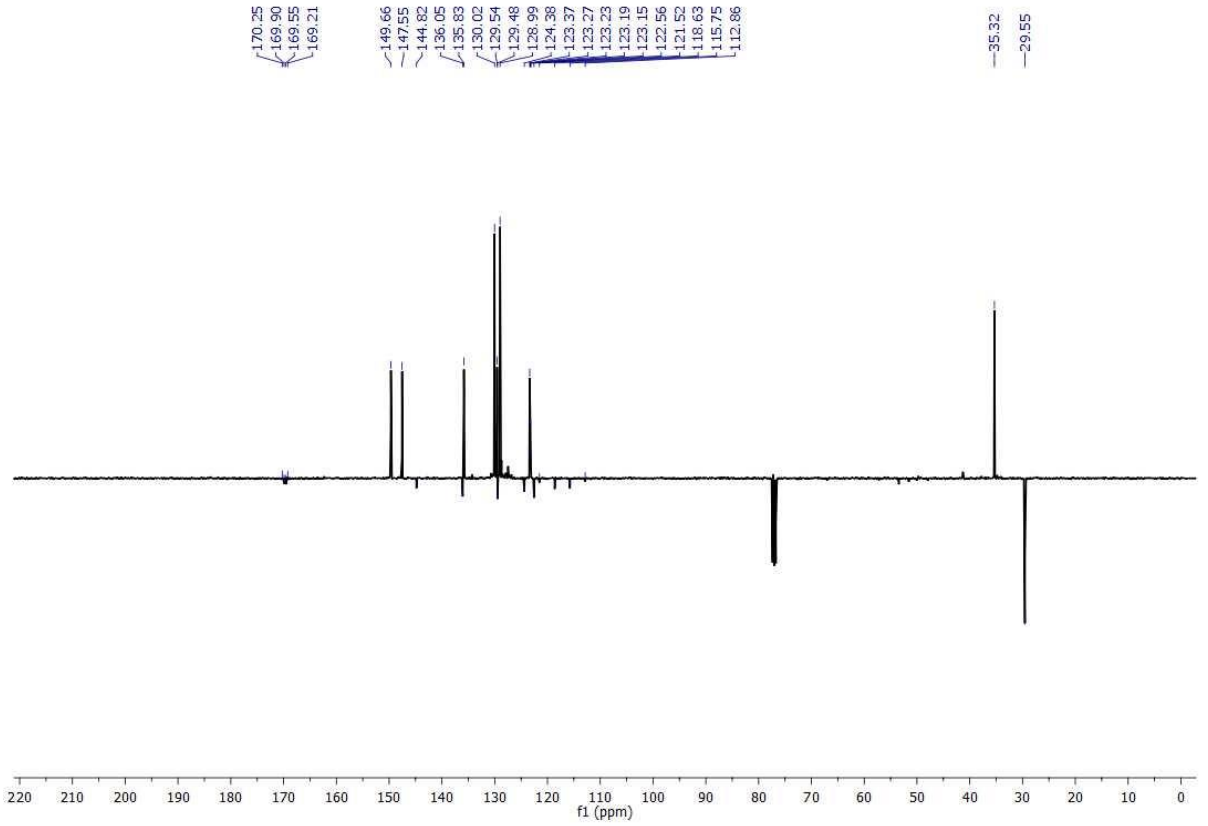
-71.20
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

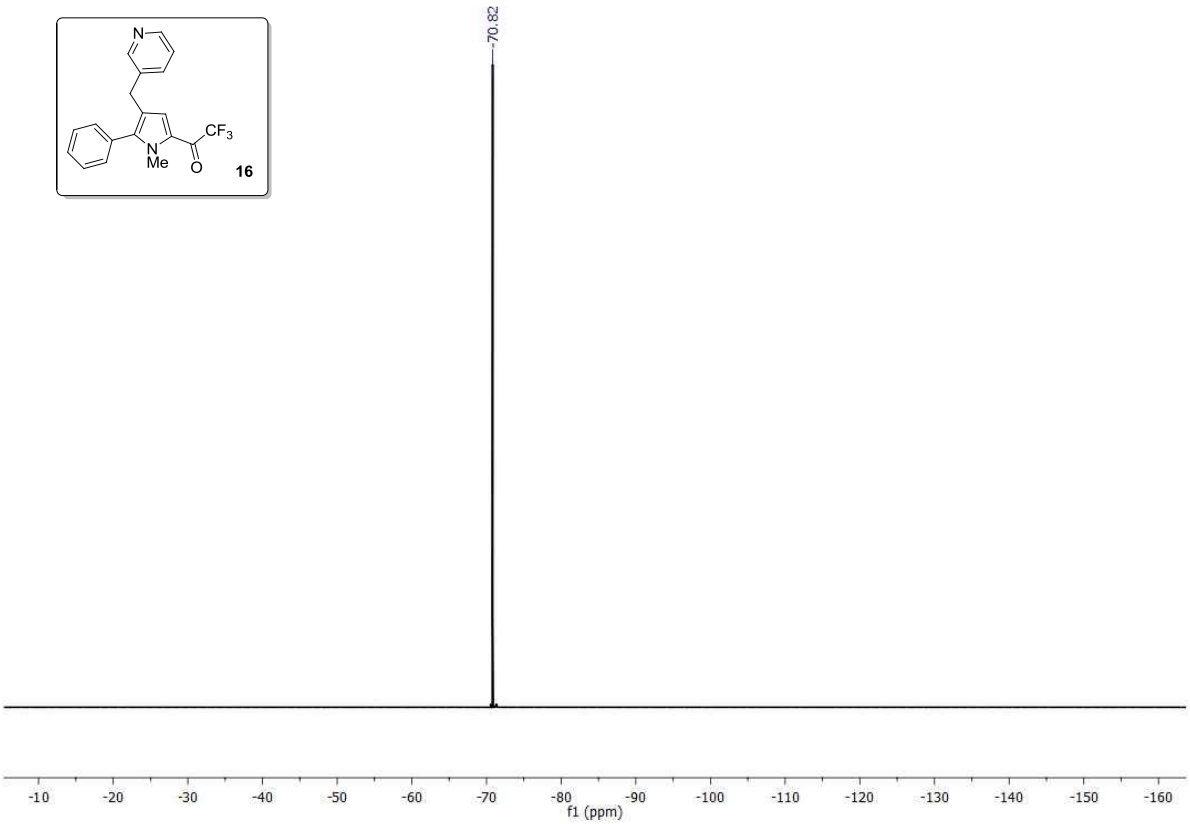

CF3
N
Me
O
15
7.51
7.51
7.51
7.50
7.49
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.22
7.21
7.20
7.20
7.19
7.18
7.15
7.15
7.14
7.09
7.08
7.06
3.81
3.75
3.22
4.37
1.07
0.97
1.92
3.00
2.02
f1 (ppm)
170.16
169.82
169.48
169.13
144.99
140.68
130.15
129.75
129.31
128.82
128.45
128.34
126.09
124.38
123.88
123.70
123.67
123.63
123.59
121.62
118.73
115.84
112.96
35.33
32.18
f1 (ppm)

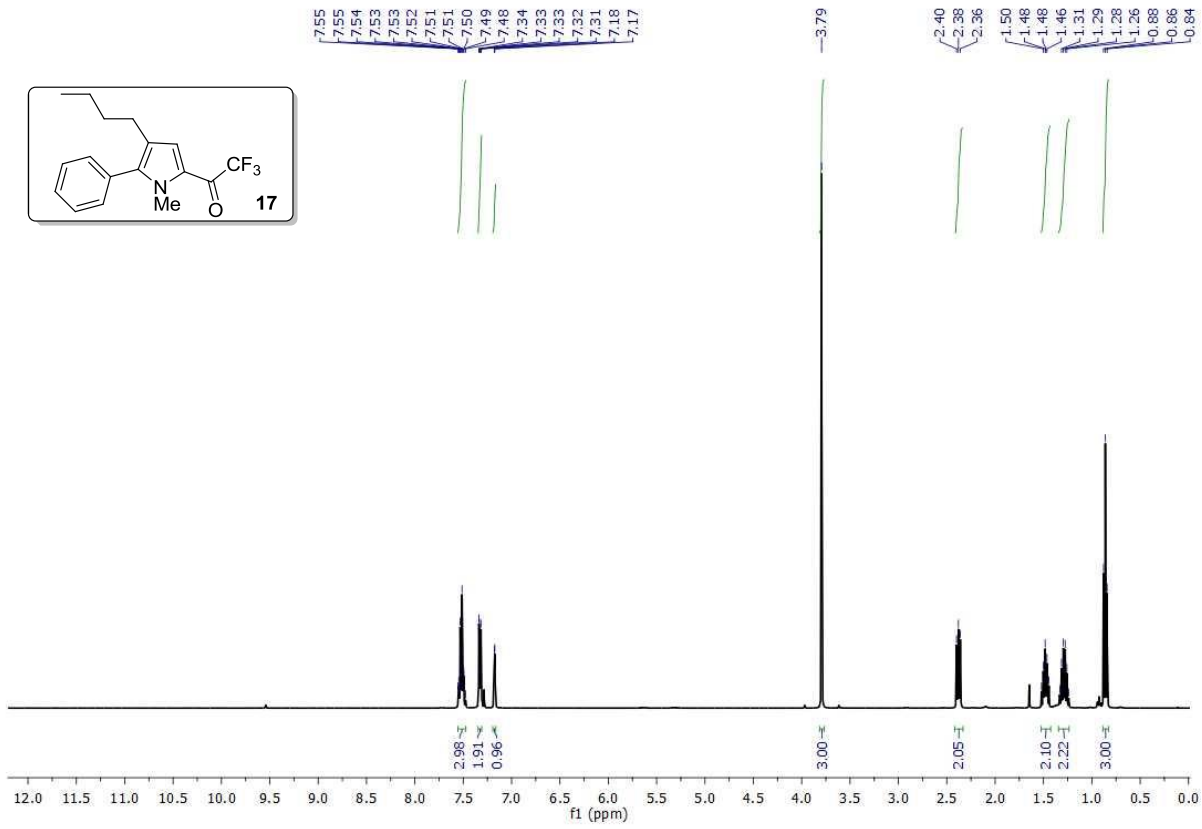

-71.17
CF3
N
Me
O
15
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

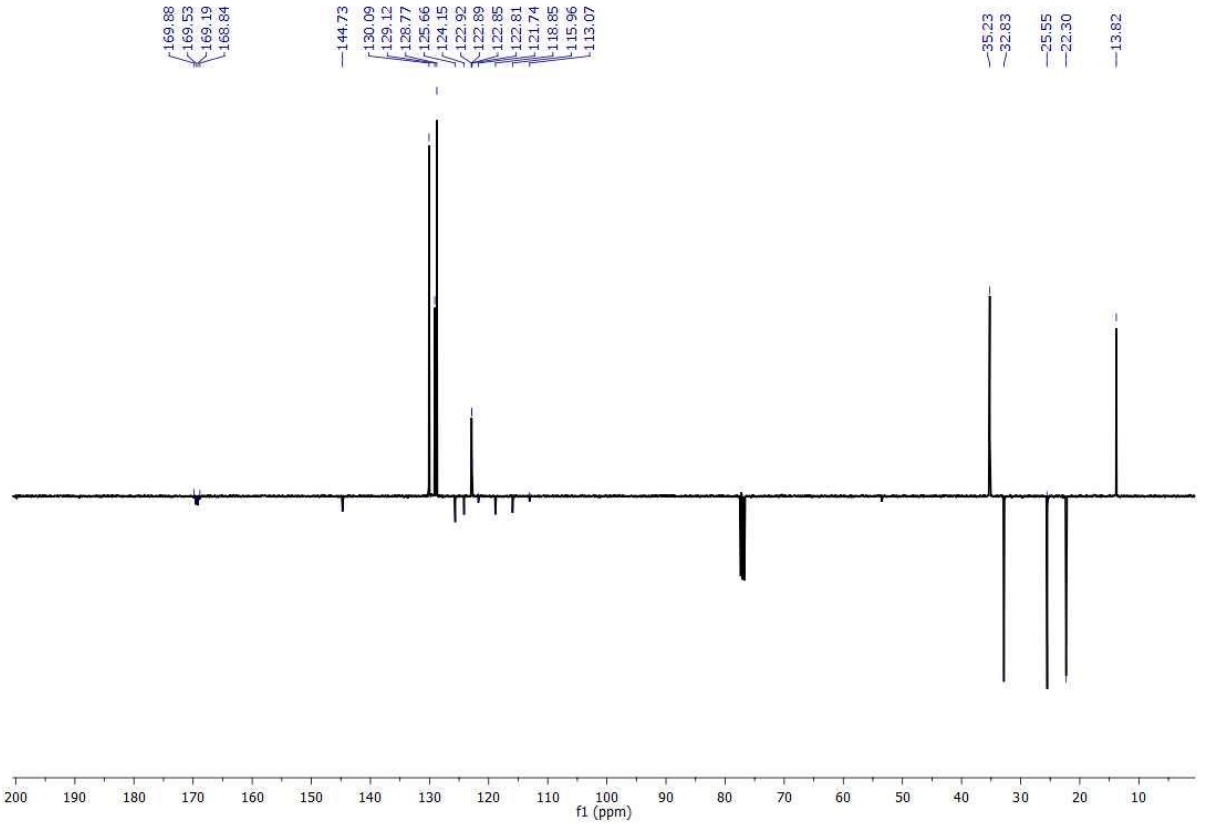

N
CF3
N
Me
O
16

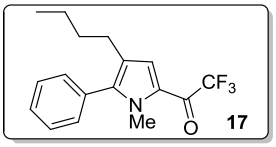
8.44
8.43
8.43
8.42
8.30
8.29
7.51
7.50
7.49
7.37
7.35
7.26
7.24
7.23
7.19
7.18
7.17
7.16
7.12
7.12
7.11
3.80
3.74
1.99
3.12
1.31
1.96
2.02
3.00
2.00
f1 (ppm)


170.25
169.90
169.55
169.21
149.66
147.55
144.82
136.05
135.83
130.02
129.54
129.48
128.99
124.38
123.37
123.27
123.23
123.19
123.15
122.56
121.52
118.63
115.75
112.86
35.32
29.55
f1 (ppm)

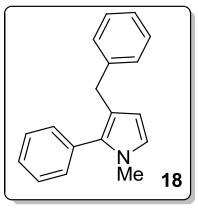

N
CF3
N
Me
O
16
-70.82
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.48
7.34
7.33
7.33
7.32
7.31
7.18
7.17
3.79
2.40
2.38
2.36
1.50
1.48
1.48
1.46
1.31
1.29
1.28
1.26
0.88
0.86
0.84
CF3
N
Me
O
17
2.98
1.91
0.96
3.00
2.05
2.10
2.22
3.00
f1 (ppm)

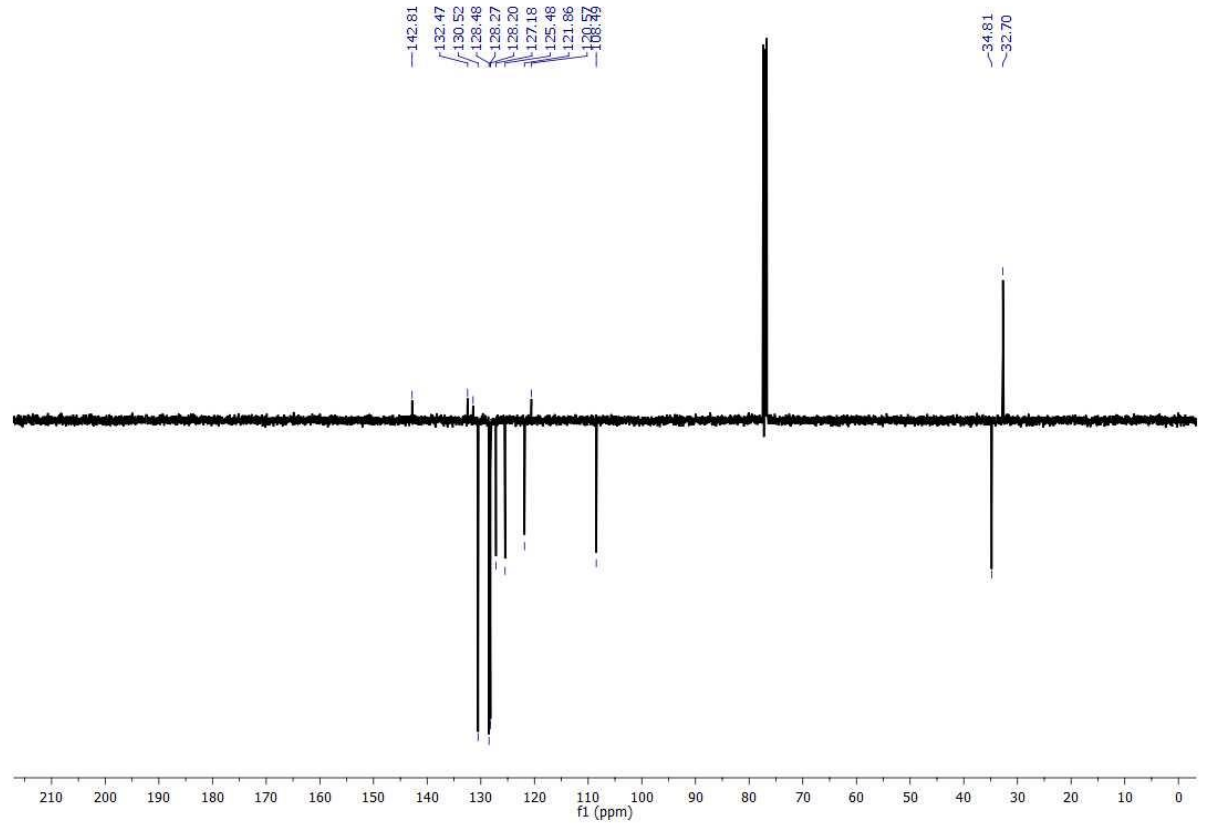

169.88
169.53
169.19
168.84
144.73
130.09
129.12
128.77
125.66
124.15
122.92
122.89
122.85
122.81
121.74
118.85
115.96
113.07
35.23
32.83
25.55
22.30
13.82
f1 (ppm)

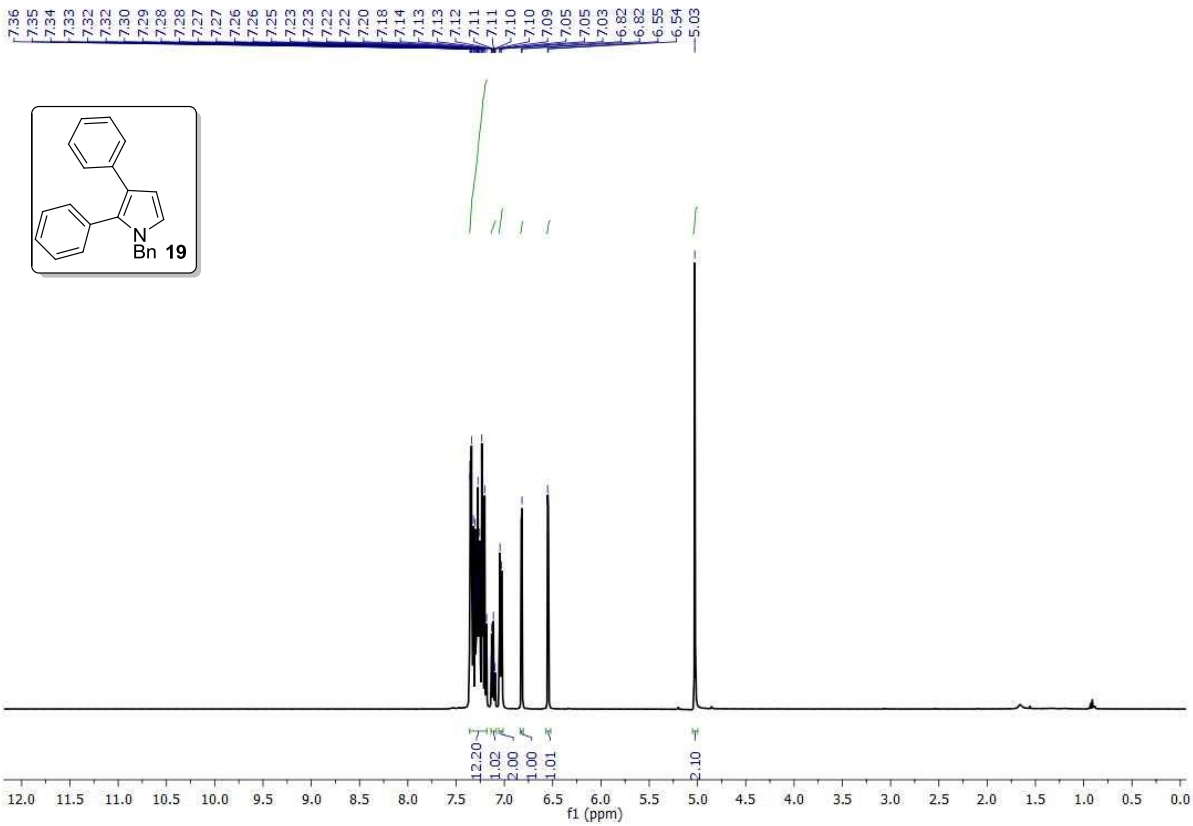

CF3
N
Me
O
17

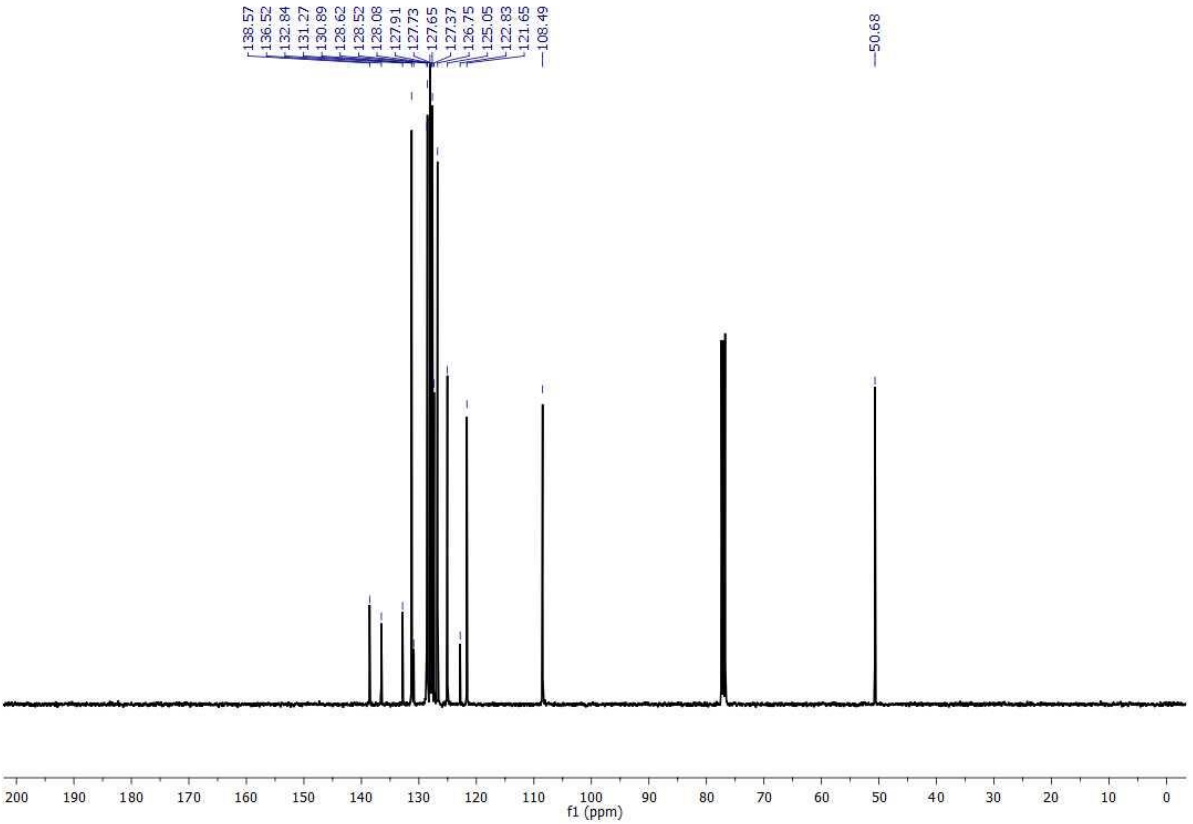
-71.03
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

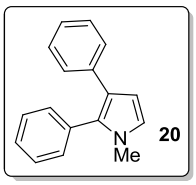

N
Me
18

7.45
7.43
7.41
7.38
7.36
7.34
7.33
7.32
7.27
7.25
7.19
7.17
7.15
6.67
6.67
6.05
6.04
3.79
3.54
2.13
3.31
5.12
1.02
1.00
2.13
3.17
f1 (ppm)


142.81
132.47
130.52
128.48
128.27
128.20
127.18
125.48
121.86
34.81
32.70
f1 (ppm)

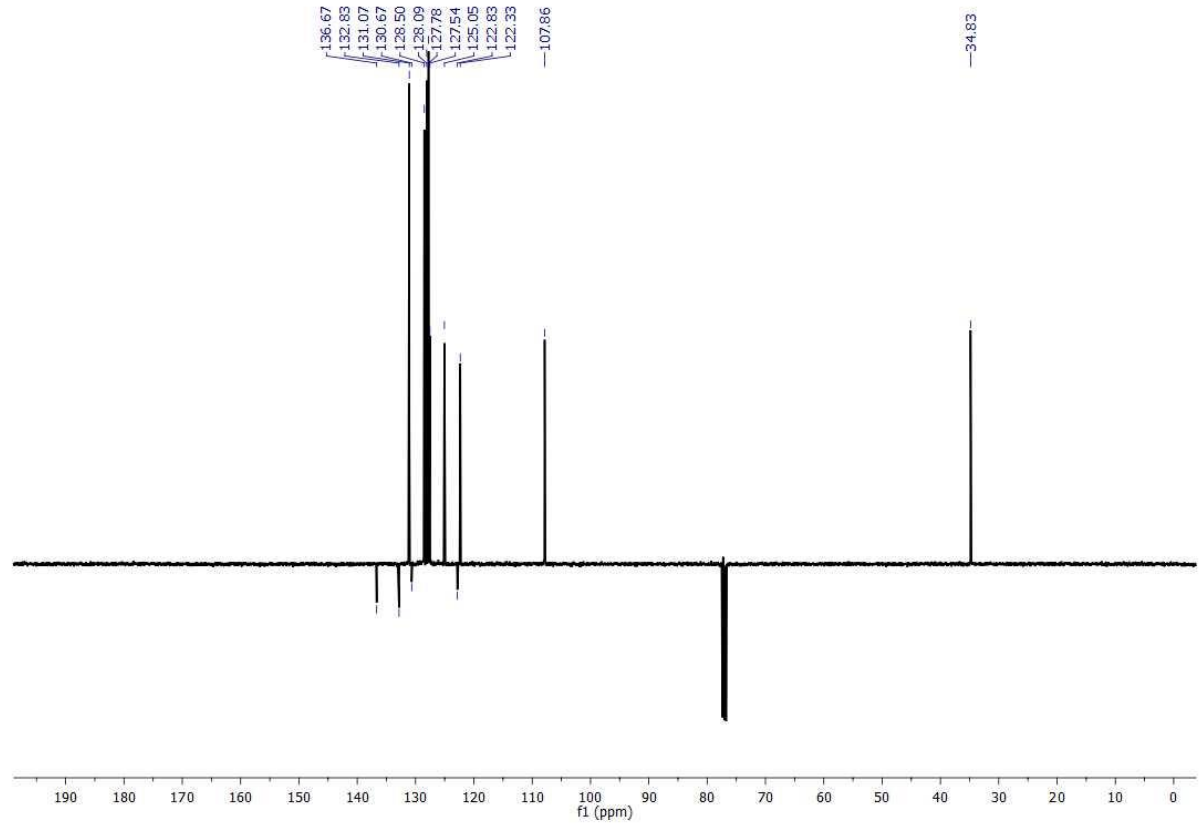

7.36
7.35
7.34
7.33
7.32
7.32
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.23
7.23
7.22
7.22
7.20
7.18
7.14
7.13
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.05
7.05
7.03
6.82
6.82
6.55
6.54
5.03
N
Bn 19
12.20
1.02
2.00
1.00
1.01
2.10
f1 (ppm)

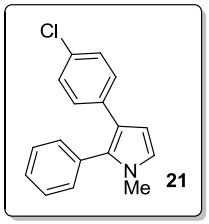

138.57
136.52
132.84
131.27
130.89
128.62
128.52
128.08
127.91
127.73
127.65
127.37
126.75
125.05
122.83
121.65
108.49
50.68
f1 (ppm)


N
Me

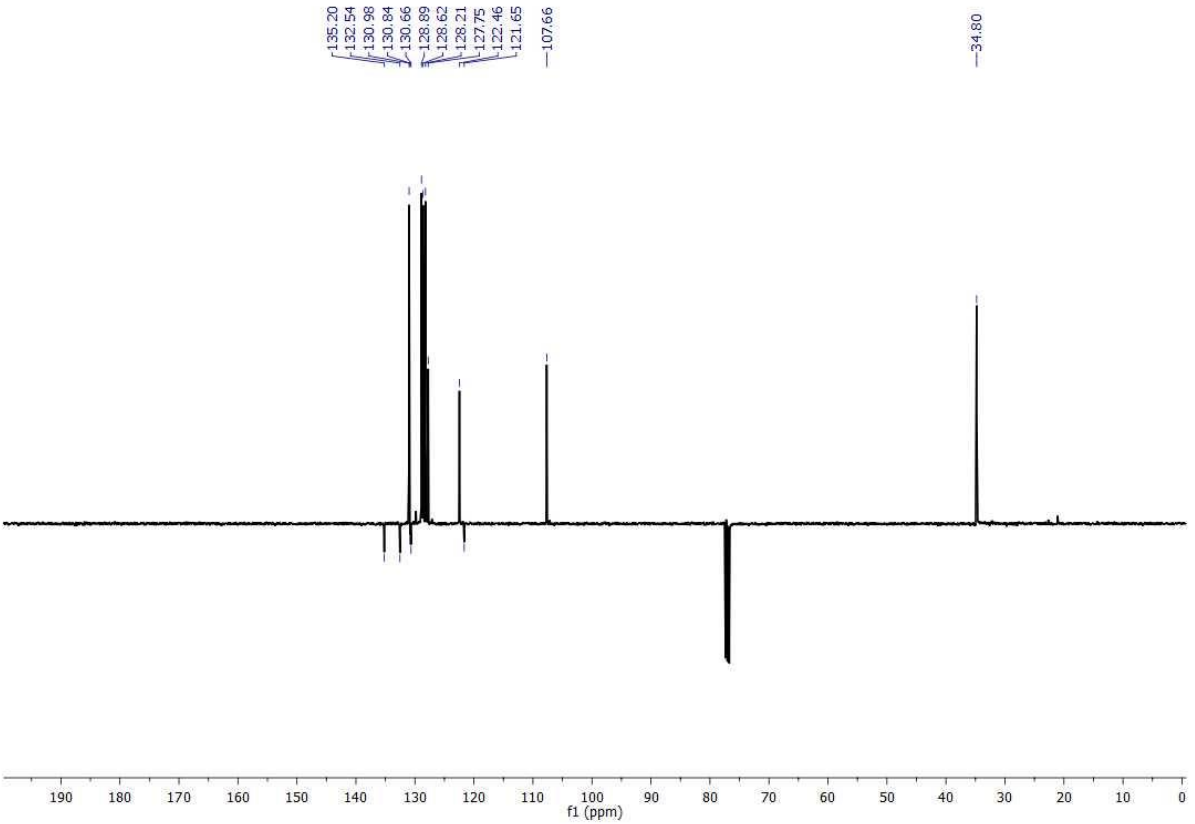
20

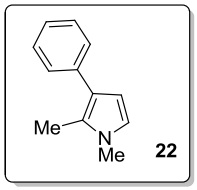
7.44
7.43
7.42
7.40
7.39
7.39
7.38
7.35
7.34
7.33
7.33
7.32
7.22
7.21
7.21
7.19
7.14
7.13
7.13
7.12
7.11
7.11
7.10
6.79
6.78
6.47
6.46
3.56
5.35
4.07
1.07
0.98
0.99
3.00
f1 (ppm)


136.67
132.83
131.07
130.67
128.50
128.09
127.78
127.54
125.05
122.83
122.33
107.86
34.83
f1 (ppm)


Cl
N
Me
21

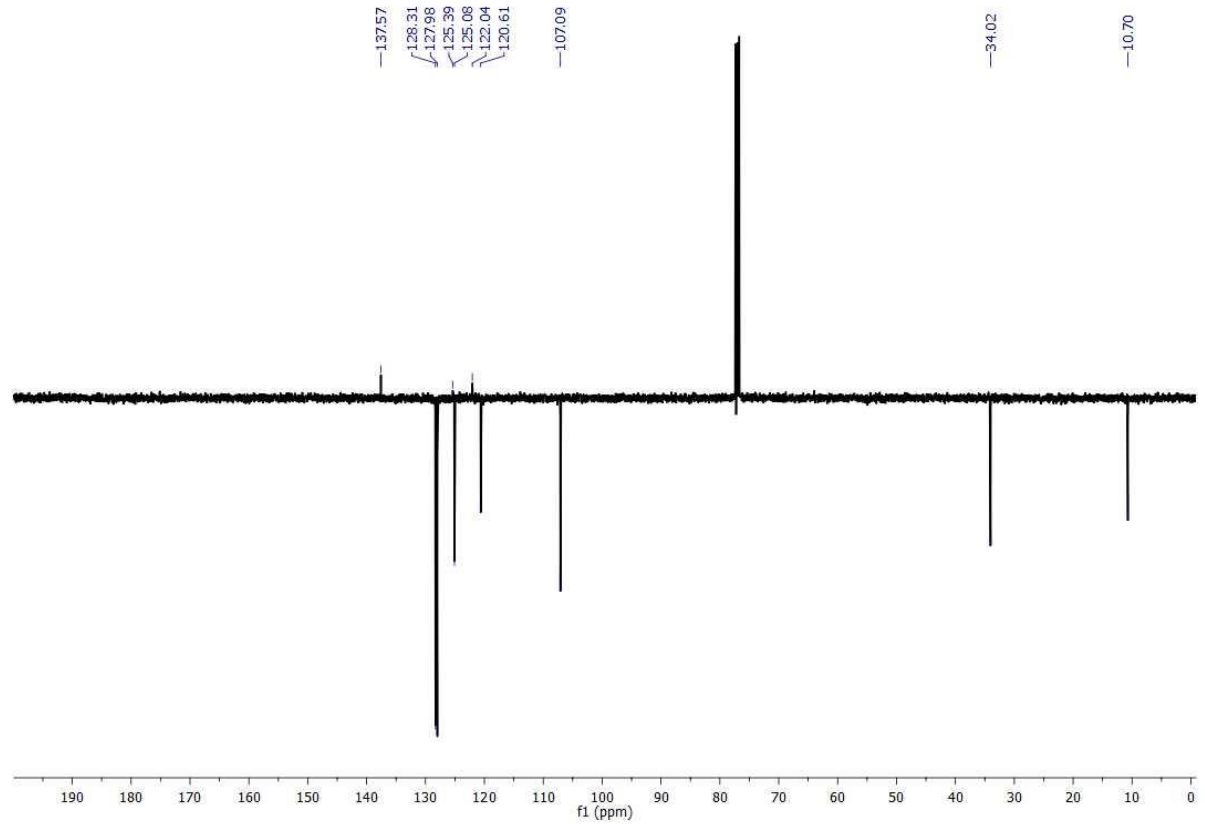
7.44
7.43
7.42
7.40
7.39
7.38
7.36
7.31
7.31
7.29
7.28
7.16
7.16
7.15
7.14
7.12
7.10
7.10
6.77
6.77
6.42
6.41
3.54
3.28
2.19
4.14
0.96
0.95
3.00
f1 (ppm)

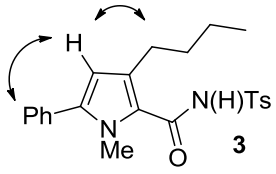

135.20
132.54
130.98
130.84
130.66
128.89
128.62
128.21
127.75
122.46
121.65
107.66
34.80
f1 (ppm)

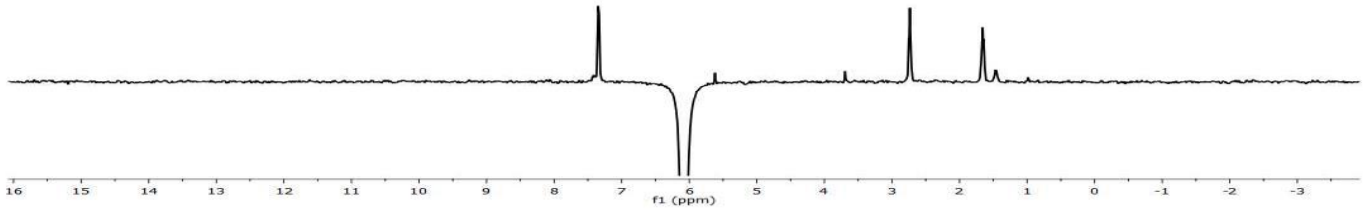

Me
N
Me

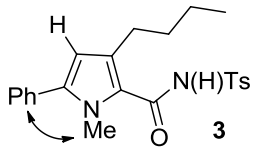
22

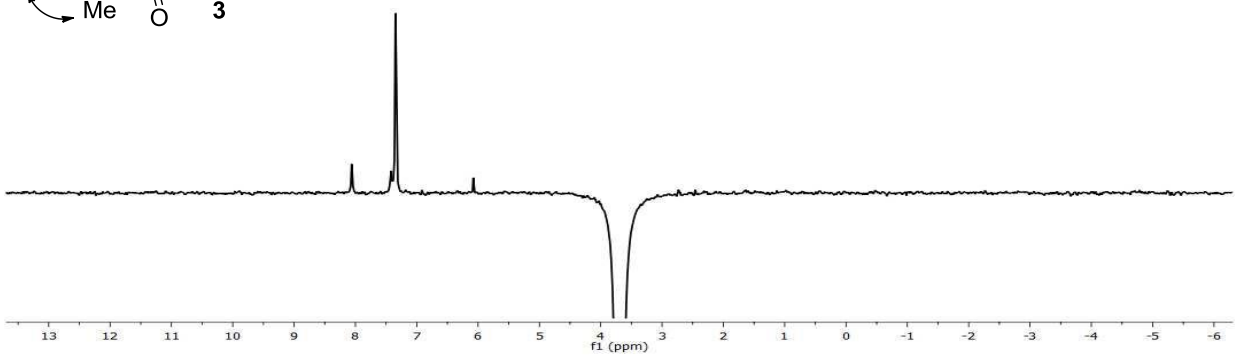
7.43
7.41
7.41
7.39
7.37
7.25
7.24
7.23
7.22
7.21
7.21
6.64
6.64
6.28
6.27
3.61
2.37
4.09
1.01
0.93
0.95
3.01
3.00
f1 (ppm)

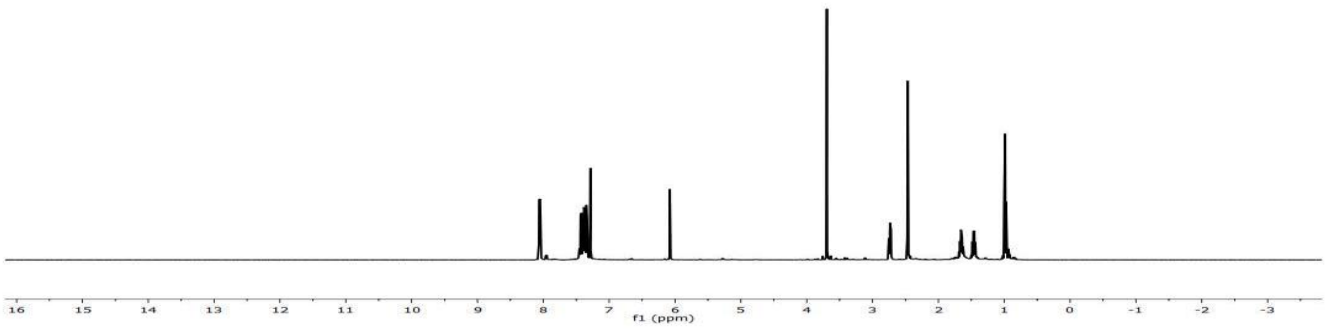

137.57
128.31
127.98
125.39
125.08
122.04
120.61
107.09
34.02
10.70
f1 (ppm)

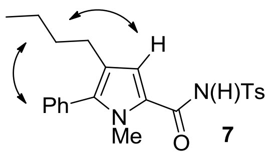

H
Ph
N
Me
O
N(H)Ts
3

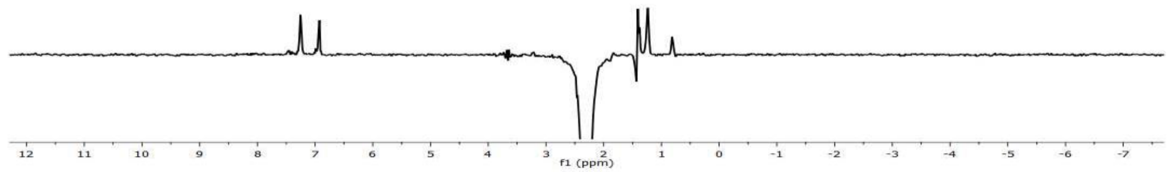

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

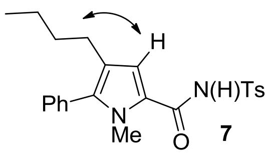

H
Ph
N
Me
O
N(H)Ts
3

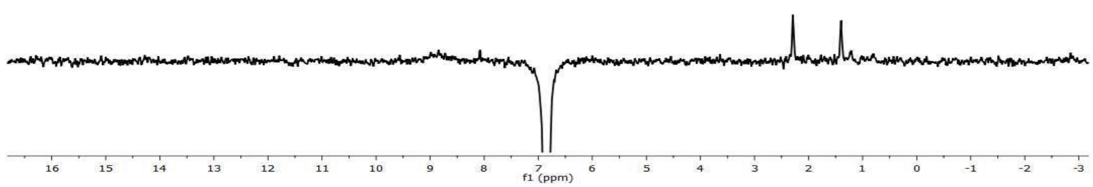

13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6
f1 (ppm)

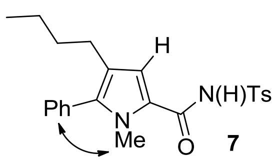

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

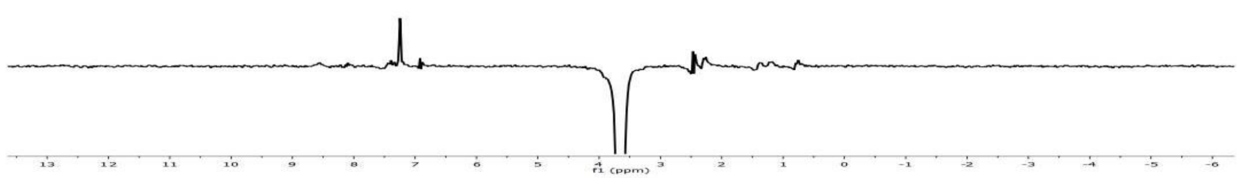

H
N(H)Ts
Ph
N
Me
O
7

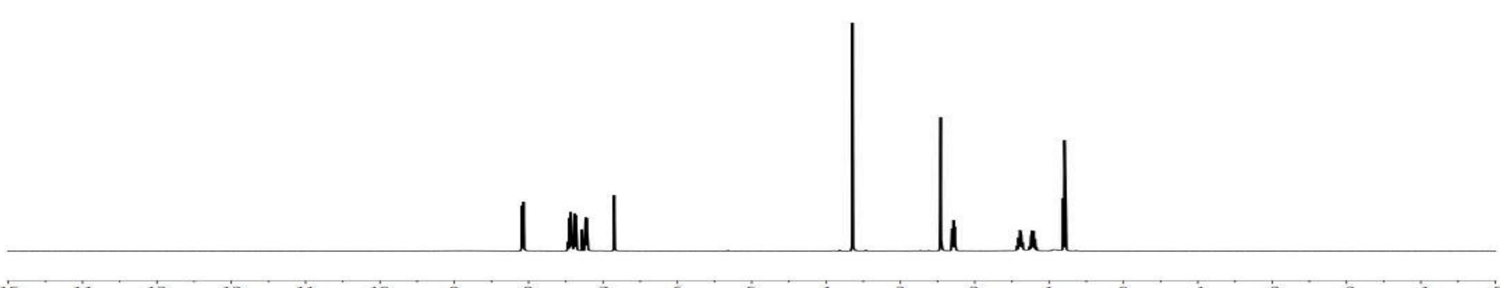

f1 (ppm)

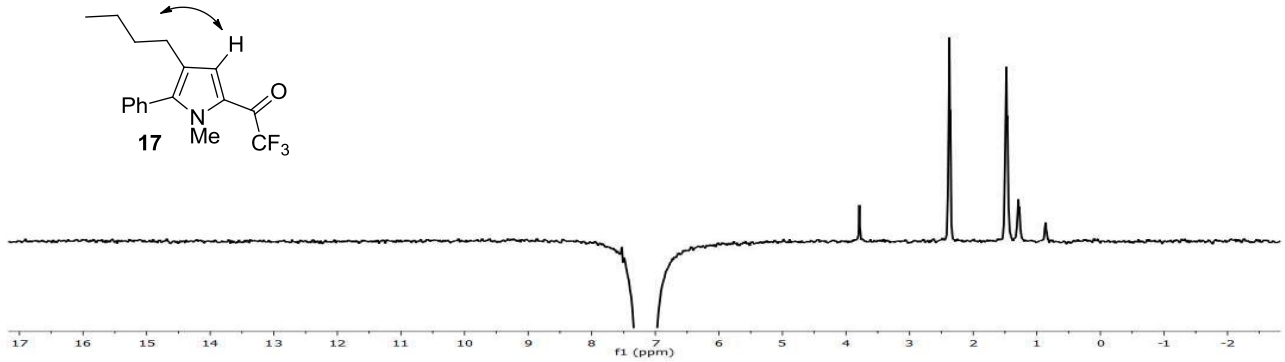

H
N(H)Ts
Ph
N
Me
O
7

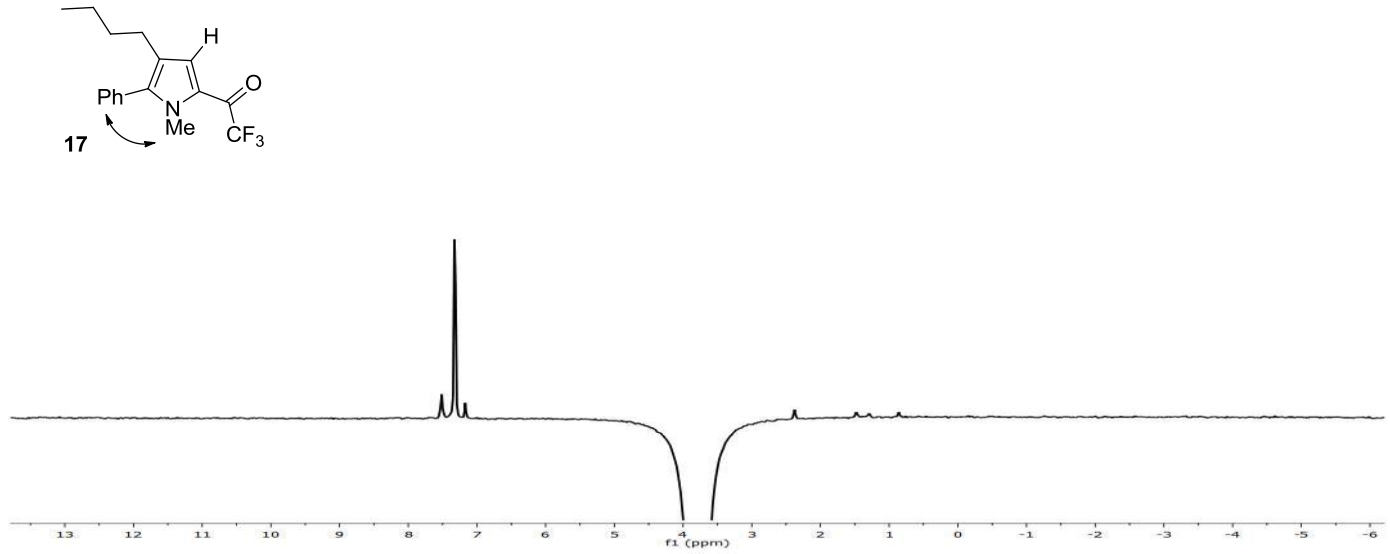

f1 (ppm)

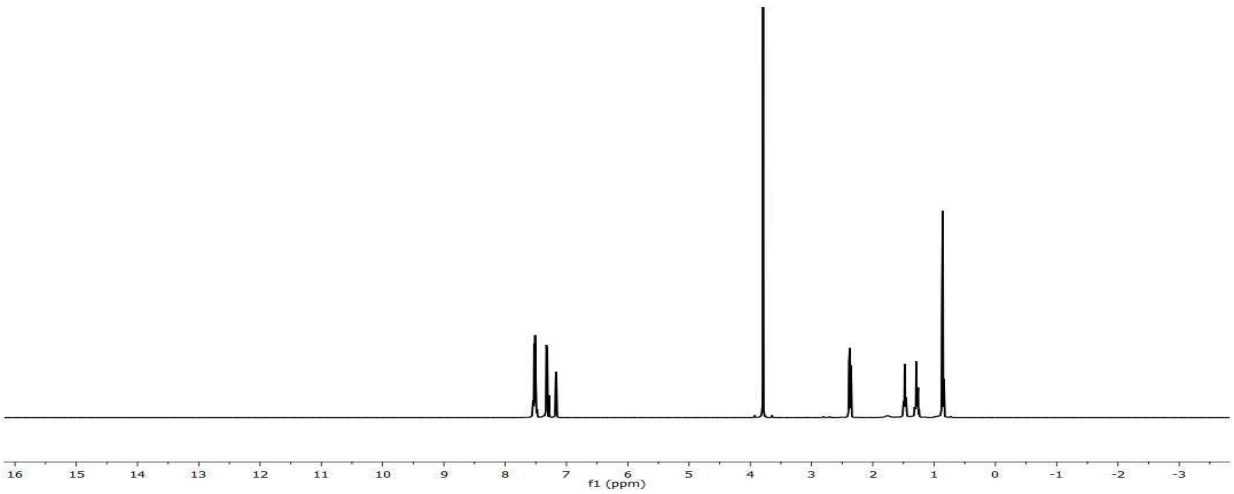

H
N(H)Ts
Ph
N
Me
O
7

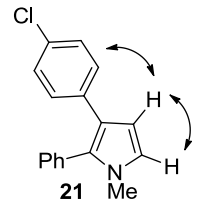

f1 (ppm)


f1 (ppm)

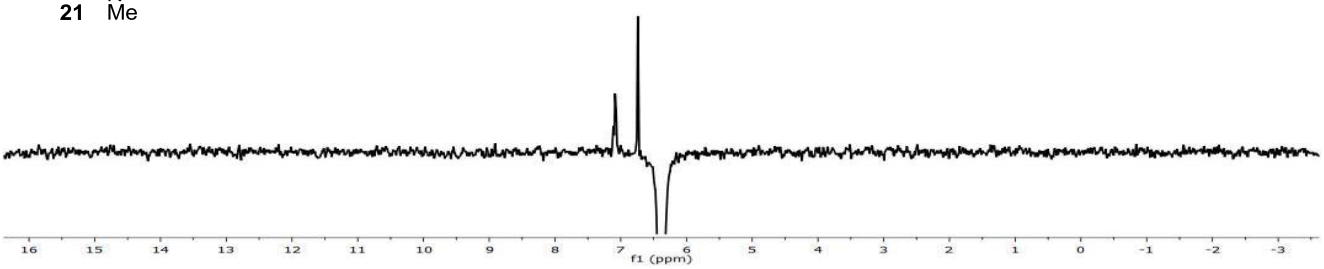

H
Ph
N
Me
O
CF3
17
f1 (ppm)

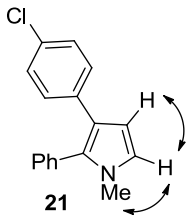

H
Ph
N
Me
O
CF3
17
f1 (ppm)


f1 (ppm)

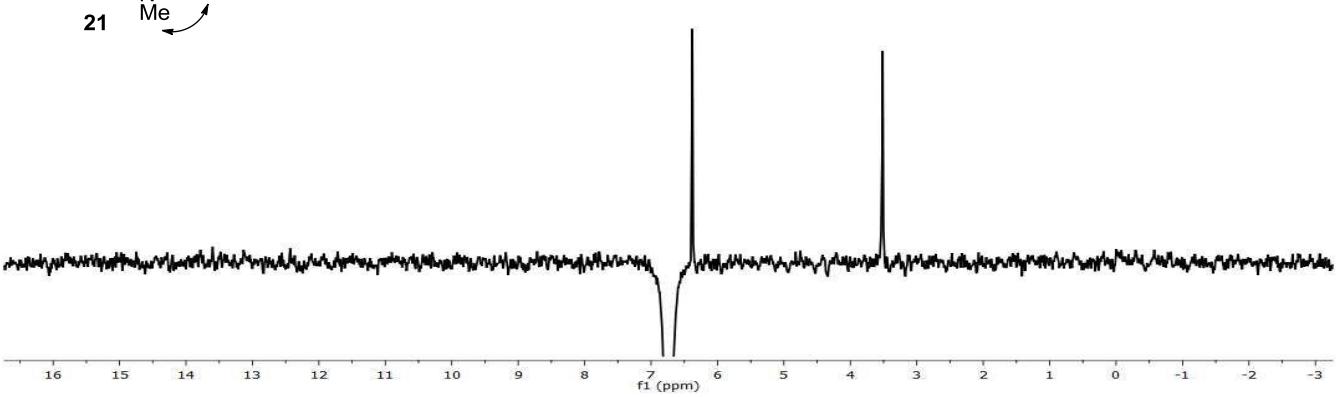

Cl
H
Ph
N
H
Me

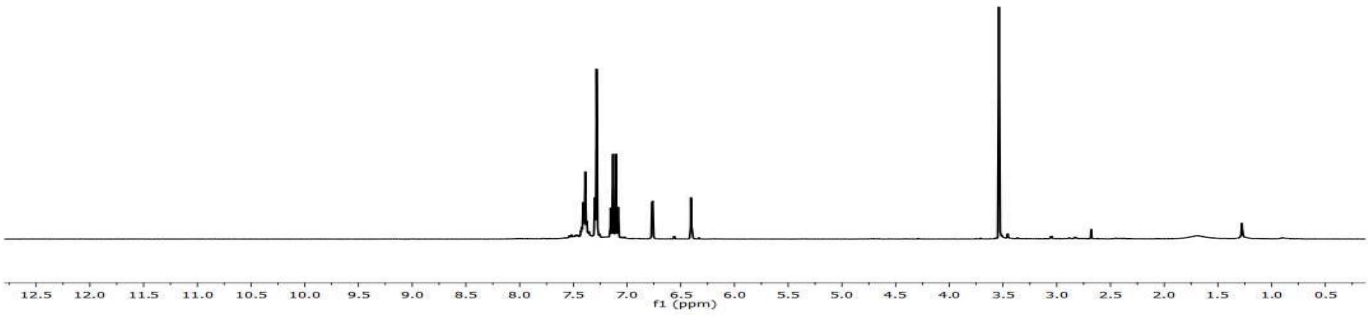
21


16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Cl
H
Ph
N
H
Me

21


16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)