Supporting Information

Phosphine-Catalyzed One-Pot Isomerization of 3-Alkynoates and [2+3]-Cycloaddition with Imines: Formal Synthesis of *Securinega* alkaloid (±)-Allosecurinine

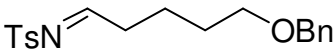
General:

Phosphine includes PPh_3, BINAP, (2*S*, 3*S*)-CHIRAPHOS, (*S*, *S*)-Et-DUPHOS, (*R*, *R*)-Et-DUPHOS, (*R*, *R*)-Et-BPE (+)-DIOP, (*S*)-(-)-2-[2-(Di phenylphosphino)-phenyl]-4-isopropyl-2-oxazoline and (*R*, *R*)-DIPAMP were purchased from commercial suppliers. Alkynes, Ethyl-diazo-acetate, Copper iodide, Aldehydes and Sulphonamides were purchased from commercial suppliers. All alkynoates [1] and imines [2] were synthesized using the previous reports. All reactions were carried out under nitrogen atmosphere unless otherwise stated. Commercial solvents and reagents were used without further purification with following exceptions: toluene and dichloromethane was distilled from calcium hydride prior to use. Reactions were monitored through thin layer chromatography [Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate or acidic solution of ceric molybdate as stain, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. All HPLC chromatograms were recorded using Agilent 1100 and 1200 series. Infrared spectra were recorded on a Shimadzu IR Prestige-21 FT-IR. Liquid samples were examined as film between NaCl salt plates. HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance 300, 400 and 500 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.260, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); td (triplet of doublet); m (multiplets); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00, triplet).

General procedure for aliphatic aldimines[2c]:

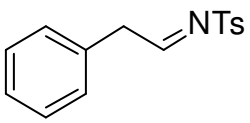
A mixture of aldehyde (1 mmol), *p*-toluenesulfonamide (1 mmol) and benzenesulfinic acid sodium salt (1.1 mmol) in formic acid and H_2O was stirred at room temperature. The resulting white precipitate was filtered off, washed with H_2O, then pentane. The resulting solid was dissolved in CH_2Cl_2, then Sat. aq. $NaHCO_3$ was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH_2Cl_2 and the combined organic layers dried over anhydrous $NaHCO_3$, filtered off and the solvent removed under vacuum to yield the corresponding aldimines. All the imines were taken as such to next step without further purification.

N-(5-(benzyloxy)pentylidene)-4-methylbenzenesulfonamide (6a):



The product was prepared by using above general procedure, employing 5-(benzyloxy)pentanal (1.0 g, 5.20 mmol), *p*-toluenesulfonamide (890 mg, 5.20 mmol) and benzenesulfinic acid sodium salt (940 mg, 5.72 mmol). After 24 h, the resulting white precipitate was filtered off, washed with H_2O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH_2Cl_2 (50 mL), then sat. aq. $NaHCO_3$ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried over anhydrous $NaHCO_3$, filtered off and the solvent removed under vacuum to yield the aldimines **6a** (1.15 g, 64% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 8.59 (t, *J*=4.3 Hz; 1H), 7.78-7.82 (m, 2H), 7.25-7.35 (m, 7H), 4.45 (s, 2H), 3.45 (t, *J*=5.9 Hz, 2H), 2.25-2.35 (m, 2H), 2.42 (s, 3H), 1.55-1.75 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 178.1, 144.7, 138.4, 134.6, 129.8 (2), 128.4 (2), 128.1 (2), 127.63 (2), 127.6, 72.9, 69.5, 35.6, 29.0, 21.6, 21.5 ppm.

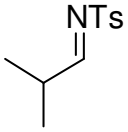
4-methyl-N-(2-phenylethylidene)benzenesulfonamide (6b):



The product was prepared by using above general procedure, employing 2-phenylacetaldehyde (1.0 g, 8.33 mmol), *p*-toluenesulfonamide (1.42 g, 8.33 mmol) and benzenesulfinic acid sodium salt (1.50 g, 9.16 mmol). After 48 h, the resulting white precipitate was filtered off, washed with H_2O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH_2Cl_2 (50 mL), then sat. aq $NaHCO_3$ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried

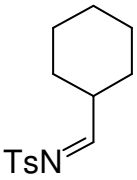
over anhydrous $NaHCO_3$, filtered off and the solvent removed under vacuum to yield the aldimines **6b** (840 g, 37% yield); **NMR (400 MHz, $CDCl_3$):** δ= 8.60 (t, *J*=5.3 Hz; 1H), 7.78-7.82 (m, 2H), 7.25-7.35 (m, 7H), 3.79 (d, J=5.3 Hz; 2H), 2.44 (s, 3H) ppm.

4-methyl-N-(2-methylpropylidene)benzenesulfonamide (6c):



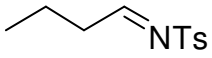
The product was prepared by using above general procedure, employing isobutyraldehyde (1.0 g, 13.9 mmol), *p*-toluenesulfonamide (2.38 g, 13.9 mmol) and benzenesulfinic acid sodium salt (2.50 g, 15.2 mmol). After 12 h, the resulting white precipitate was filtered off, washed with H_2O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH_2Cl_2 (50 mL), then sat. aq $NaHCO_3$ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried over anhydrous $NaHCO_3$, filtered off and the solvent removed under vacuum to yield the aldimines **6c** (2.22 g, 71% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 8.47 (d, *J*=4.2 Hz; 1H), 7.77 (d, *J*= 8.2 Hz; 2H), 7.30 (d, *J*= 8.1 Hz; 2H), 2.63-2.67 (m, 1H), 2.42 (s, 3H), 1.12 (d, *J*=6.9 Hz; 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 181.8, 144.6, 134.7, 129.8 (2), 128.0 (2), 34.6, 21.6, 17.9 (2) ppm.

N-(cyclohexylmethylene)-4-methylbenzenesulfonamide (6d):



The product was prepared by using above general procedure, employing cyclohexanecarbaldehyde (1.0 g, 8.9 mmol), *p*-toluenesulfonamide (1.52 g, 8.9 mmol) and benzenesulfinic acid sodium salt (1.60 g, 9.8 mmol). After 12 h, the resulting white precipitate was filtered off, washed with H_2O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH_2Cl_2 (50 mL), then sat. aq $NaHCO_3$ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried over anhydrous $NaHCO_3$, filtered off and the solvent removed under vacuum to yield the aldimines **6d** (1.75 g, 74% yield); **^{1}H NMR (500 MHz, $CDCl_3$):** δ= 8.47 (d, *J*=4.4 Hz; 1H), 7.79 (d, *J*= 8.2 Hz; 2H), 7.33 (d, *J*= 8.0 Hz; 2H), 2.44 (brs, 4H), 1.60-1.90 (m, 5H), 1.10-1.40 (m, 5H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 181.0, 144.6, 134.8, 129.7 (2), 128.0 (2), 43.6, 28.3 (2), 25.6, 25.0 (2), 21.6 ppm.

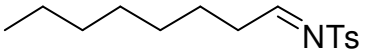
N-butylidene-4-methylbenzenesulfonamide (6e):



The product was prepared by using above general procedure, employing

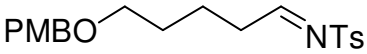
isobutyraldehyde (1.0 g, 13.9 mmol), *p*-toluenesulfonamide (2.38 g, 13.9 mmol) and benzenesulfinic acid sodium salt (2.50 g, 15.2 mmol). After 16 h, the resulting white precipitate was filtered off, washed with H_2O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH_2Cl_2 (50 mL), then sat. aq $NaHCO_3$ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried over anhydrous $NaHCO_3$, filtered off and the solvent removed under vacuum to yield the aldimines **6e** (2.12 g, 68% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 8.60 (t, *J*=4.4 Hz; 1H), 7.80 (d, *J*= 8.0 Hz; 2H), 7.32 (d, *J*= 7.9 Hz; 2H), 2.48-2.52(m, 2H), 2.43(s, 3H), 1.60-1.69 (m, 2H), 0.94 (t, *J*=7.4 Hz; 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 178.3, 144.7, 134.7, 129.8 (2), 128.1 (2), 37.7, 21.6, 18.1, 13.6 ppm.

4-methyl-N-octylidenebenzenesulfonamide (6f):



The product was prepared by using above general procedure, employing isobutyraldehyde (1.0 g, 7.8 mmol), *p*-toluenesulfonamide (1.33 g, 7.8 mmol) and benzenesulfinic acid sodium salt (1.40 g, 8.58 mmol). After 24 h, the resulting white precipitate was filtered off, washed with H_2O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH_2Cl_2 (50 mL), then sat. aq $NaHCO_3$ (40 mL) was added and the solution was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried over anhydrous $NaHCO_3$, filtered off and the solvent removed under vacuum to yield the aldimines **6f** (1.34 g, 61% yield); **^{1}H NMR (500 MHz, $CDCl_3$):** δ= 8.60 (t, *J*=4.6 Hz; 1H), 7.80 (d, *J*= 8.3 Hz; 2H), 7.34 (d, *J*= 8.0 Hz; 2H), 2.48-2.52(m, 2H), 2.43(s, 3H), 1.57-1.67 (m, 2H), 1.20-1.35 (m, 8H), 0.84 (t, *J*=7.1 Hz; 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 178.6, 144.6, 134.7, 129.8 (2), 128.1 (2), 35.9, 31.5, 28.9, 28.8, 24.6, 22.5, 21.6, 14.0 ppm.

N-(5-(4-methoxybenzyloxy)pentylidene)-4-methylbenzenesulfonamide (9):



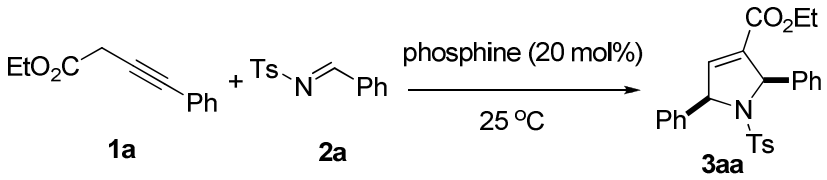
The product was prepared by using above general procedure, employing 5-(4-methoxybenzyloxy)pentanal (1.0 g, 4.5 mmol), *p*-toluenesulfonamide (770 mg, 4.5 mmol) and benzenesulfinic acid sodium salt (812 mg, 4.95 mmol). After 24 h, the resulting white precipitate was filtered off, washed with H_2O (2 x 10 mL), then pentane (2 x 10 mL). The solid was dissolved in CH_2Cl_2 (50 mL), then sat. aq $NaHCO_3$ (40 mL) was added and the solution

was well stirred for 2 h at r.t. The organic phase was decanted, the aqueous phase extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried over anhydrous $NaHCO_3$, filtered off and the solvent removed under vacuum to yield the aldimines **9** (1.1 g, 66% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 8.59 (t, *J*= 4.3 Hz; 1H), 7.78 (d, *J*= 8.2 Hz;2H), 7.33 (d, *J*= 8.1Hz; 2H), 7.23 (d, *J*= 8.5Hz; 2H), 6.87 (d, *J*=8.5Hz; 2H), 4.40 (s, 2H), 3.80 (s, 3H), 3.42 (t, *J*= 6.0 Hz; 2H), 2.49-2.55 (m, 2H), 2.42 (s, 3H), 1.59-1.75 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 178.1, 159.2, 144.8, 134.7, 130.5 (2), 129.9 (2), 129.3 (2), 128.2 (2), 113.8, 72.6, 69.3, 55.4, 35.7, 29.1, 21.7, 21.6 ppm.

General procedure for [2+3]-Cycloaddition reaction:

To a solution of alkynoates and imines in toluene (4 mL) cooled to 0°C, phosphine catalyst in toluene was added dropwise for 10 min. The solution was warmed to room temperature and stirred until then disappearance of alkynoates. Flash column chromatography using hexane and ethyl acetate was done to obtain pyrrolines.

Table 1: Optimization of reaction condition

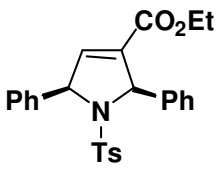


1a **2a** **3aa**

S. No	Phosphines	Solvents	Yield (%)
1.	Triphenylphosphine	toluene	0
2.	Tricyclohexylphosphine	toluene	51
3.	Trimethoxyphosphine	toluene	27
4.	Tri-*n*-butylphosphine	toluene	71
5	Tri-*t*-butylphosphine	toluene	69
6.	**Trimethylphosphine**	**toluene**	**84**
7.	Trimethylphosphine	CH_2Cl_2	77
8.	Trimethylphosphine	Diethyl ether	68
9.	Trimethylphosphine	Dimethoxymethane	trace
10.	Trimethylphosphine	THF	81
11.	Trimethylphosphine	DMF	trace
12.	Triethylphosphine	toluene	75

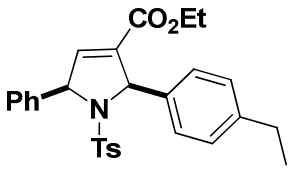
13.	Ethylenebis(diphenylphosphine)	toluene	64
14.	1,3-bis(diphenylphosphino)propane	toluene	69
15.	1,5-Bis(diphenylphosphino)pentane	toluene	71

Ethyl 2,5-diphenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3aa):



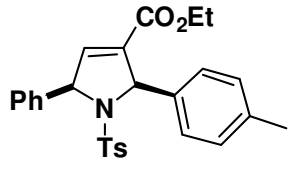
The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), *(E)*-N-benzylidene-4-methylbenzenesulfonamide (82 mg, 0.318 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (100 mg, 0.223 mmol, 84% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.25 – 7.30 (m, 10H), 7.19 – 7.21 (m, 2H), 6.99 – 7.01 (m, 2H), 6.75 (t, *J*=2.1 Hz, 1H), 5.95 (t, *J*=2.5 Hz, 1H), 5.87 (t, *J*=2.5 Hz, 1H), 3.93 - 4.13 (m, 2H), 2.31 (s, 3H), 1.07 (t, J = 7.13 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 162.0, 143.1, 139.3, 139.2, 138.2, 136.0, 133.9, 129.1(2), 128.55(2), 128.50(2), 128.1(2), 128.0, 127.7(2), 127.2(2), 69.8, 69.5, 60.8, 29.6, 21.3, 13.8ppm. **FTIR (neat): ν** = 3053, 2986, 2926, 2304, 1721, 1454, 1421, 1341, 1265, 1165, 1093 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{26}H_{26}NO_4S$ $[M+H]^+$ 448.1583, found: 448.1585.

Ethyl 2-(4-ethylphenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ab):

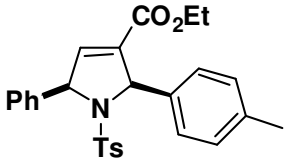


The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (*E*)-N-(4-ethylbenzylidene)-4-methylbenzenesulfonamide (92 mg, 0.318 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (96 mg, 0.202 mmol, 76% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.16 – 7.30 (m, 9H). 6.97 – 7.09 (m, 4H), 6.72 – 6.73 (m, 1H), 5.85 – 5.90 (m, 2H), 3.92 - 4.07 (m, 2H), 2.61 (q, *J* = 7.60, 2H), 2.30 (s, 3H), 1.22 (t, *J* = 7.60 Hz, 3H), 1.08 (t, J = 7.12 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 162.2 (1C), 144.1 (1C), 143.1 (1C), 139.1 (1C), 138.4 (1C), 136.6 (1C), 136.2 (1C), 134.1 (1C), 129.1 (2C), 128.6 (2C), 128.5 (2C), 128.2 (1C), 127.8 (2C), 127.7 (2C), 127.3 (2C), 69.8 (1C), 69.4 (1C), 60.8 (1C), 28.6 (1C), 21.4 (1C), 15.7 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3055, 2984, 2968, 2932, 1721, 1599, 1454, 1422, 1340, 1265, 1165, 1093 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{28}H_{30}NO_4S$ $[M+H]^+$ 476.1896, found: 476.1896.

Ethyl 5-phenyl-2-p-tolyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ac):

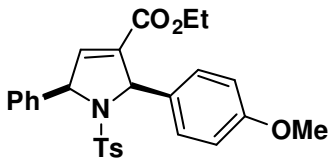


The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (*E*)-4-methyl-N-(4-



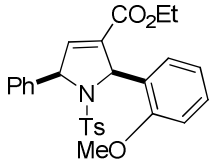
methylbenzylidene) benzenesulfonamide (87 mg, 0.318 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (83 mg, 0.181 mmol, 68% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.22 – 7.37 (m, 9H). 7.01 – 7.08 (m, 4H), 6.72 – 6.73 (m, 1H), 5.88 – 5.89 (m, 1H), 5.82 – 5.84 (m, 1H), 3.97 - 4.08 (m, 2H), 2.32 (s, 6H), 1.09 (t, *J*=7.12 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ= 162.2 (1C), 143.2 (1C), 139.1 (1C), 138.4 (1C), 137.8 (1C), 136.5 (1C), 136.0 (1C), 134.0 (1C), 129.2 (2C), 128.9 (2C), 128.6 (2C), 128.4 (2C), 128.1 (1C), 127.7 (2C), 127.4 (2C), 69.9 (1C), 69.4 (1C), 60.9 (1C), 21.4 (1C), 21.2 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3053, 2986, 2305, 1721, 1454, 1341, 1265, 1165, 1092 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{27}H_{28}NO_4S$ $[M+H]^+$ 462.1705, found: 462.1712.

Ethyl 2-(4-methoxyphenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ad):



The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (*E*)-N-(4-methoxybenzylidene)-4-methylbenzenesulfonamide (92 mg, 0.318 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (90 mg, 0.189 mmol, 71% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.21 – 7.36 (m, 9H), 7.00 – 7.03 (m, 2H), 6.79 – 6.81 (m, 2H), 6.72 – 6.73 (m, 1H), 5.89 – 5.90 (m, 1H), 5.82 – 5.83 (m, 1H), 3.98 - 4.09 (m, 2H), 3.79 (s, 3H), 2.31 (s, 3H), 1.09 (t, *J* = 7.50 Hz, 3H) ppm. **^{13}C NMR (100MHz, $CDCl_3$):** δ= 162.4 (1C), 159.6 (1C), 143.3 (1C), 139.3 (1C), 138.6 (1C), 136.3 (1C), 134.1 (1C), 131.8 (1C), 129.9 (2C), 129.4 (2C), 128.8 (2C), 128.3 (1C), 127.8 (2C), 127.5 (2C), 113.8 (2C), 69.9 (1C), 69.3 (1C), 61.0 (1C), 55.4 (1C), 21.7 (1C), 14.1 (1C) ppm. **FTIR (neat): ν** = 3053, 2986, 2305, 1719, 1512, 1341, 1265, 1165, 1094, 1034 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{27}H_{28}NO_5S$ $[M+H]^+$ 478.1688, found: 478.1681.

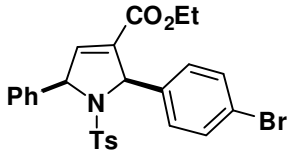
Ethyl 2-(2-methoxyphenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ae):



The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (*E*)-N-(2-methoxybenzylidene)-4-methylbenzenesulfonamide (92 mg, 0.318 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (89 mg, 0.186 mmol, 70% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.47 – 7.53 (m, 4H). 7.30 – 7.38 (m, 3H), 7.12 – 7.21 (m, 4H),

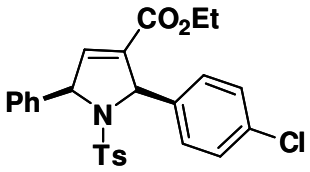
6.83 – 6.85 (m, 2H), 6.71 (m, 1H), 6.33 (m, 1H), 5.82 (m, 1H), 3.89 - 4.09 (m, 2H), 3.85 (s, 3H), 2.34 (s, 3H), 1.01 (t, J = 7.50 Hz, 3H) ppm. **^{13}C NMR (100MHz, $CDCl_3$):** δ= 162.1 (1C), 157.5 (1C), 143.4 (1C), 139.2 (1C), 138.9 (1C), 135.0 (1C), 134.3 (1C), 129.3 (3C), 129.2 (1C), 128.6 (2C), 128.4 (1C), 128.0 (1C), 127.8 (2C), 127.5 (2C), 120.5 (1C), 111.1 (1C), 69.8 (1C), 62.6 (1C), 60.7 (1C), 55.8 (1C), 21.5 (1C), 13.8 (1C) ppm. **FTIR (neat): ν** = 3055, 2984, 2839, 2305, 1719, 1598, 1493, 1352, 1265, 1167, 1094cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{27}H_{28}NO_5S$ $[M+H]^+$ 478.1688, found: 478.1681.

Ethyl 2-(4-bromophenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3af):



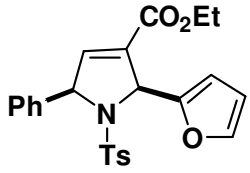
The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (*E*)-N-(4-bromobenzylidene)-4-methylbenzenesulfonamide (108 mg, 0.318 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (76 mg, 0.143 mmol, 54% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.32 – 7.34 (m, 7H), 7.20 – 7.23 (m, 4H), 7.03 – 7.05 (m, 2H), 6.76 (brs, 1H), 5.86 (brs, 2H), 3.99 - 4.10 (m, 2H), 2.34 (s, 3H), 1.11 (t, J = 7.20 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 162.1 (1C), 143.7 (1C), 139.8 (1C), 138.7 (1C), 138.3 (1C), 135.9 (1C), 133.8 (1C), 131.5 (2C), 130.4 (2C), 129.5 (2C), 128.9 (2C), 128.5 (1C), 127.8 (2C), 127.5 (2C), 122.3 (1C), 70.1 (1C), 69.1 (1C), 61.2 (1C), 21.6 (1C), 14.1 (1C) ppm. **FTIR (neat): ν** = 3053, 2986, 2305, 1719, 1421, 1341, 1265, 1165, 1092 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{26}H_{25}BrNO_4S$ $[M+H]^+$ 526.0688, found: 526.0682.

Ethyl 2-(4-chlorophenyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ag):



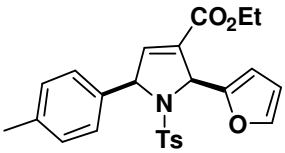
The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (*E*)-N-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (94 mg, 0.318 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (114 mg, 0.236 mmol, 89% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.36 – 7.37 (m, 2H), 7.24 – 7.29 (m, 4H), 7.06 – 7.08 (m, 2H), 6.93 – 6.94 (m, 2H), 6.73 (t, J = 2.18 Hz, 1H), 6.43 – 6.44 (m, 1H), 6.31 – 6.32 (m, 1H), 6.07 (t, J = 2.35 Hz, 1H), 5.79 (t, J = 2.60 Hz, 1H), 4.02 - 4.19 (m, 2H), 2.27 (s, 3H), 1.14 (t, J = 7.13 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 162.0 (1C), 151.6 (1C), 142.9 (1C), 142.4 (2C), 140.5 (2C), 138.1 (1C), 136.8 (1C), 131.1 (1C), 128.3 (4C), 110.6 (2C), 110.0 (2C), 69.8 (2C), 62.3(2C), 61.0 (2C), 21.5 (2C) ppm. **FTIR (neat): ν** = 3063, 2982, 2928, 2905, 1715, 1655, 1599, 1495, 1456, 1341, 1258, 1161 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{26}H_{25}ClNO_4S$ $[M+H]^+$ 482.1193, found: 482.1163.

Ethyl 2-(furan-2-yl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ah):



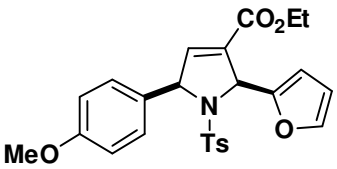
The product was prepared by above general procedure, employing ethyl-4-phenylbut-3-ynoate (50 mg, 0.265 mmol), (*E*)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (79 mg, 0.318 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (74 mg, 0.170 mmol, 64% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.22 – 7.37 (m, 10H), 7.04 – 7.05 (m, 2H), 6.76 – 6.77 (m, 1H), 5.88 – 5.89 (m, 1H), 5.85 – 5.86 (m, 1H), 3.99 – 4.09 (m, 2H), 2.33 (s, 3H), 1.10 (t, J = 7.13 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 161.9, 143.4, 139.6, 138.1, 137.9, 135.7, 133.8, 133.6, 129.8 (2), 129.2 (2), 128.6 (2), 128.3, 128.2, 127.6 (2), 127.2 (2), 69.8, 68.8, 21.4, 13.8 ppm. **FTIR (neat): ν** = 3053, 2986, 1719, 1597, 1422, 1341, 1265, 1165, 1092 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{24}H_{24}NO_5S$ $[M+H]^+$ 438.1341, found: 438.1345.

Ethyl 2-(furan-2-yl)-5-p-tolyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3bh):



The product was prepared by above general procedure, employing ethyl 4-p-tolylbut-3-ynoate (50 mg, 0.247 mmol), (*E*)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (74 mg, 0.297 mmol) and PMe_3 (5 mg, 0.049 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (86 mg, 0.190 mmol, 77% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 6.90 – 7.30 (m, 9H), 6.76 (*t*, J=2.1 Hz, 1H), 6.45 – 6.49 (m, 1H), 6.25 – 6.35 (m, 1H), 6.05 (t, J=2.5 Hz, 1H), 5.75 (t, J=2.6 Hz, 1H), 3.99 – 4.09 (m, 2H), 2.33 (s, 3H), 2.28 (s, 3H), 1.14 (t, J = 7.20 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ= 162.0 (1C), 151.6 (1C), 142.8 (1C), 142.2 (1C), 140.6 (1C), 138.0 (1C), 136.7 (1C), 135.1 (1C), 130.9 (1C), 129.1 (2C), 128.9 (2C), 128.0 (2C), 127.0 (2C), 110.5 (1C), 109.8 (1C), 69.5 (1C), 62.1 (1C), 60.9 (1C), 21.4 (1C), 21.1 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3055, 2984, 2968, 1721, 1599, 1340, 1265, 1165, 1094 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{25}H_{26}NO_5S$ $[M+H]^+$ 452.1524, found: 452.1521.

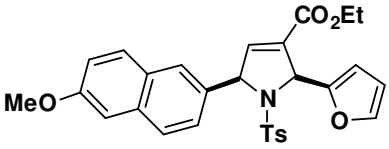
Ethyl 2-(furan-2-yl)-5-(4-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3ch):



The product was prepared by above general procedure, employing ethyl 4-(4-methoxyphenyl)but-3-ynoate (50 mg, 0.229 mmol), (*E*)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (69 mg, 0.275 mmol) and PMe_3 (5 mg, 0.046 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (73 mg, 0.156 mmol, 68% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.26 – 7.31 (m, 3H),

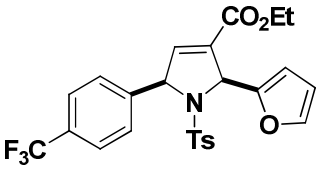
7.04 – 7.06 (m, 2H), 6.93 – 6.95 (m, 2H), 6.77 – 6.79 (m, 2H), 6.71 – 6.72 (m, 1H), 6.41 – 6.42 (m, 1H), 6.30 – 6.32 (m, 1H), 6.04 – 6.05 (m, 1H), 5.75 – 5.77 (m, 1H), 4.04 – 4.17 (m, 2H), 3.78 (s, 3H), 2.28 (s, 3H), 1.15 (t, *J* = 7.20 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 162.0 (1C), 159.6 (1C), 151.5 (1C), 142.7 (1C), 142.3 (1C), 140.5 (1C), 136.9 (1C), 130.9 (1C), 130.2 (1C), 129.5 (2C), 128.9 (2C), 127.0 (2C), 113.8 (2C), 110.5 (1C), 109.9 (1C), 69.2 (1C), 62.0 (1C), 60.9 (1C), 55.3 (1C), 21.4 (1C), 14.0 (1C) ppm. **FTIR (neat): ν** = 3055, 2984, 2305, 1719, 1512, 1265, 739 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{25}H_{26}NO_6S$ $[M+H]^+$ 468.1481, found: 468.1480.

Ethyl 2-(furan-2-yl)-5-(6-methoxynaphthalen-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3dh):



The product was prepared by above general procedure, employing ethyl 4-(6-methoxynaphthalen-2-yl)but-3-ynoate (50 mg, 0.186 mmol), (*E*)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (56 mg, 0.224 mmol) and PMe_3 (3 mg, 0.037 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (59 mg, 0.114 mmol, 61% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.58 – 7.68 (m, 3H), 7.34 – 7.45 (m, 2H), 6.98 – 7.14 (m, 4H), 6.76 – 6.80 (m, 3H), 6.47 – 6.48 (m, 1H), 6.35 – 6.36 (m, 1H), 6.13 – 6.14 (m, 1H), 5.93 (t, *J*=2.3 Hz, 1H), 4.05 – 4.19 (m, 2H), 3.92 (s, 3H), 2.17 (s, 3H), 1.16 (t, J = 7.20 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ= 162.0 (1C), 158.0 (1C), 151.7 (1C), 142.7 (1C), 142.2 (1C), 140.5 (1C), 136.8 (1C), 134.4 (1C), 132.9 (1C), 131.0 (1C), 129.6 (1C), 128.8 (2C), 128.5 (1C), 127.4 (1C), 127.1 (1C), 126.9 (2C), 125.9 (1C), 118.9 (1C), 110.6 (1C), 110.0 (1C), 105.5 (1C), 69.8 (1C), 62.2 (1C), 60.9 (1C), 55.3 (1C), 21.3 (1C), 14.0 (1C) ppm. **FTIR (neat): ν** = 3053, 2986, 2305, 1719, 1609, 1421, 1341, 1265, 1161, 1094 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{29}H_{27}NO_6S$ $[M+H]^+$ 518.1637, found: 518.1636.

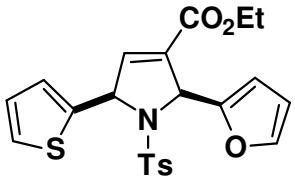
Ethyl- 2-(furan-2-yl)-1-tosyl-5-(4-(trifluoromethyl) phenyl)-2,5-dihydro-1H-pyrrole-3-carboxylate (3eh):



The product was prepared by above general procedure, employing ethyl 4-(4-(trifluoromethyl) phenyl) but-3-ynoate (50 mg, 0.195 mmol), (*E*)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (58 mg, 0.234 mmol) and PMe_3 (3 mg, 0.039 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (82 mg, 0.162 mmol, 83% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.46 (brs, 4H), 7.35

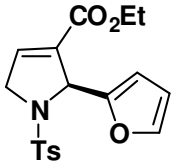
(m, 1H), 6.90-7.10 (m, 4H), 6.70 (t, *J*=2.2Hz, 1H), 6.50 (m, 1H), 6.40(m, 1H), 6.10 (t, =2.6Hz, 1H), 5.81 (t, J=2.7Hz, 1H), 4.00-4.22 (m, 2H), 2.28 (s, 3H), 1.16 (t, *J* = 7.20 Hz, 3H) ppm. **^{13}C NMR (100MHz, $CDCl_3$):** δ= 162.0 (1C), 159.6 (1C), 151.5 (1C), 142.7 (1C), 142.3 (1C), 140.5 (1C), 136.9 (1C), 130.9 (1C), 130.2 (1C), 129.5 (2C), 128.9 (2C), 127.0 (2C), 113.8 (2C), 110.5 (1C), 109.9 (1C), 69.2 (1C), 62.0 (1C), 60.9 (1C), 55.3 (1C), 21.4 (1C), 14.0 (1C) ppm. **FTIR (neat): ν** = 3055, 2986, 2305, 1722, 1325, 1265, 1167, 1128, 1067, 1016 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{25}H_{23}F_3NO_5S$ $[M+H]^+$ 506.1249, found: 506.1250.

Ethyl-2-(furan-2-yl)-5-(thiophen-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate(3fh):



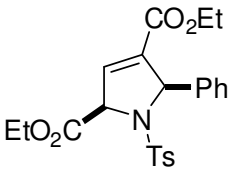
The product was prepared by above general procedure, employing ethyl 4-(thiophen-2-yl)but-3-ynoate (50 mg, 0.257 mmol), (*E*)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (77 mg, 0.309 mmol) and PMe_3 (5 mg, 0.051 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (103 mg, 0.203 mmol, 79% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.25 – 7.28 (m, 2H), 7.10 – 7.15 (m, 1H), 7.00 - 7.05 (m, 3H), 6.94 – 6.96 (m, 2H), 6.75 – 6.77 (m, 1H), 6.41 – 6.42 (m, 1H), 6.29 – 6.31 (m, 1H), 6.05 – 6.07 (m, 1H), 5.93 – 5.95 (m, 1H), 3.99 – 4.17 (m, 2H), 2.29 (s, 3H), 1.16 (t, J = 7.20 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ= 161.9 (1C), 151.4 (1C), 142.7 (1C), 142.3 (1C), 139.7 (1C), 139.1 (1C), 137.0 (1C), 131.3 (1C), 128.9 (2C), 127.1 (1C), 126.8 (2C), 126.0 (1C), 124.3 (1C), 110.5 (1C), 109.9 (1C), 64.7 (1C), 61.9 (1C), 61.0 (1C), 21.4 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3055, 2984, 1719, 1340, 1265, 1161, 1094, 1013, 737 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{22}H_{22}NO_5S_2$ $[M+H]^+$ 444.0939, found: 444.0938.

Ethyl 2-(furan-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (3gh):



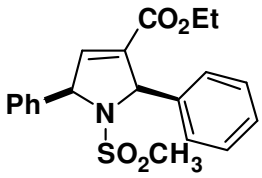
The product was prepared by above general procedure, employing ethyl but-3-ynoate (50 mg, 0.446 mmol), (*E*)-N-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (77 mg, 0.309 mmol) and PMe_3 (7 mg, 0.089 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (158 mg, 0.312 mmol, 70% yield);**^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.45 – 7.48 (m, 2H), 7.15 - 7.20 (m, 3H), 6.82 (q, *J*=2.01 Hz, 1H), 6.34 – 6.37 (m, 1H), 6.25 – 6.30 (m, 1H), 5.87 (td, *J*=5.5, 1.7Hz, 1H), 4.25 – 4.55 (m, 2H), 4.00 – 4.20 (m, 2H), 2.38 (s, 3H), 1.59 (t, *J*=7.12 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ= 161.6, 151.3, 143.2, 142.1, 136.9, 135.6, 133.0, 129.5 (2), 127.0 (2), 110.4, 109.1, 61.7, 60.8, 54.2, 21.4, 13.9 ppm. **FTIR (neat): ν** = 3053, 2986, 2305, 1721, 1422, 1265, 1165, 895 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{18}H_{20}NO_5S$ $[M+H]^+$ 362.1062, found: 362.1067.

Triethyl 1-tosyl-2, 5-dihydro-1H-pyrrole-2,3,5-tricarboxylate (3ha):



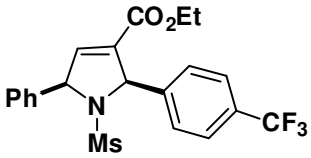
The product was prepared by above general procedure, employing diethyl pent-2-ynedioate (50 mg, 0.271 mmol), (E)-N-benzylidene-4-methylbenzenesulfonamide (84 mg, 0.326 mmol) and PMe_3 (5 mg, 0.054 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product as colorless oil (75 mg, 0.149 mmol, 55% yield); **^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.42 – 7.45 (m, 2H), 7.32 – 7.35 (m, 2H), 7.26 (brs, 3H), 7.15 - 7.17 (m, 2H), 6.70 (t, *J*=2.3 Hz, 1H), 5.80 – 5.82 (m, 1H), 5.51 (t, *J*=2.7 Hz, 1H), 4.15 – 4.35 (m, 2H), 3.95 – 4.10 (m, 2H), 2.30 (s, 3H), 1.30 (t, J=7.14 Hz, 3H), 1.10 (t, J=7.14 Hz, 3H)ppm. **NMR (100 MHz, $CDCl_3$):** δ= 168.3, 161.4, 143.4, 138.2, 137.2, 135.8, 132.8 (2), 128.9 (2), 128.5 (2), 127.89 (2), 127.83(2), 69.5, 67.9, 62.1, 61.0, 21.4, 14.0, 13.7ppm.

Ethyl 1-(methylsulfonyl)-2,5-diphenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5aa):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-benzylidene methanesulfonamide (58 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (113 mg, 0.223 mmol, 84% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.30 – 7.51 (m, 10H), 6.83 – 6.84 (m, 1H), 6.03 – 6.04 (m, 1H), 5.96 – 5.98 (m, 1H), 3.99 – 4.17 (m, 2H), 2.04 (s, 3H), 1.10 (t, *J* = 7.05 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 162.1 (1C), 139.2 (1C), 139.1 (1C), 138.3 (1C), 134.1 (1C), 129.0 (1C), 128.7 (2C), 128.6 (1C), 128.4 (2C), 128.4 (2C), 128.0 (2C), 69.4 (1C), 68.9 (1C), 60.9 (1C), 42.6 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3055, 2986, 2305, 1719, 1456, 1422, 1334, 1265, 1151 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{20}H_{22}NO_4S$ $[M+H]^+$ 372.1270, found: 372.1270.

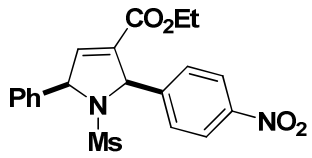
Ethyl- 1-(methylsulfonyl)-5-phenyl-2-(4-(trifluoromethyl) phenyl)-2,5-dihydro-1H-pyrrole-3-carboxylate (5ab):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-(4-(trifluoromethyl)benzylidene)methanesulfonamide (80 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (102 mg, 0.202 mmol, 76% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.59 – 7.66 (m, 4H), 7.38 – 7.50 (m, 5H), 6.88 – 6.90 (m, 1H), 6.08 – 6.09 (m, 1H), 5.97 – 5.99 (m, 1H), 4.03 – 4.16 (m, 2H),

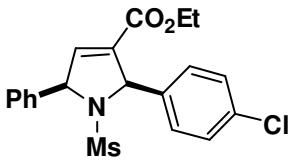
2.25 (s, 3H), 1.13 (t, J = 7.20 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 161.8 (1C), 143.4 (1C), 139.7 (1C), 138.0 (1C), 133.8 (1C), 129.2 (2C), 129.0 (1C), 128.8 (2C), 128.0 (2C), 125.7 (1C), 125.6 (1C), 125.6 (1C), 125.6 (1C), 69.6 (1C), 68.5 (1C), 61.2 (1C), 42.3 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3053, 2986, 2305, 1721, 1422, 1325, 1067, 895 cm^{-1}.

Ethyl 1-(methylsulfonyl)-2-(4-nitrophenyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5ac):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-(4-nitrobenzylidene) methanesulfonamide (73 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (63 mg, 0.125 mmol, 47% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 8.23 – 8.26 (m, 2H), 7.67 – 7.69 (m, 2H), 7.40– 7.47 (m, 5H), 6.91 – 6.93 (m, 1H), 6.11 – 6.12 (m, 1H), 5.98 – 6.00 (m, 1H), 4.05 – 4.17 (m, 2H), 2.29 (s, 3H), 1.16 (t, J = 7.12 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 161.6 (1C), 147.7 (1C), 146.6 (1C), 140.0 (1C), 137.7 (1C), 133.5 (1C), 129.4 (2C), 129.3 (2C), 129.2 (1C), 127.9 (2C), 123.8 (2C), 69.7 (1C), 68.2 (1C), 61.3 (1C), 42.2 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3053, 2986, 2305, 1719, 1526, 1348, 1265, 1152, 1074 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{20}H_{21}N_2O_6S$ $[M+H]^+$ 417.1127, found: 417.1129.

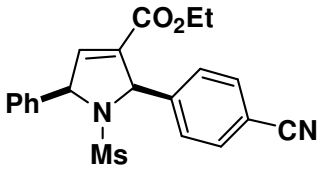
Ethyl 2-(4-chlorophenyl)-1-(methylsulfonyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5ad):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-(4-chlorobenzylidene) methanesulfonamide (69 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (95 mg, 0.189 mmol, 71% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.34– 7.47 (m, 9H), 6.84 – 6.86 (m, 1H), 6.00 – 6.02 (m, 1H), 5.94 – 5.96 (m, 1H), 4.03 – 4.16 (m, 2H), 2.23 (s, 3H), 1.14 (t, *J* = 7.05 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 161.9 (1C), 139.5 (1C), 138.1 (1C), 138.0 (1C), 134.3 (1C), 133.8 (1C), 129.8 (2C), 129.1 (2C), 128.9 (3C), 127.9 (2C), 69.5 (1C), 68.3 (1C), 61.1 (1C), 42.5 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3053, 2986, 2305, 1721, 1491, 1335, 1265, 1152, 1090 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{20}H_{21}ClNO_4S$ $[M+H]^+$ 406.0880, found: 406.0723.

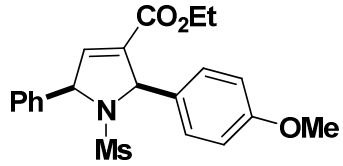
Ethyl 2-(4-cyanophenyl)-1-(methylsulfonyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5ae):

The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-(4-cyanobenzylidene) methanesulfonamide (66 mg, 0.319 mmol) and PMe_3



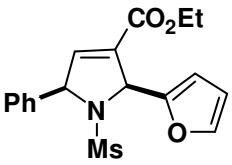
(5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (86 mg, 0.170 mmol, 64% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.73 – 7.76 (m, 2H), 7.61 – 7.65 (m, 1H), 7.40–7.52 (m, 6H), 6.90 – 6.91 (m, 1H), 6.03 – 6.05 (m, 1H), 5.95 – 5.97 (m, 1H), 4.04 – 4.18 (m, 2H), 2.27 (s, 3H), 1.16 (t, *J* = 7.20 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 161.6 (1C), 141.2 (1C), 139.9 (1C), 137.7 (1C), 133.5 (1C), 133.0 (1C), 132.1 (1C), 131.8 (1C), 129.5 (1C), 129.3 (2C), 129.2 (1C), 127.9 (2C), 118.4 (1C), 112.8 (1C), 69.6 (1C), 68.2 (1C), 61.3 (1C), 42.2 (1C), 13.9 (1C) ppm. **FTIR (neat): ν** = 3055, 2986, 2305, 1719, 1339, 1265, 1153 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{21}H_{21}N_2O_4S$ $[M+H]^+$ 397.1229, found: 397.1222.

Ethyl 2-(4-methoxyphenyl)-1-(methylsulfonyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-(4-methoxybenzylidene) methanesulfonamide (68 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (94 mg, 0.186 mmol, 70% yield);**^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.33 – 7.49 (m, 7H), 6.91 – 6.92 (m, 1H), 6.89 – 6.90 (m, 1H), 6.80 – 6.81 (m, 1H), 6.00 – 6.01 (m, 1H), 5.93 – 5.95 (m, 1H), 4.02 – 4.15 (m, 2H), 3.81 (s, 3H), 2.20 (s, 3H), 1.13 (t, *J* = 7.20 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 162.5 (1C), 159.8 (1C), 139.1 (1C), 138.7 (1C), 134.3 (1C), 131.5 (1C), 129.8 (2C), 129.1 (2C), 128.8 (1C), 128.1 (2C), 114.2 (2C), 69.5 (1C), 68.6 (1C), 61.2 (1C), 55.5 (1C), 42.9 (1C), 14.2 (1C) ppm. **HRMS (ESI, m/z):** calcd for $C_{21}H_{23}NO_5S$ $[M+H]^+$ 402.1368, found: 402.1371.

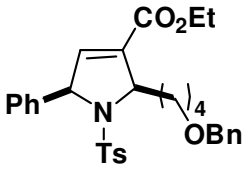
Ethyl 2-(furan-2-yl)-1-(methylsulfonyl)-5-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5ag):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-(furan-2-ylmethylene) methanesulfonamide (55 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (120 mg, 0.236 mmol, 89% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.53 – 7.56 (m, 2H), 7.34 – 7.46 (m, 4H), 6.81 – 6.83 (m, 1H), 6.53 – 6.54 (m, 1H), 6.40 – 6.41 (m, 1H), 6.08 – 6.10 (m, 1H), 5.82 – 5.84 (m, 1H), 4.06 – 4.25 (m, 2H), 2.10 (s, 3H), 1.18 (t, *J* = 7.05 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 161.9 (1C), 151.0 (1C), 142.7 (1C), 140.2 (1C), 137.8 (1C), 131.3 (1C), 128.9 (2C), 128.8 (1C), 128.4 (2C), 110.8 (1C), 110.2 (1C), 69.3

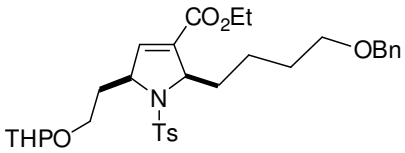
(1C), 61.7 (1C), 61.0 (1C), 42.1 (1C), 14.0 (1C) ppm. **HRMS (ESI, m/z):** calcd for $C_{18}H_{20}NO_5S$ $[M+H]^+$ 362.1062, found: 362.1061.

Ethyl 2-(4-(benzyloxy)butyl)-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7aa):



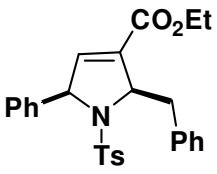
The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-(5-(benzyloxy)pentylidene)-4-methylbenzenesulfonamide (110 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (103 mg, 0.194 mmol, 73% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.63 – 7.65 (m, 2H), 7.38 – 7.39 (m, 2H), 7.22 – 7.34 (m, 10H), 6.59 – 6.61 (m, 1H), 5.58 (s, 1H), 4.82 – 4.86 (m, 1H), 4.46 (s, 2H), 4.12 – 4.19 (m, 2H), 3.39 – 3.43 (m, 2H), 2.38 (s, 3H), 1.88 – 1.97 (m, 1H), 1.72 – 1.82 (m, 1H), 1.45 – 1.64 (m, 4H), 1.23 (t, *J* = 7.20 Hz, 3H) ppm. **^{13}C NMR (500MHz, $CDCl_3$):** δ= 162.5 (1C), 143.8(1C), 139.0 (1C), 138.8 (1C), 138.7 (1C), 135.1 (1C), 134.8 (1C), 129.7 (2C), 128.6 (2C), 128.3 (2C), 128.0 (1C), 127.7 (2C), 127.6 (2C), 127.4 (1C), 127.3 (2C), 72.9 (1C), 70.3 (1C), 69.5 (1C), 66.8 (1C), 60.9 (1C), 34.9 (1C), 29.6 (1C), 22.0 (1C), 21.5 (1C), 14.1 (1C) ppm. **FTIR (neat): ν** = 3053, 2984, 2938, 2864, 1717, 1647, 1599, 1495, 1454, 1350, 1265, 1165, 1090, 1028 $cm^{-1;}$ **HRMS (ESI, m/z):** calcd for $C_{31}H_{35}NO_5S$ $[M+H]^+$ 534.2314, found: 534.2317.

Ethyl-2-(4-(benzyloxy)butyl)-5-(2-(tetrahydro-2H-pyran-2-yloxy)ethyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7oa):



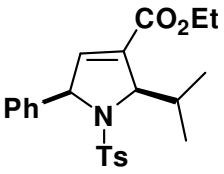
The product was prepared by above general procedure, employing ethyl 6-(tetrahydro-2H-pyran-2-yloxy)hex-3-ynoate (50 mg, 0.208 mmol), (*E*)-N-(5-(benzyloxy)pentylidene)-4-methylbenzenesulfonamide (86 mg, 0.250 mmol) and PMe_3 (3 mg, 0.042 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (85 mg, 0.146mmol, 70% yield);**^{1}H NMR (400 MHz, $CDCl_3$):** δ= 7.60 – 7.70 (m, 2H), 7.20 – 7.35 (m, 7H), 6.50 – 6.65 (m, 1H), 4.57 – 4.70 (m, 2H), 4.47 (s, 2H), 4.40 – 4.45 (m, 1H), 4.10 (q, *J*=7.13 Hz, 2H),3.75 – 3.90 (m, 2H), 3.47 – 3.67 (m, 2H), 3.45 (t, *J*=6.6 Hz, 2H), 2.37 (s, 3H), 2.10 – 2.30 (m, 1H), 1.44 – 2.00 (m, 12H), 1.32 – 1.42 (m, 1H), 1.20 (t, *J*=7.1 Hz, 3H)ppm. **FTIR (neat): ν** = 3053, 2941, 2866, 1717, 1346, 1265, 1165, 1092, 1076, 1034 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{27}H_{36}NO_6S$ $[M+H]^+$ 502.2246, found: 502.2263 (THP cleaved mass).

Ethyl-2-benzyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ab):



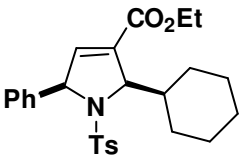
The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-4-methyl-N-(2-phenylethylidene) benzenesulfonamide (87 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (109 mg, 0.236 mmol, 89% yield);**^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.67 – 7.69 (m, 2H), 7.14 – 7.29 (m, 6H), 7.02 – 7.08 (m, 4H), 6.54 – 6.57 (m, 2H), 6.40 – 6.41 (m, 1H), 5.36 – 5.38 (m, 1H), 5.05 – 5.08 (m, 1H), 4.14 – 4.25 (m, 2H), 3.30 – 3.48 (m, 2H), 2.44 (s, 3H), 1.30 (t, *J* = 7.05 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 162.8 (1C), 143.9 (1C), 139.7 (1C), 138.7 (1C), 136.4 (1C), 134.3 (1C), 133.1 (1C), 131.0 (2C), 129.9 (2C), 128.3 (2C), 128.2 (2C), 128.0 (2C), 127.9 (2C), 127.9 (1C), 126.5 (1C), 70.0 (1C), 67.7 (1C), 61.1 (1C), 39.6 (1C), 21.6 (1C), 14.2 (1C) ppm. **FTIR (neat): ν** = 3055, 2984, 1717, 1599, 1350, 1265, 1165, 1092 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{27}H_{28}NO_4S$ $[M+H]^+$ 462.1739, found: 462.1698.

Ethyl 2-isopropyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ac):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-4-methyl-N-(2-methylpropylidene) benzenesulfonamide (72 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (92 mg, 0.223 mmol, 84% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.70 – 7.72 (m, 2H), 7.46 – 7.48 (m, 2H), 7.33 – 7.36 (m, 2H), 7.26 – 7.29 (m, 3H), 6.70 – 6.71 (m, 1H), 5.56 – 5.57 (m, 1H), 4.73 (d, J = 5.00 Hz, 1H), 4.11 – 4.19 (m, 2H), 2.40 (s, 3H), 1.97 – 2.01 (m, 1H), 1.26 (t, *J* = 7.25 Hz, 3H), 0.93 (d, *J* = 7.00 Hz, 3H), 0.79 (d, *J* = 7.00 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 163.0 (1C), 143.9 (1C), 139.0 (1C), 138.2 (1C), 136.0 (1C), 134.2 (1C), 129.7 (2C), 128.5 (2C), 127.9 (2C), 127.8 (1C), 127.1 (2C), 72.4 (1C), 68.9 (1C), 60.9 (1C), 33.6 (1C), 21.5 (1C), 19.5 (1C), 19.4 (1C), 14.1 (1C) ppm. **FTIR (neat): ν** = 3057, 2968, 2934, 2907, 1719, 1647, 1599, 1348, 1265, 1165, 1090, 895, 816 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{23}H_{28}NO_4S$ $[M+H]^+$ 414.1739, found: 414.1738.

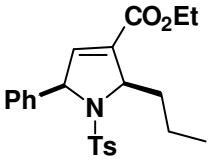
Ethyl 2-cyclohexyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ad):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-(cyclohexylmethylene)-4-methylbenzenesulfonamide (85 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (108 mg, 0.239 mmol,

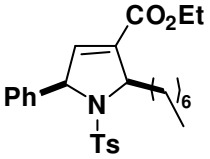
90% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.68 – 7.70 (m, 2H), 7.45 – 7.47 (m, 2H), 7.30 – 7.34 (m, 2H), 7.23 – 7.27 (m, 3H), 6.67 (brs, 1H), 5.56 (brs, 1H), 4.70 – 4.71 (m, 1H), 4.12 – 4.17 (m, 2H), 2.37 (s, 3H), 1.61 – 1.69 (m, 6H), 1.26 (t, J = 7.00 Hz, 3H), 0.85 – 1.16 (m, 5H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 163.0 (1C), 143.8 (1C), 139.0 (1C), 138.1 (1C), 136.0 (1C), 134.3 (1C), 129.7 (2C), 128.5 (2C), 127.8 (2C), 127.8 (1C), 127.2 (2C), 71.8 (1C), 68.9 (1C), 60.9 (1C), 43.6 (1C), 29.9 (1C), 29.8 (1C), 26.4 (1C), 26.4 (1C), 26.1 (1C), 21.5 (1C), 14.1 (1C) ppm. **FTIR (neat): ν** = 3055, 2984, 2930, 2853, 1719, 1647, 1599, 1495, 1449, 1348, 1265, 1165, 1092 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{26}H_{32}NO_4S$ $[M+H]^+$ 454.2018, found: 454.2029.

Ethyl 5-phenyl-2-propyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7ae):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-N-butylidene-4-methylbenzenesulfonamide (72 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (85 mg, 0.205 mmol, 77% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.60 – 7.70 (m, 2H), 7.20 – 7.40 (m, 7H), 6.55 – 6.60 (m, 1H), 5.55 – 5.60 (m, 1H), 4.80 - 4.85 (m, 1H), 4.10 – 4.25 (m, 2H), 2.40 (s, 3H), 1.65 – 1.75 (m, 2H), 1.35 – 1.50 (m, 2H), 1.25 (t, *J*=7.1 Hz, 3H), 0.87 (t, *J*=7.3 Hz, 3H). 5.96 – 5.98 (m, 1H), 3.99 – 4.17 (m, 2H), 2.04 (s, 3H), 1.10 (t, J = 7.05 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 162.8 (1C), 144.0 (1C), 139.3 (1C), 138.8 (1C), 135.4 (1C), 135.0 (1C), 129.9 (2C), 128.8 (2C), 128.2 (1C), 127.9 (2C), 127.5 (2C), 69.7 (1C), 67.0 (1C), 61.1 (1C), 37.6 (1C), 21.7 (1C), 18.8 (1C), 14.3 (1C), 14.2 (1C) ppm. **FTIR (neat): ν** = 3055, 2982, 2963, 2934, 2872, 1719, 1647, 1599, 1350, 1265, 1165, 1092 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{23}H_{27}NO_4S$ $[M+H]^+$ 414.1739, found: 414.1720.

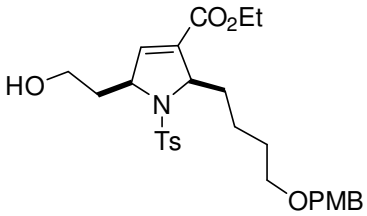
Ethyl 2-heptyl-5-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (7af):



The product was prepared by above general procedure, employing ethyl 4-phenylbut-3-ynoate (50 mg, 0.266 mmol), (*E*)-4-methyl-N-octylidenebenzenesulfonamide (90 mg, 0.319 mmol) and PMe_3 (5 mg, 0.053 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (25 – 30% ethyl acetate in hexane) to afford product (101 mg, 0.215 mmol, 81% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.61 – 7.64 (m, 2H), 7.41 – 7.43 (m, 2H), 7.28 – 7.36 (m, 3H), 7.24 – 7.26 (m, 2H), 6.60 (brs, 1H), 5.60 (brs, 1H), 4.84 – 4.86 (m, 1H), 4.13 – 4.22 (m, 2H), 2.40

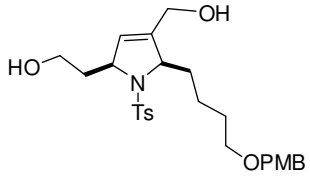
(s, 3H), 1.84 – 1.91 (m, 1H), 1.70 – 1.77 (m, 1H), 1.29 – 1.43 (m, 2H) 1.26 (m, 5H), 1.20 (s, 6H), 0.86 (t, J = 7.20 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 162.6 (1C), 143.7 (1C), 139.0 (1C), 138.7 (1C), 135.2 (1C), 135.0 (1C), 129.7 (2C), 128.6 (2C), 128.0 (1C), 127.7 (2C), 127.4 (2C), 69.4 (1C), 66.9 (1C), 60.9 (1C), 34.9 (1C), 31.7 (1C), 29.4 (1C), 29.0 (1C), 25.1 (1C), 22.7 (1C), 21.5 (1C), 14.1 (2C) ppm. **FTIR (neat): ν** = 3053, 2986, 2957, 2928, 2857, 1715, 1422, 1350, 1265, 1165, 1092 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{27}H_{35}NO_4S$ $[M+H]^+$ 470.2291, found: 470.2302.

Ethyl-5-(2-hydroxyethyl)-2-(4-(4-methoxybenzyloxy)-butyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (10):



The product was prepared by above general procedure, employing ethyl 6-hydroxyhex-3-ynoate (2 g, 12.0 mmol), (*E*)-N-(5-(4-methoxybenzyloxy) pentylidene)-4-methylbenzenesulfonamide (5.76 g, 14.4 mmol) and PMe_3 (200 mg, 2.5 mmol). After 2 h, solvent was removed; the residue was purified through flash column chromatography (30% ethyl acetate in hexane) to afford product (5.5 g, 81% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.66 - 7.69 (m, 2H), 7.24 - 7.27 (m, 4H), 6.85 – 6.88 (m, 2H), 6.48 (brs, 1H), 4.60 – 4.65 (m, 2H), 4.42 (s, 2H), 4.07 – 4.15 (m, 3H), 3.93 – 4.01 (m, 1H), 3.77 (s, 3H), 3.69 – 3.75 (m, 1H), 3.46 (t, *J*=6.4Hz, 2H), 2.38 (s, 3H), 1.48 - 2.00 (m, 9H), 1.18-1.21 (m, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 162.2, 159.0, 144.0, 140.2, 134.5, 133.5, 130.7, 129.8, 127.6, 113.7, 72.5, 69.9, 66.6, 64.2, 60.8, 58.5, 55.2, 39.0, 35.4, 29.5, 21.9, 21.5, 14.0 ppm. **FTIR (neat): ν** = 3053, 2985, 2304, 1716, 1555, 1344, 1265, 1163, 738 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{20}H_{30}NO_6S$ $[M+H]^+$ 412.1794, found: 412.1800 (PMB cleaved mass).

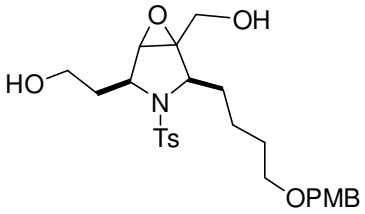
4-(hydroxymethyl)-5-(4-(4-methoxybenzyloxy)-butyl)-1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)ethanol (11):



DIBAL-H (1.0 M in THF, 2.7 g, 18.8 mmol) was added dropwise to a solution of ethyl 5-(2-hydroxyethyl)-2-(4-(4-methoxybenzyloxy)butyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (5 g, 9.4 mmol) in dry THF (100 mL) at 0 °C. After 2 h, ethanol (2 mL) was added slowly, and then stirred with aq. solution of sodium potassium tartarate for 5 h. Organic layers were evaporated to get crude residue, that was purified through flash column chromatography (50% ethyl acetate in hexane) to afford product (3.4 g, 74% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.68 (d, J=8.1, 2H), 7.24 – 7.28 (m, 4H), 6.88 (d, J=8.5, 2H), 5.42 (s, 1H), 5.30 (s, 1H), 4.51 (brs, 1H), 4.38 – 4.42 (m, 3H), 3.88 – 4.02 (m, 3H), 3.80 (s, 3H), 3.68 – 3.72 (m, 1H), 3.40 – 3.50 (m, 2H), 2.40 (s, 3H), 1.40-2.00 (m, 11H)

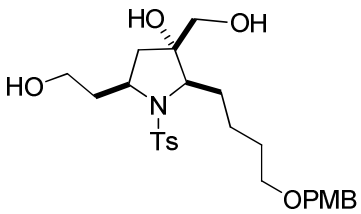
ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 159.1, 143.8, 141.9, 133.7, 130.5, 129.6, 129.2, 127.6, 124.5, 113.7, 72.5, 69.7, 67.1, 64.0, 58.9(2), 55.2, 39.9, 34.5, 29.4, 21.6, 21.5 ppm. **FTIR (neat): ν** = 3055, 2933, 2304, 1512, 1421, 1340, 1265, 1161, 1093, 894, 815, 744 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{18}H_{28}NO_5S$ $[M+H]^+$ 370. 1688, found: 370.1689 (PMB cleaved mass).

2-(5-(hydroxymethyl)-4-(4-(4-methoxybenzyloxy)-butyl)-3-tosyl-6-oxa-3-azabicyclo[3.1.0]hexan-2-yl)ethanol (12):



m-CPBA (2.75 g, 61.3 mmol; 77%) was added to a solution of 4-(hydroxymethyl)-5-(4-(4-methoxybenzyloxy)butyl)-1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)ethanol (3 g, 6.1 mmol) in CH_2Cl_2 (50 mL) at 0 ^oC. After 12 h, saturated $NaHCO_3$ solution was added, extracted with ethyl acetate. Organic layers were evaporated to get crude residue, that was purified through flash column chromatography (40% ethyl acetate in hexane) to afford product (2.5 g, 81% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.62 (d, J=8.1, 2H), 7.25 – 7.29 (m, 4H), 6.88 (d, J=8.5, 2H), 4.43 (s, 2H), 3.85 – 4.05 (m, 4H), 3.79 (s, 3H), 3.65 – 3.75 (m, 1H), 3.55 – 3.65 (m, 1H), 3.45 – 3.50 (m, 2H), 3.31 (brs, 1H), 2.41 (s, 3H), 1.35 – 1.85 (m, 9H) ppm. ^{13}C **NMR (125 MHz, $CDCl_3$):** δ= 159.0, 143.6, 134.7, 130.4, 129.3, 129.2, 127.9, 113.7, 72.5, 69.6, 68.2, 61.5, 61.3, 58.5, 58.1, 57.6, 55.1, 35.6, 32.9, 29.3, 23.0, 21.5 ppm. **FTIR (neat): ν** = 3053, 2985, 2303, 1512, 1421, 1342, 1265, 1159, 1093, 894, 740 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{18}H_{28}NO_6S$ $[M+H]^+$ 386.1657, found: 386.1647 (PMB cleaved mass).

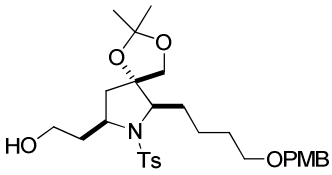
5-(2-hydroxyethyl)-3-(hydroxymethyl)-2-(4-(4-methoxybenzyloxy)butyl)-1-tosylpyrrolidin-3-ol (13):



DIBAL-H (1.0 M in THF, 2.24 g, 15.8 mmol) was added dropwise to a solution of 5-(hydroxymethyl)-4-(4-(4-methoxybenzyloxy)butyl)-3-tosyl-6-oxa-3-azabicyclo[3.1.0]hexan-2-yl)ethanol (2 g, 3.9 mmol) in dry THF (100 mL) at -78 ^oC then increased the temperature to -25 ^oC. After 24 h, ethanol (2 mL) was added slowly, and then stirred with aq. solution of sodium potassium tartarate for 5 h. Organic layers were evaporated to get crude residue, that was purified through flash column chromatography (80% ethyl acetate in hexane) to afford product (1.28 g, 64% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.75 (d, J=8.2, 2H), 7.24 – 7.28 (m, 4H), 6.88 (d, J=8.5, 2H), 4.41 (s, 2H), 3.95 – 4.05 (m, 1H), 3.79 (s, 3H), 3.73 – 3.78 (m, 1H), 3.58 – 3.66 (m, 2H), 3.38 – 3.53 (m, 4H), 2.42 - 2.52 (brs, 1H), 2.39 (s, 3H), 2.28 – 2.33 (brs, 1H), 2.05 – 2.10 (m, 1H), 1.95 – 2.03 (m, 1H), 1.70 -1.80 (m, 1H), 1.50 – 1.65 (m, 5H), 1.30 – 1.38 (m, 1H), 1.17 – 1.25 (m, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 159.1, 143.7, 134.9, 130.5, 129.3, 129.2, 128.3, 113.7, 82.0,

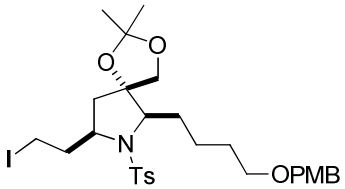
72.4, 69.8, 69.3, 64.6, 59.6, 56.4, 55.2, 40.6, 40.5, 33.0, 29.3, 22.6, 21.5 ppm. **FTIR (neat): ν** = 3053, 2981, 2304, 1421, 1265, 1159, 1091, 1033, 894, 738 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{18}H_{30}NO_6S$ $[M+H]^+$ 388.1794, found: 388.1769 (PMB cleaved mass).

6-(4-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-7-tosyl-1,3-dioxa-7-azaspiro[4.4]nonan-8-yl)ethanol (14):



To a solution of 2-2-dimethoxy propane (2.63 g, 25 mmol)and 5-(2-hydroxyethyl)-3-(hydroxymethyl)-2-(4-(4-methoxybenzyloxy)butyl)-1-tosylpyrrolidin-3-ol (1.2 g, 2.5 mmol) in CH_2Cl_2, camphorsulfonic acid (58 mg, 0.25 mmol) was added and stirred for 1h at 25 ^oC. Saturated solution of NaHCO3 (2 mL) was added, extracted with CH2Cl2. Organic layer was concentrated to get crude product that was purified using column chromatography (70% ethyl acetate in hexane) to get pure product (1.0 g, 77% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.71 (d, J=8.2Hz, 2H), 7.23 – 7.28 (m, 4H), 6.88 (d, J=8.6Hz, 2H), 4.44 (s, 2H), 3.80 – 3.85 (m, 2H), 3.79 (s, 3H), 3.77 – 3.78 (m, 1H), 3.62 – 3.70 (m, 2H), 3.57 (dd, J= 9.7, 3.7Hz, 1H), 3.45 - 3.52 (m, 2H), 2.41 (s, 3H), 2.20 – 2.27 (m, 1H), 2.09 (dd, J=9.7, 3.7Hz, 1H), 1.65 – 1.85 (m, 4H), 1.55 -1.62 (m, 2H), 1.38 – 1.48 (m, 1H), 1.27 – 1.37 (m, 1H), 0.99 (s, 3H), 0.95 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 159.0, 142.8, 134.9, 130.5, 129.2, 128.7, 128.5, 113.6, 109.0, 88.0, 72.4, 69.8, 68.7, 67.3, 59.6, 56.9, 55.1, 42.3, 40.3, 33.5, 29.5, 26.7, 25.5, 22.5, 21.3 ppm. **FTIR (neat): ν** = 3055, 2983, 2968, 1720, 1598, 1454, 1340, 1265, 1165, 1093, 813, 742 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{29}H_{42}NO_7S$ $[M+H]^+$ 548.2682, found: 548.2677.

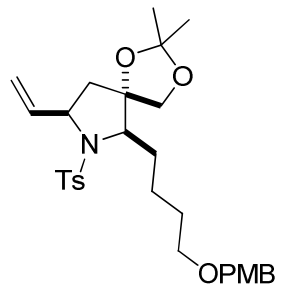
8-(2-iodoethyl)-6-(4-(4-methoxybenzyloxy)-butyl)-2,2-dimethyl-7-tosyl-1,3-dioxa-7-azaspiro[4.4]nonane (15):



To a solution of 6-(4-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-7-tosyl-1,3-dioxa-7-azaspiro[4.4]nonan-8-yl)ethanol (1 g, 1.8 mmol), imidazole (375 mg, 5.4 mmol) and triphenylphosphine (710 mg, 2.7 mmol) in CH_2Cl_2, was added I_2 (685 mg, 2.7 mmol) at 25 ^oC then continued stirring for 12 h. Saturated solution of $Na_2S_2O_3$ (2 mL) and $NaHCO_3$ (2 mL) was added, extracted with ethyl acetate. Organic layer was concentrated to get crude product that was purified using column chromatography (25% ethyl acetate in hexane) to get pure product (1.0 g, 87% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.74 (d, J=8.2Hz, 2H), 7.25 – 7.28 (m, 4H), 6.87-6.89 (m, 2H), 4.44 (s, 2H), 3.81 – 3.83 (m, 1H), 3.80 (s, 3H), 3.62 – 3.72 (m, 2H), 3.59 (dd, J= 9.6, 3.4Hz, 1H), 3.48 (t, J=5.7Hz, 2H), 3.21 – 3.31 (m, 1H), 2.98 – 3.05 (m, 1H), 2.69 – 2.79 (m, 1H), 2.42 (s, 3H), 1.95 – 2.10

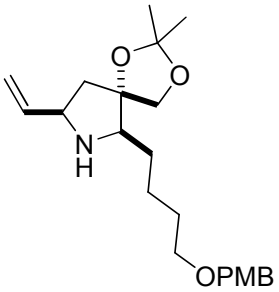
(m, 2H), 1.50 – 1.70 (m, 6H), 1.38 – 1.48 (m, 1H), 1.02 (s, 3H), 0.98 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 159.0, 142.9, 134.5, 130.6, 129.2, 128.8, 128.7, 113.7, 109.2, 87.6, 72.5, 69.8, 68.9, 67.2, 59.6, 55.2, 40.9, 40.6, 33.8, 29.5, 26.8, 25.5, 22.6, 21.4, 14.1, 0.92 ppm. **FTIR (neat): ν** = 3444, 2983, 2933, 1512, 1454, 1342, 1247, 1159, 1089, 1004, 815, 738 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{21}H_{33}NIO_5S$ $[M+H]^+$ 538.1124, found: 538.1116 (PMB cleaved mass).

6-(4-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-7-tosyl-8-vinyl-1,3-dioxa-7-azaspiro[4.4]nonane (16):



To a slurry of NaH (120 mg, 3.0 mmol, 60%) and TBAI (55.3 mg, 0.15 mmol) in THF (10 mL) was added 8-(2-iodoethyl)-6-(4-(4-methoxybenzyloxy)-butyl)-2,2-dimethyl-7-tosyl-1,3-dioxa-7-azaspiro[4.4]nonane (1 g, 1.5 mmol) in THF (10 mL) at 0 °C then refluxed for 12 h. Ice-cold water was added dropwise, extracted with ethyl acetate. Organic layer was concentrated to get crude product that was purified using column chromatography (20% ethyl acetate in hexane) to get pure product (0.7 g, 88% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.72 (d, J=8.2Hz, 2H), 7.22 – 7.28 (m, 4H), 6.89 (d, J=, 2H), 5.88 – 5.97 (m, 1H), 5.24 (d, J= , 1H), 5.12 (d, J= , 1H),) 4.43 (s, 2H), 4.00 – 4.07 (m, 1H), 3.83 – 3.87 (m, 1H), 3.78 (s, 3H), 3.68 – 3.71 (m, 1H), 3.63 – 3.73 (m, 1H), 3.47 (t, J=5.7Hz, 2H), 2.4 (s, 3H), 2.00 – 2.07 (m, 1H), 1.75 -1.81 (m, 1H), 1.30 – 1.70 (m, 6H), 1.00 (s, 3H), 1.03 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 159.0, 142.7, 139.7, 134.9, 130.5, 129.1, 128.7, 128.4, 115.1, 113.6, 109.1, 87.5, 72.4, 69.7, 68.9, 67.0, 61.0, 55.1, 42.3, 33.7, 29.5, 26.7, 25.6, 22.5, 21.3 ppm. **FTIR (neat): ν** = 3053, 2985, 2304, 1421, 1265, 1159, 894, 738, 705 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{21}H_{32}NO_5S$ $[M+H]^+$ 410.1942, found: 410.945 (PMB cleaved mass).

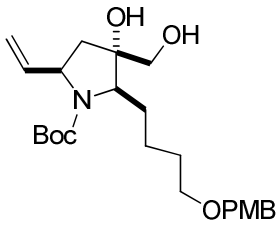
6-(4-(4-methoxybenzyloxy) butyl)-2,2-dimethyl-8-vinyl-1,3-dioxa-7-azaspiro[4.4]nonane (17) [3]**:**



To a solution of naphthalene (1.69 g, 13.2 mmol) in dry DMSO (2 mL), sodium metal (261 mg, 11.8 mmol) was added then stirred at 25 °C. After 2 h, dark green colour was observed. Above mixture was added dropwise to a pre-dissolved solution of 6-(4-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-7-tosyl-8-vinyl-1,3-dioxa-7-azaspiro[4.4]nonane (700 mg; 1.32 mmol) in dry DMSO at -78 °C. After 30 minute, saturated solution of $NaHCO_3$ (2 mL) was added then stirred with solid K_2CO_3 (6 g) for 5 h. Extracted with CH_2Cl_2 (100 mL, 3 times), combined organic layer was concentrated to get crude product that was purified using column chromatography (80% ethyl

acetate in hexane) to get pure product (340 mg, 69% yield); **^{1}H NMR (300 MHz, $CDCl_3$):** δ= 7.18 (d, J=8.4Hz, 2H), 6.80(d, J=8.4Hz, 2H), 5.62 – 5.71 (m, 1H), 4.90 -5.11 (m, 2H), 4.34 (s, 2H), 4.02 (d, J=9.0Hz, 1H), 3.71 (s, 3H), 3.57 – 3.67 (m, 2H), 3.37 – 3.40 (m, 2H), 2.95 – 2.98 (m, 1H), 2.55 (brs, 1H), 2.13 (dd, J=13.3, 7.0Hz, 1H), 1.40 – 1.70 (m, 5H), 1.31 (s, 3H), 1.28 (s, 3H), 1.15 – 1.25 (m, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 159.0, 140.3, 130.5, 129.1, 115.1, 113.6, 108.4, 88.0, 72.4, 69.9, 69.8, 66.1, 58.4, 55.1, 44.4, 30.5, 29.7, 26.8, 25.7, 24.2 ppm. **FTIR (neat): ν** = 3053, 2985, 2937, 2862, 2304, 1612, 1512, 1265, 1099, 1056, 1035, 738 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{14}H_{26}NO_3$ $[M+H]^+$ 256.1913, found: 256.1915 (PMB cleaved mass).

Tert-butyl-3-hydroxy-3-(hydroxymethyl)-2-(4-(4-methoxybenzyloxy)butyl)-5-vinylpyrrolidine-1-carboxylate (18):



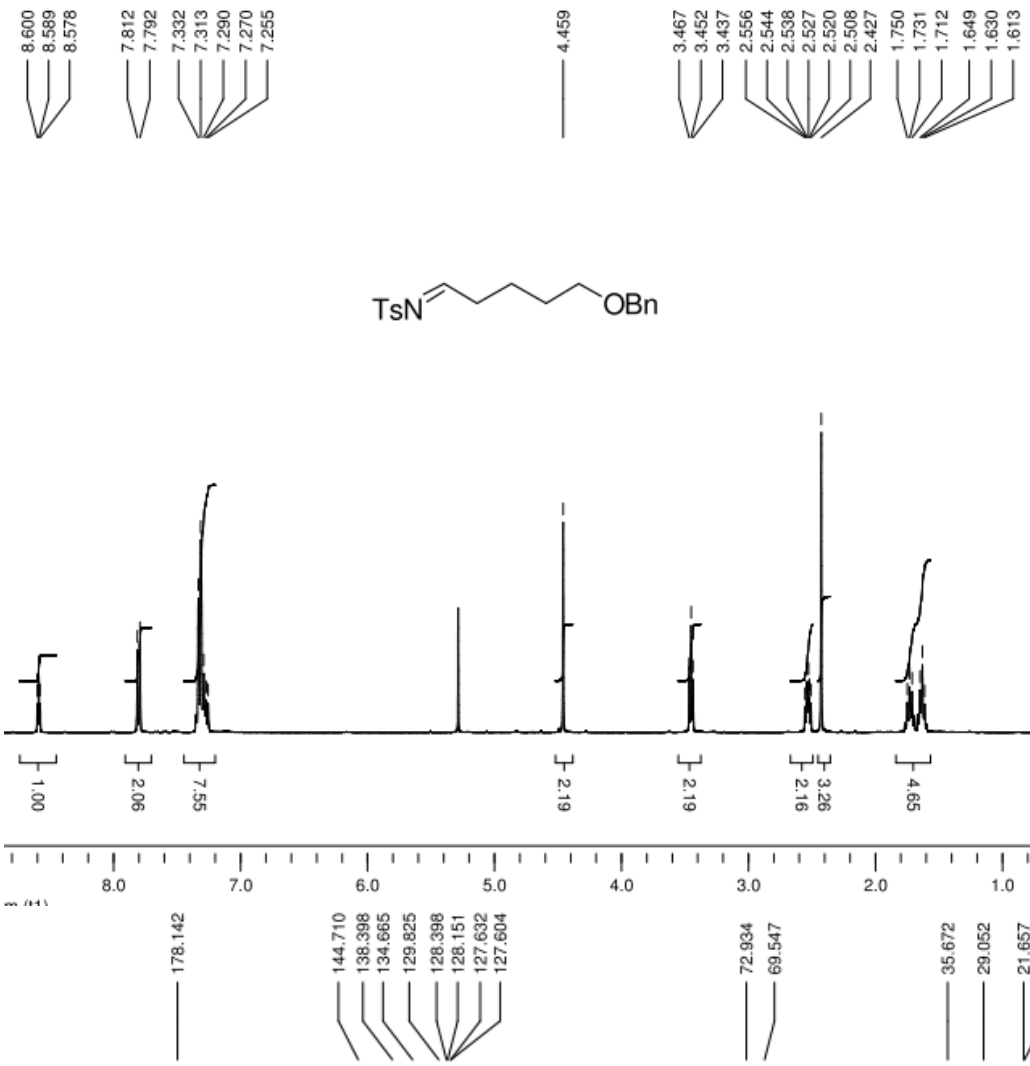
To a solution of 6-(4-(4-methoxybenzyloxy) butyl)-2,2-dimethyl-8-vinyl-1,3-dioxa-7-azaspiro[4.4]nonane (300mg; 0.8 mmol) in THF:H_2O (1:1, 10 mL), was added 3 M HCl (3.0 mL) at 0 °C. After 5 h stirring at 25 °C, adjusted the pH to 9.0 using $NaHCO_3$ then $(BOC)_2O$ (350 mg, 1.6 mmol) in THF was added dropwise at 25 °C. After 2 h, extracted with ethyl acetate, combined organic layer was concentrated to get crude product that was purified by column chromatography (90% ethyl acetate in hexane) to get pure product (330mg; 88% over 2 step); **^{1}H NMR (300 MHz, DMSO-d_6):** δ= 7.22 (d, J=8.5Hz, 2H), 6.88(d, J=8.6Hz, 2H), 5.75 (brs, 1H), 4.90 -5.05 (m, 2H), 4.50 – 4.65 (m, 2H), 4.34 (s, 2H), 4.25 (brs, 1H), 3.73 (s, 3H), 3.65 (brs, 1H), 3.35 – 3.40 (m, 4H), 1.85 -1.90 (m, 1H), 1.40 – 1.60 (m, 6H), 1.35 (s, 9H), 1.00 – 1.10 (brs, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$):** δ= 159.0, 156.4, 140.2, 130.5, 129.1(2), 114.0, 113.6(2), 81.2, 79.6, 72.4, 70.0(2), 66.3, 64.8, 58.8, 55.1(2), 39.6, 32.6, 29.6, 28.3(2) ppm. **FTIR (neat): ν** = 3053, 2980, 1683, 1612, 1512, 1392, 1265, 1033, 738 cm^{-1}; **HRMS (ESI, m/z):** calcd for $C_{16}H_{30}NO_5$ $[M+H]^+$ 316.2065, found: 316.2066 (PMB cleaved mass).

References:

[1] A. Suarez, G. C. Fu, *Angew. Chem. Int. Ed*. **2004**, *43*, 3580-3582.

[2] For synthesis of imines. see: a) T. –S. Jin, M. –J. Yu, L. –B. Liu, Y. Zhao, T. –S. Li, *Synthetic Communications* **2006**, *36*, 2339-2344; b) K. Y. Lee, C. G. Lee, J. N. Kim, *Tetrahedron Lett*. **2003**, *44*, 1231-1234; c) F. Chemla, V. Hebbe, J–. F. Normant, *Synthesis* **2000**, 75-77.

[3] For Tosyl de-protection. see: C. H. Heathcock, T. A. Blumenkopf, K. M. Smith, *J. Org. Chem*. **1989**, *54*, 1548 – 1562.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2.544
2.538
2.527
2.520
2.508
2.427
1.750
1.731
1.712
1.649
1.630
1.613
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OBn
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7.55
2.19
2.19
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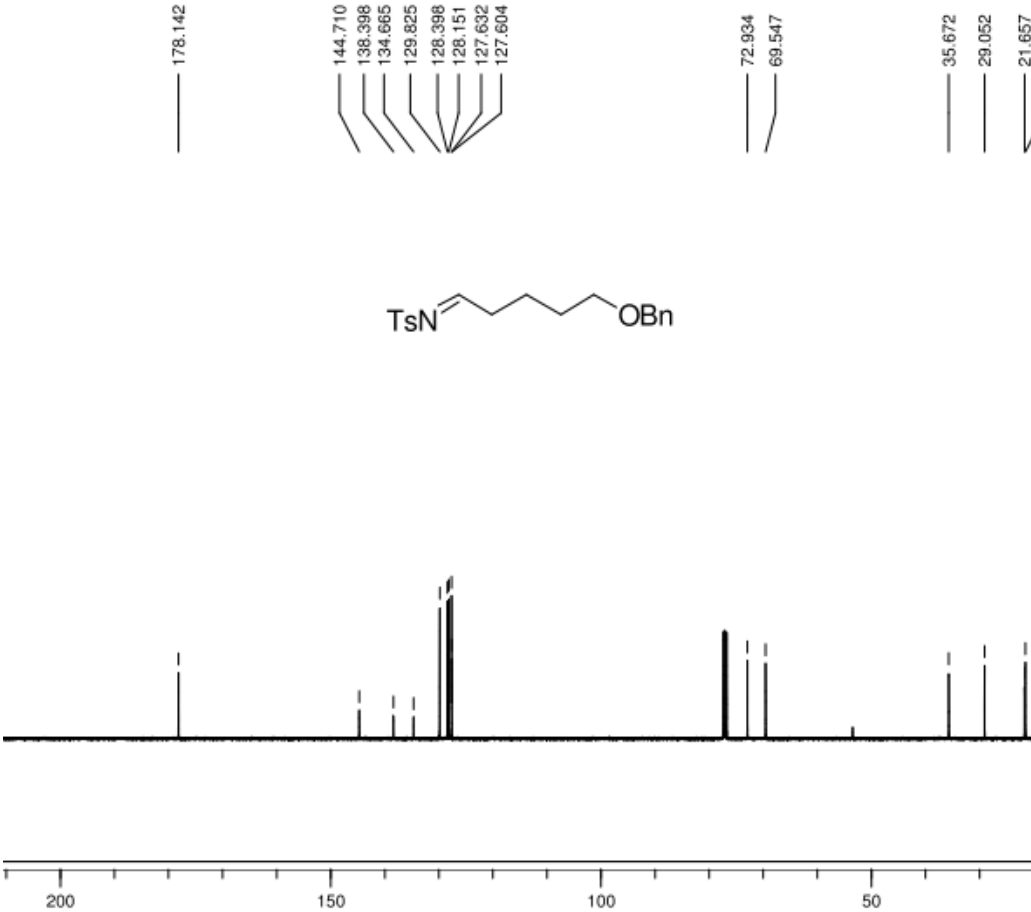
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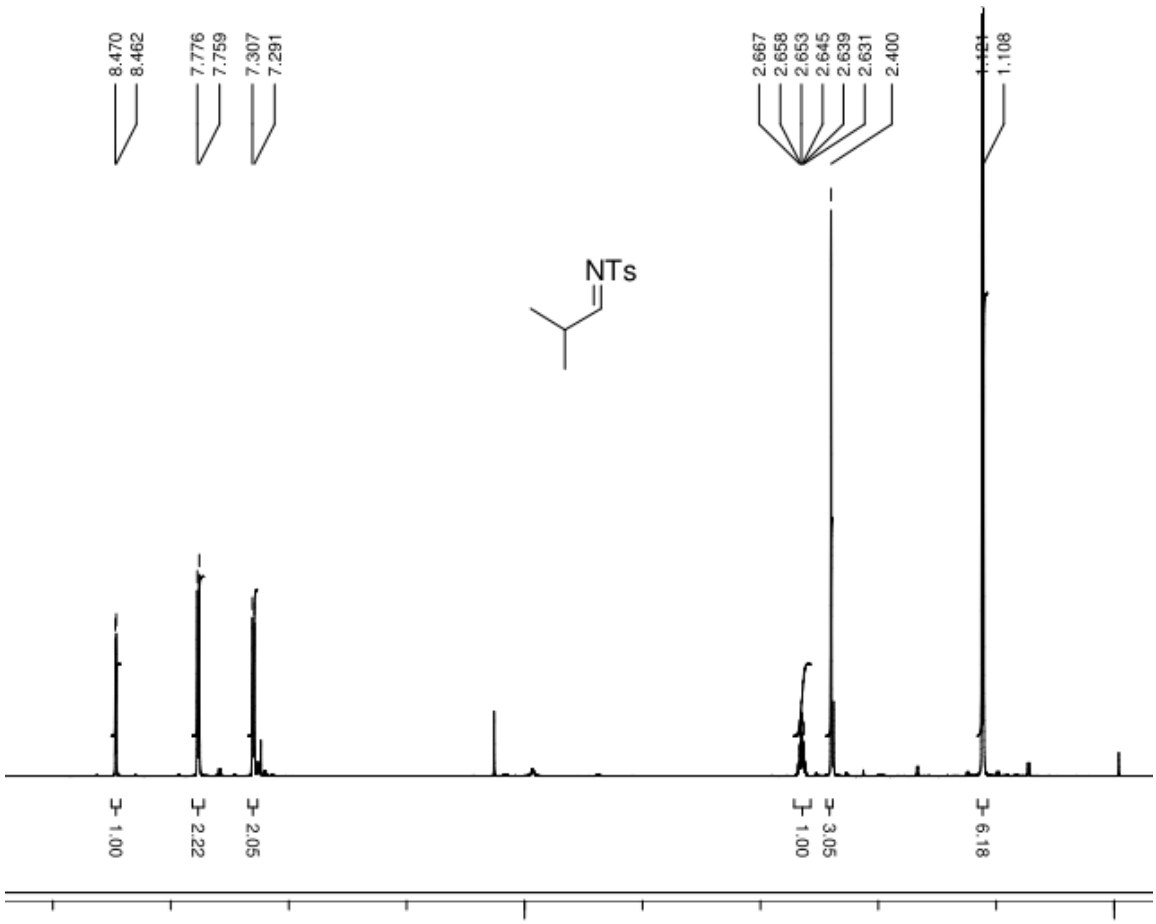
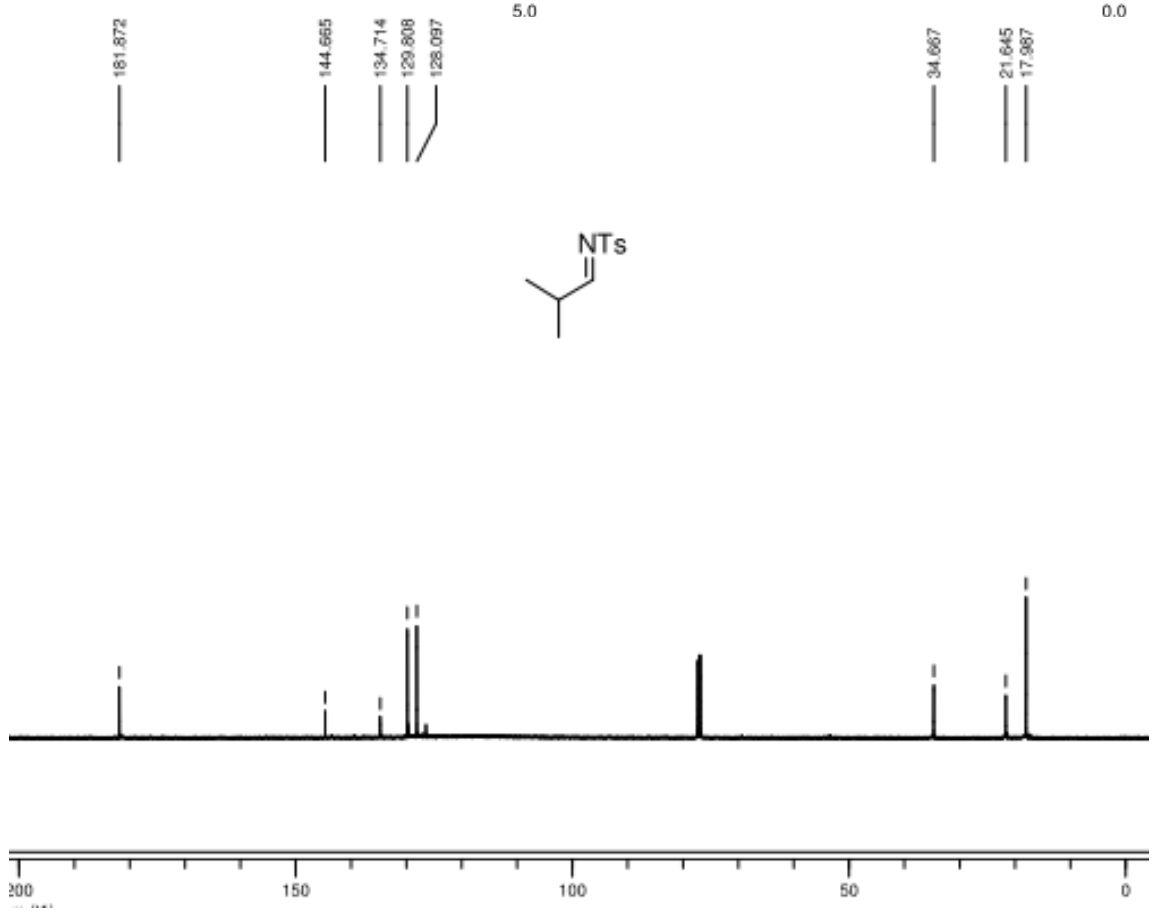
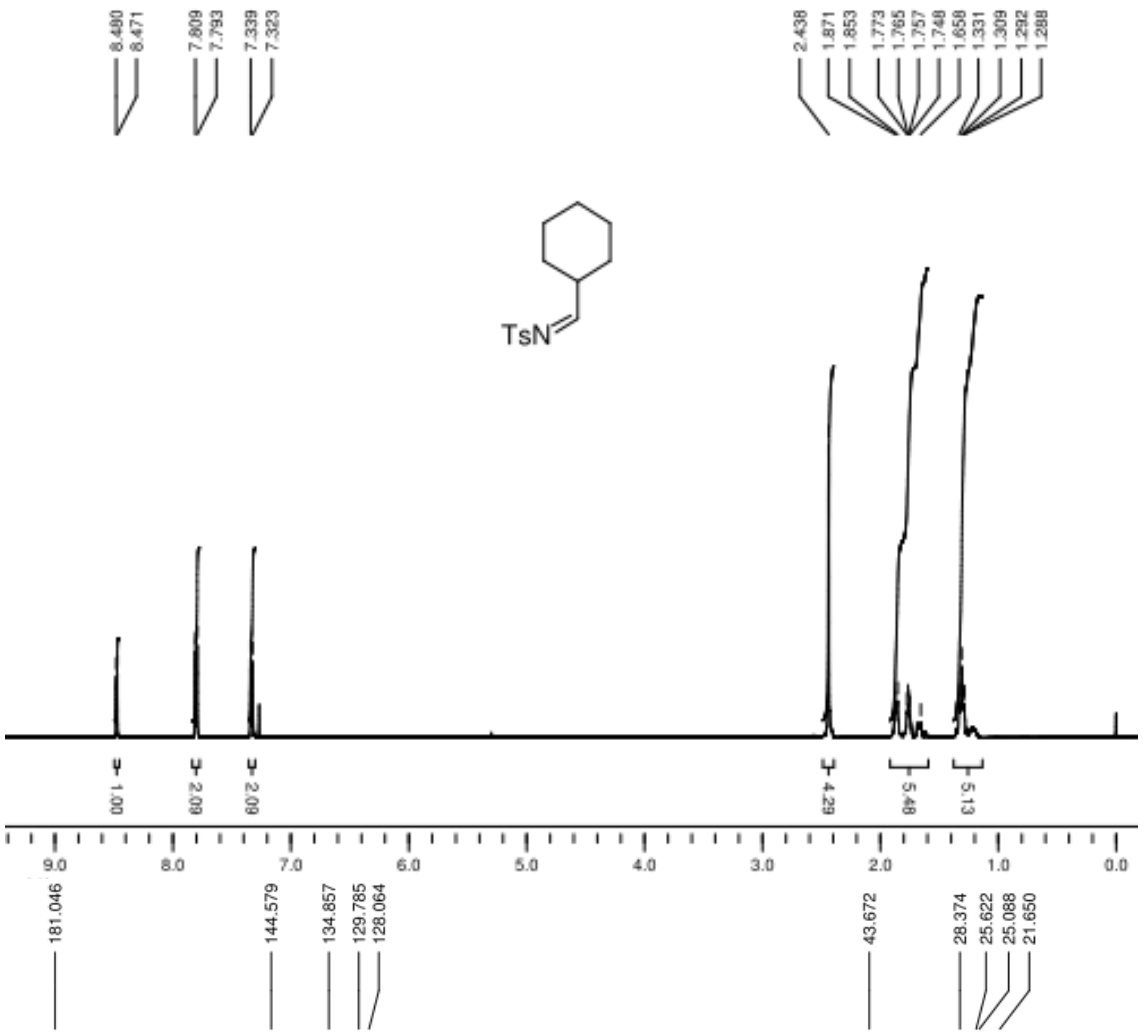
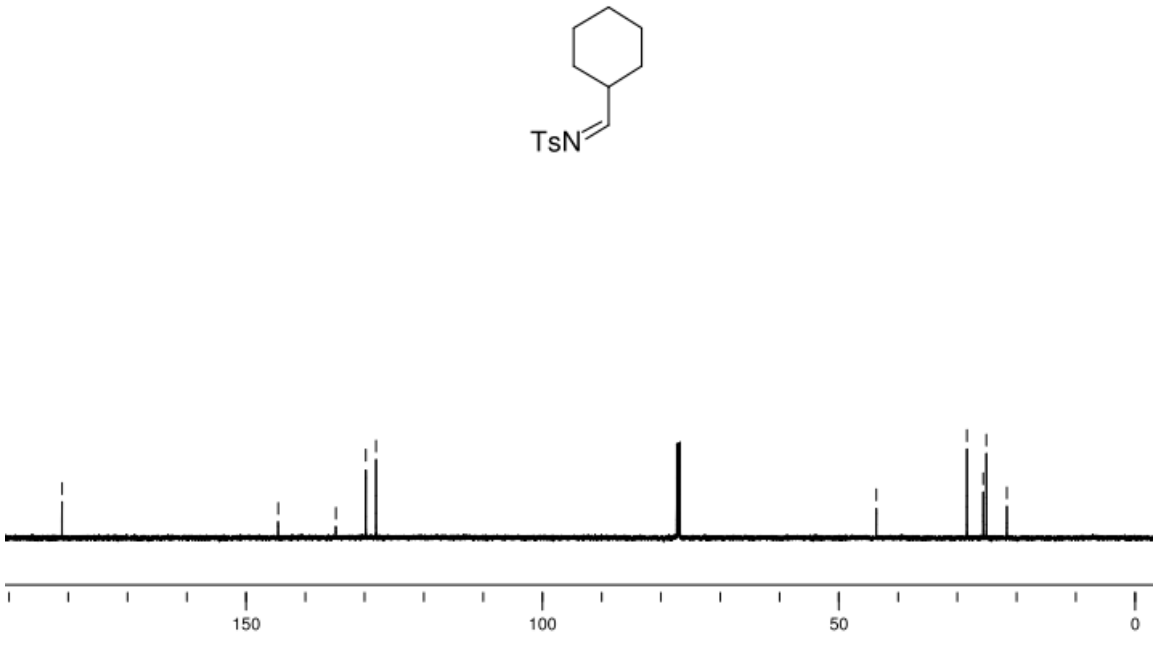
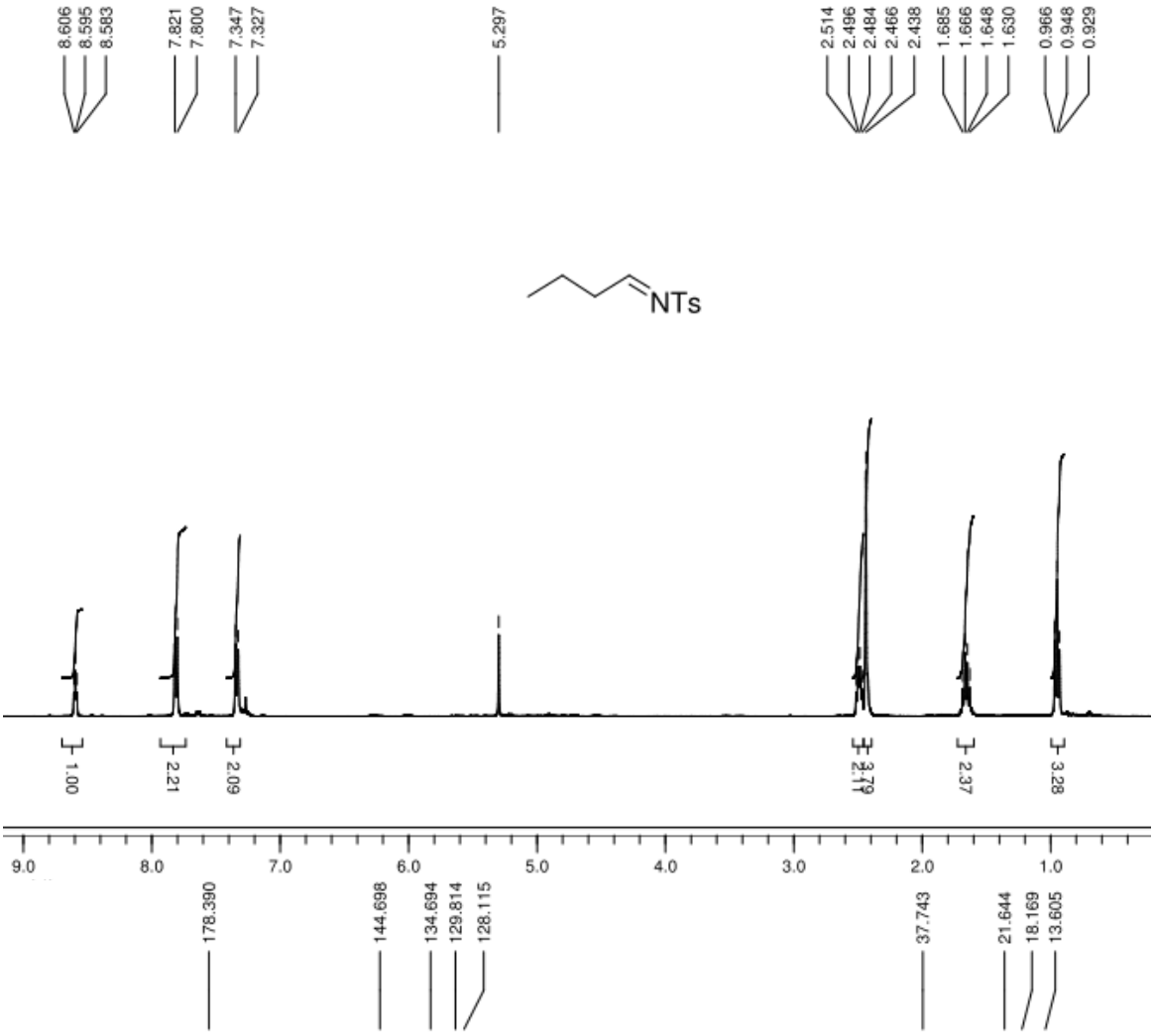
0







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0.929
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2.09
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6.0
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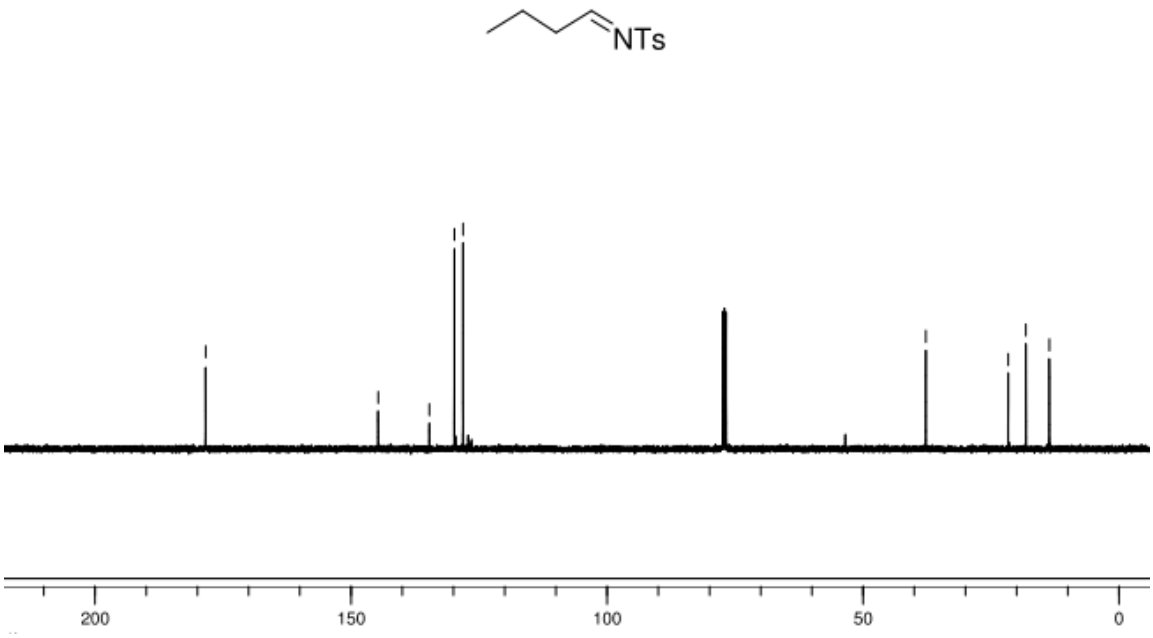
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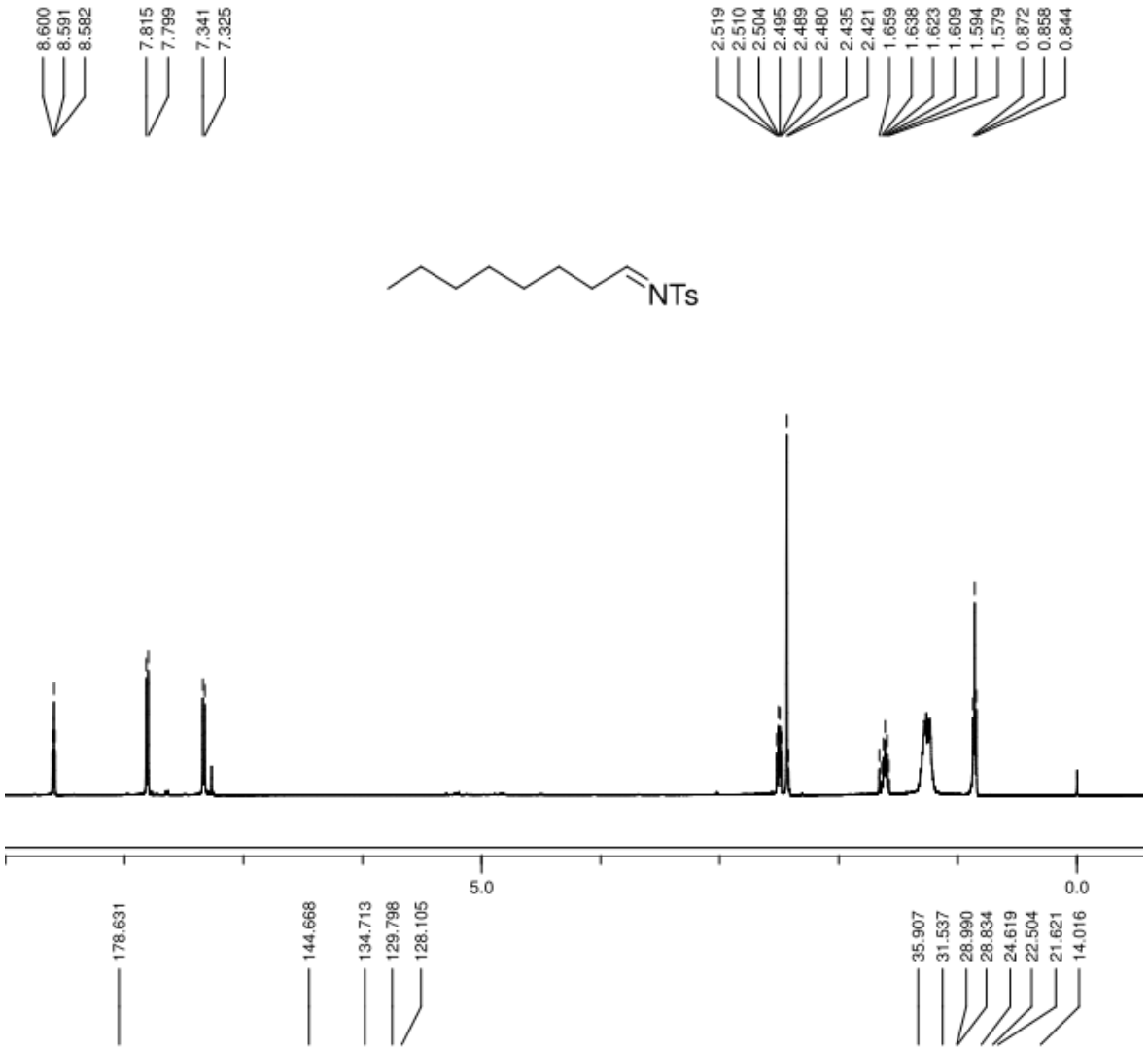

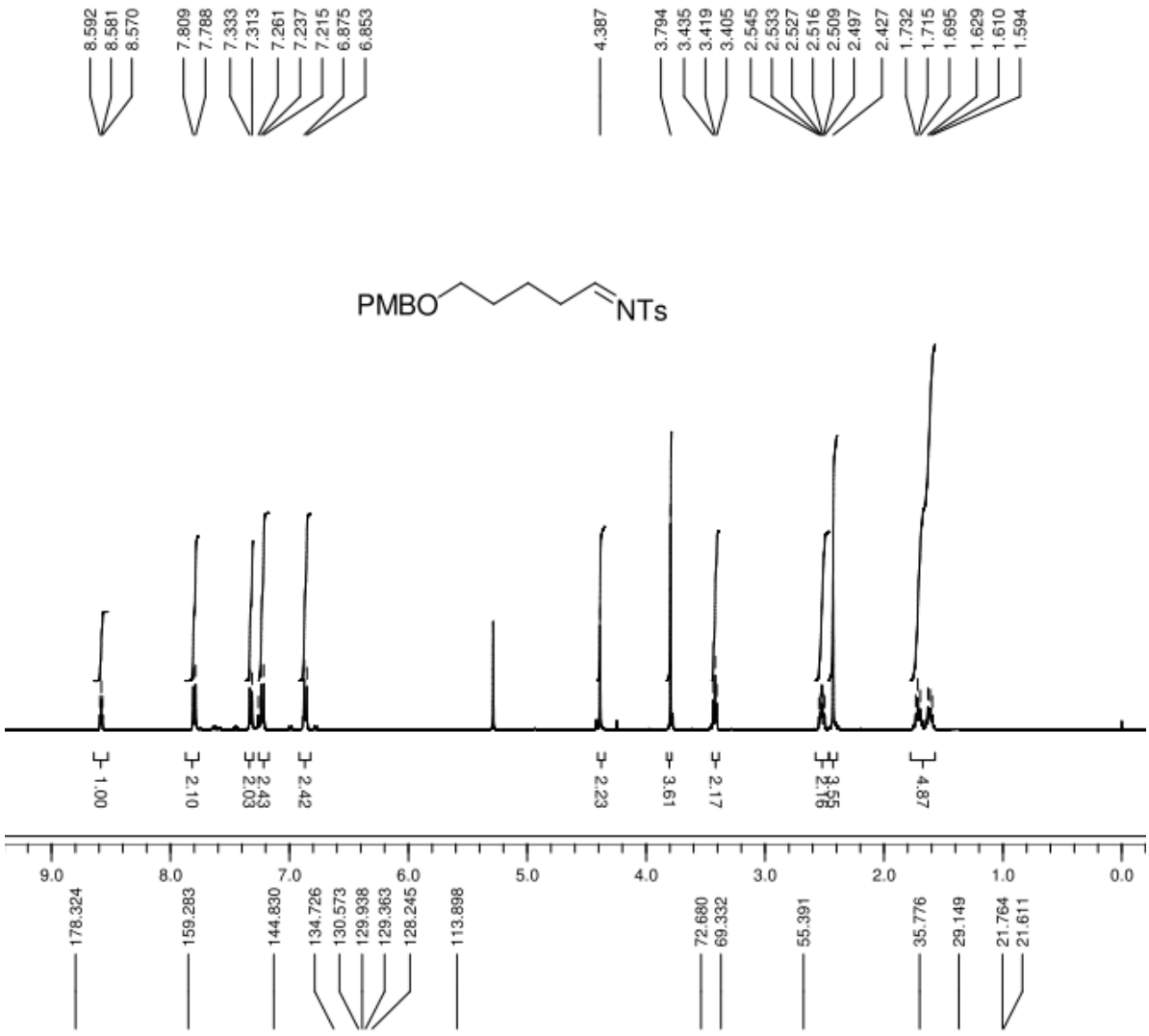
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1.594
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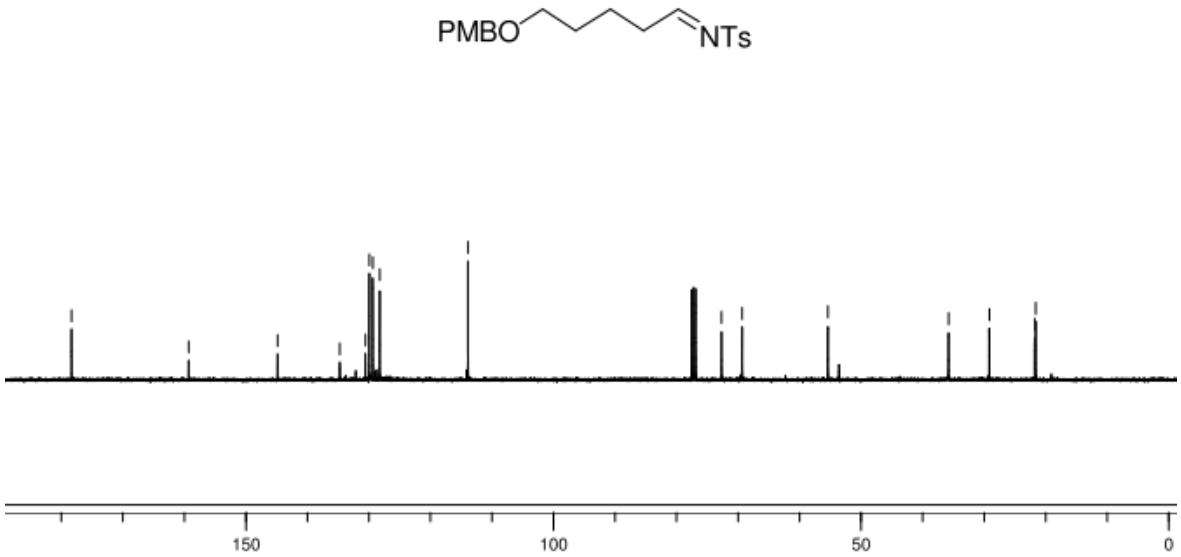
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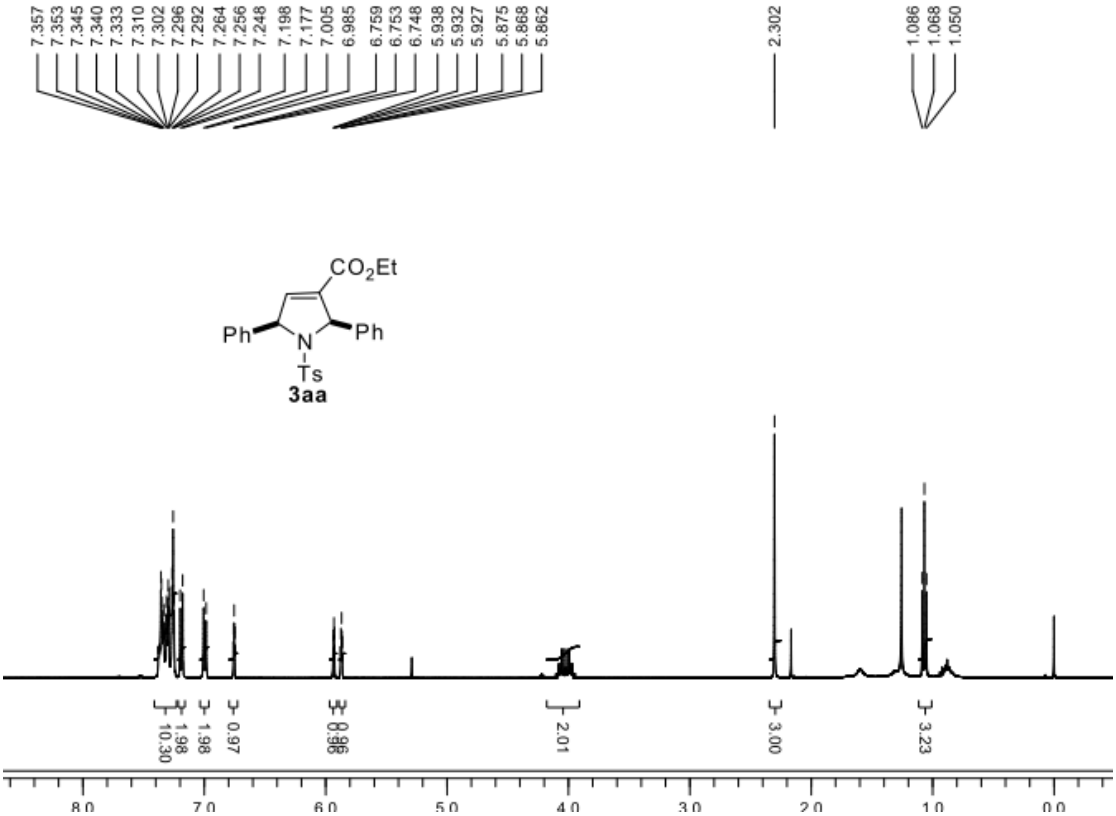
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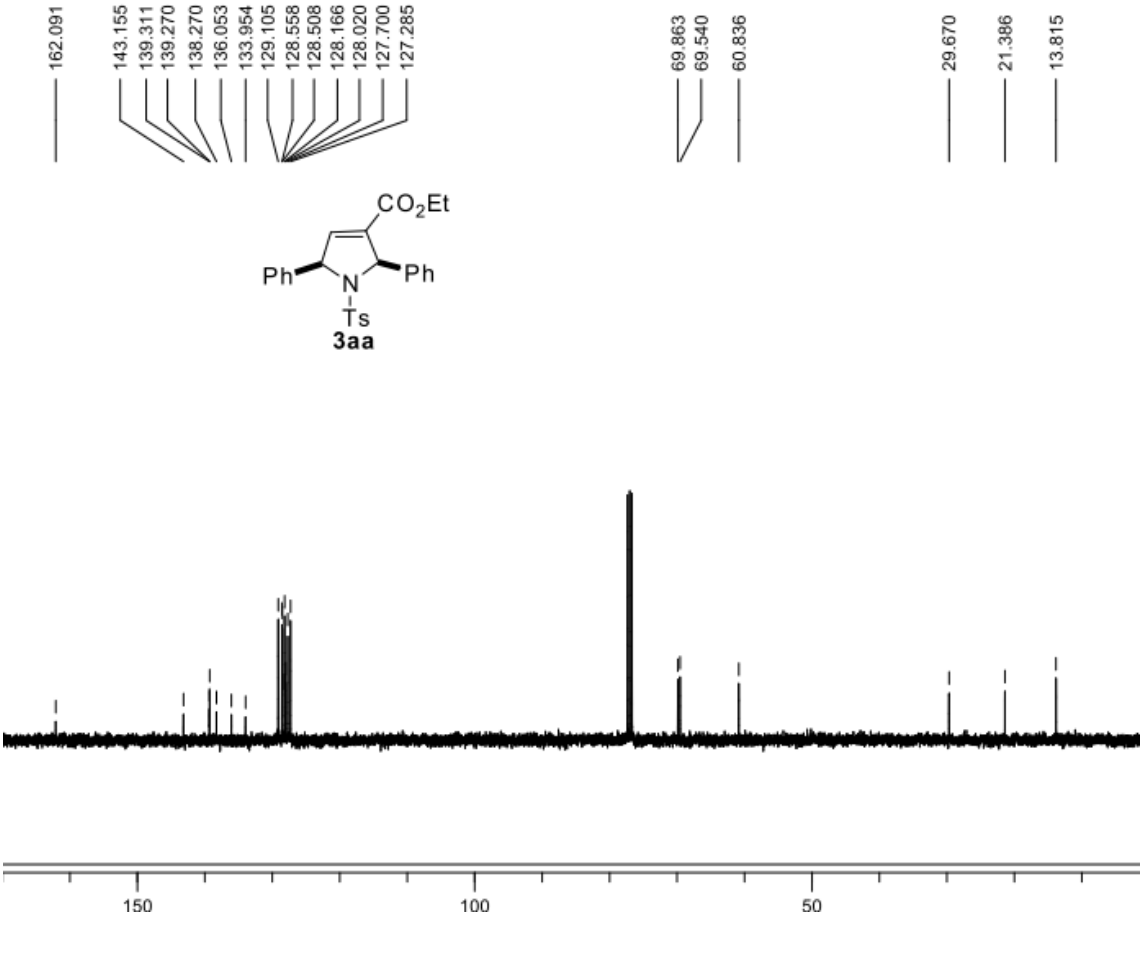
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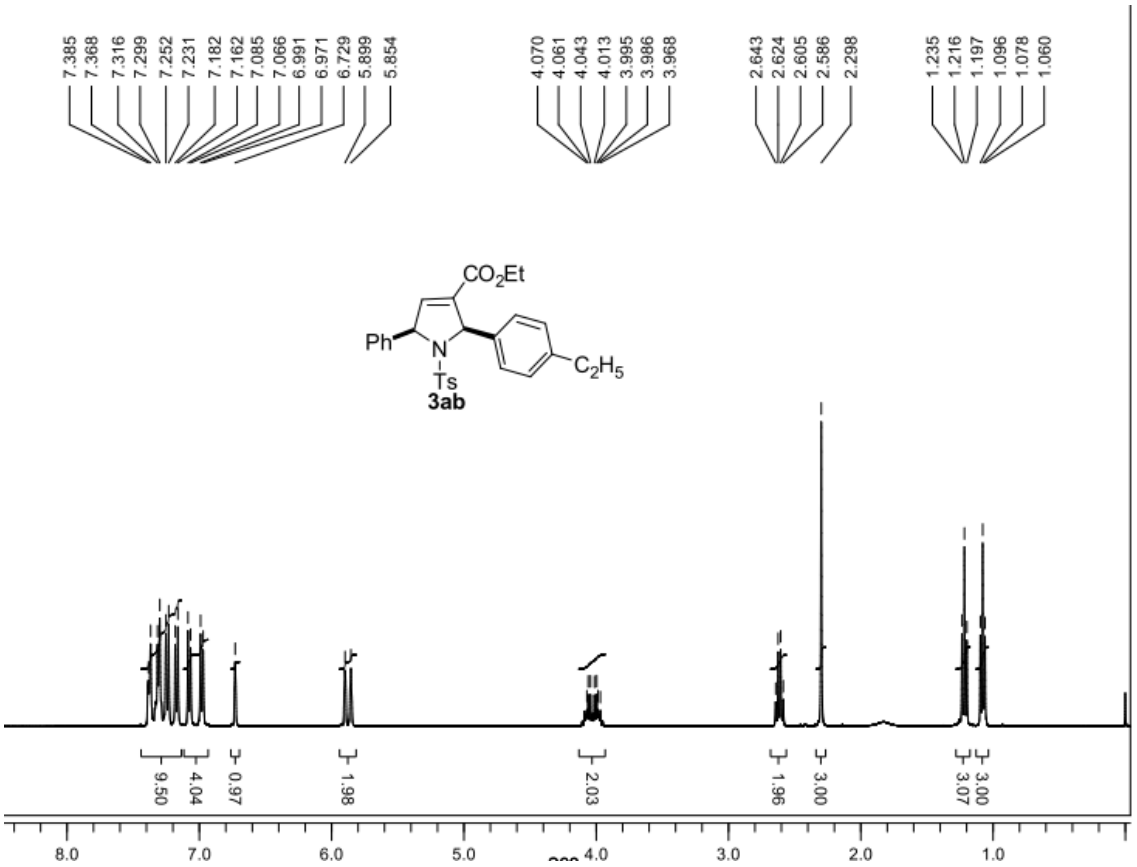
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5.854
4.070
4.061
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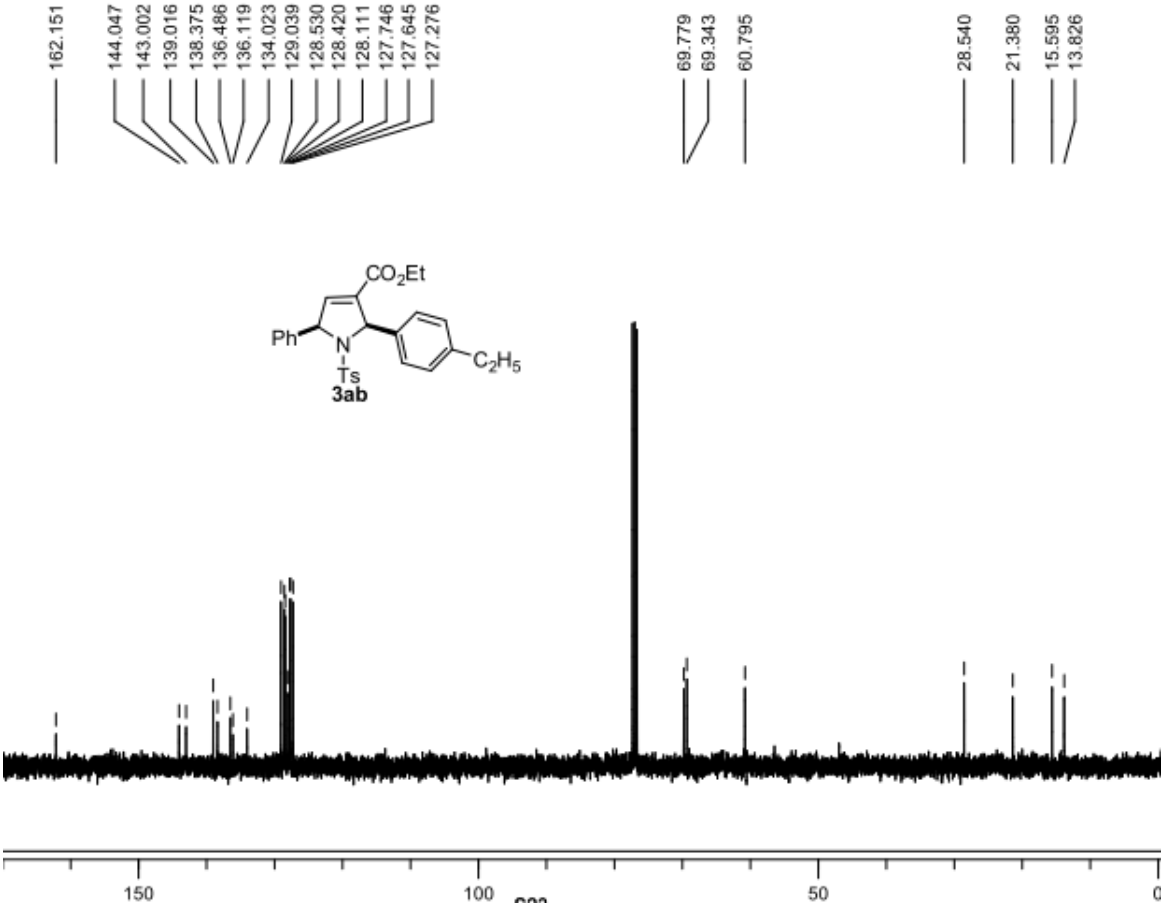
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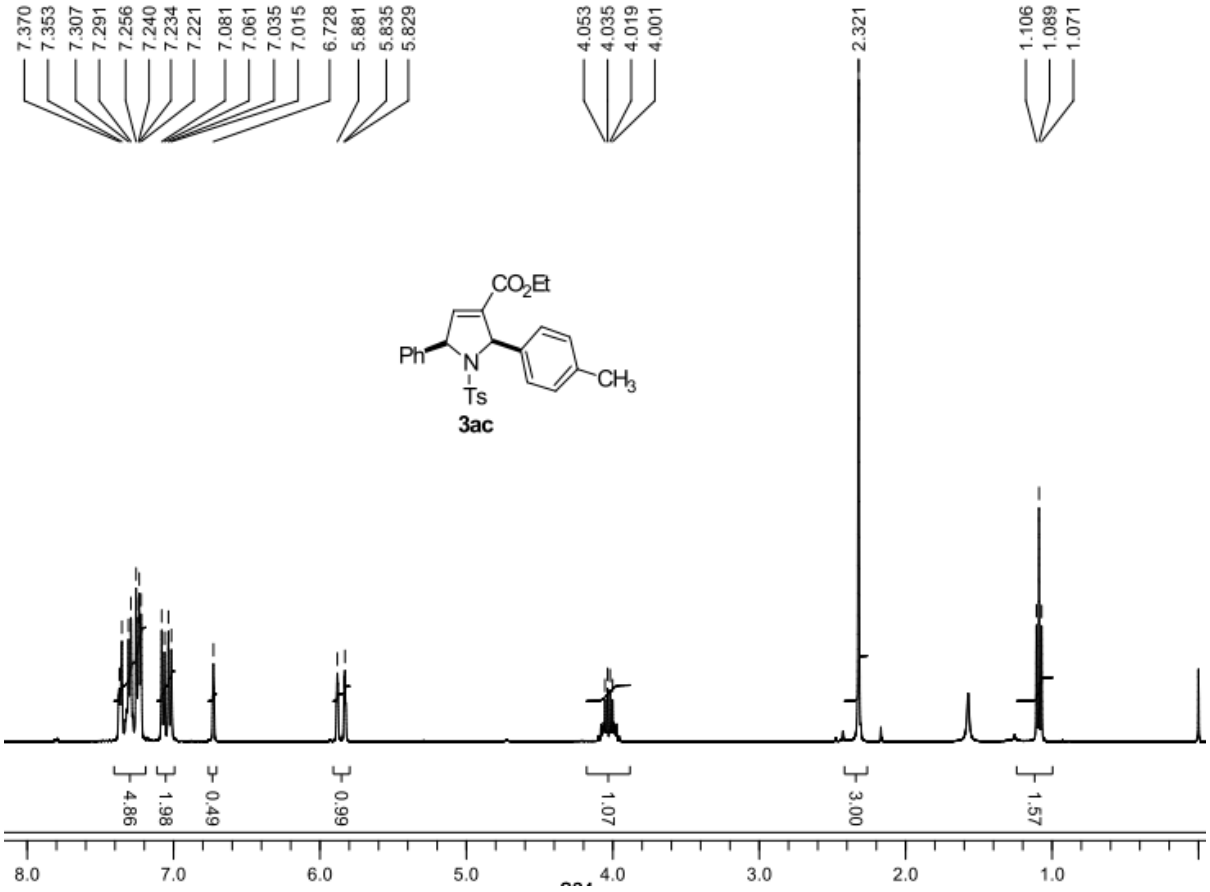
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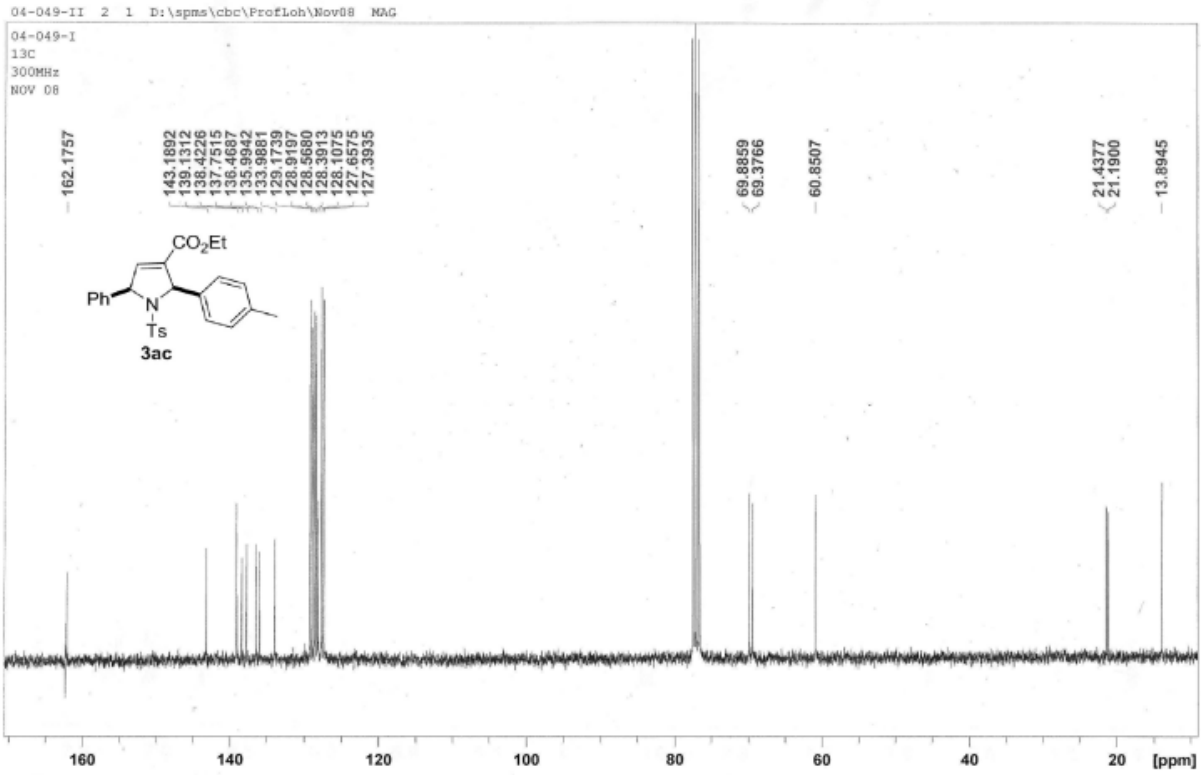
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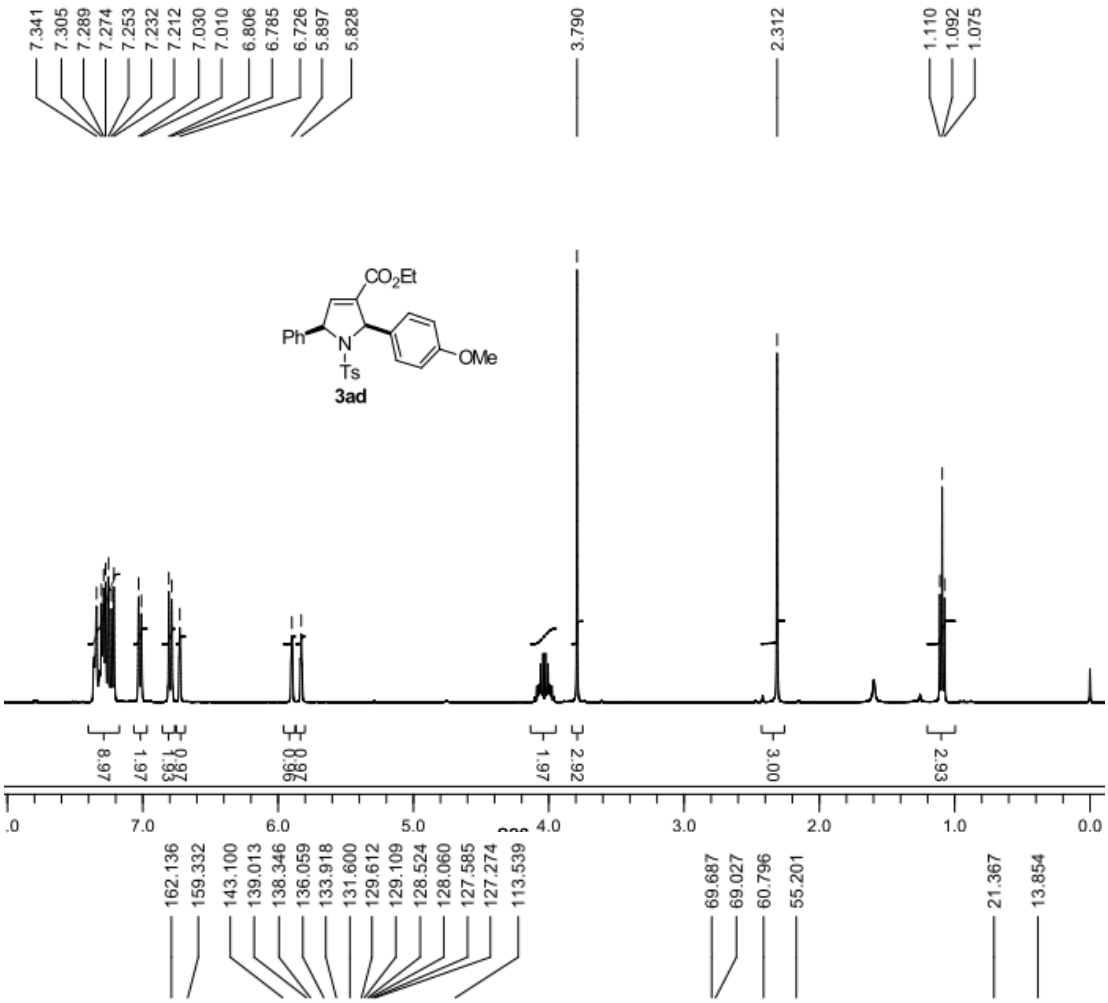
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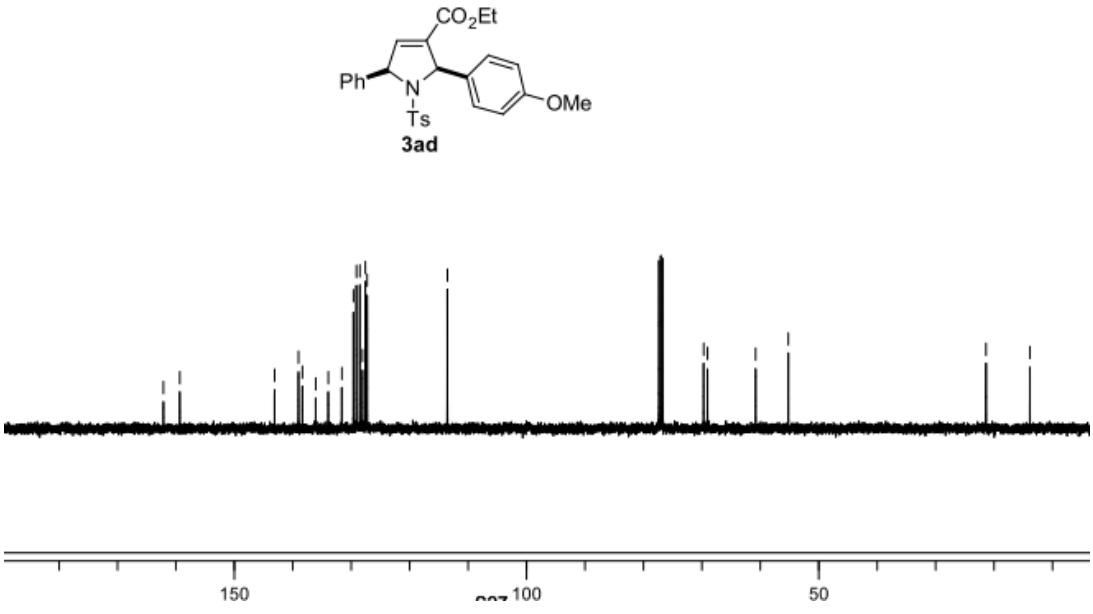
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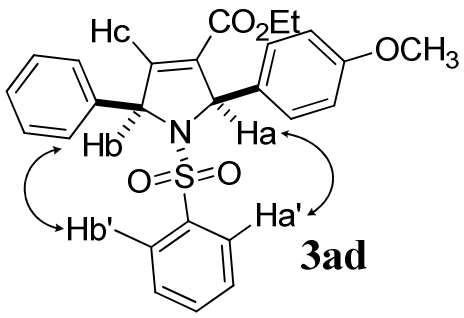

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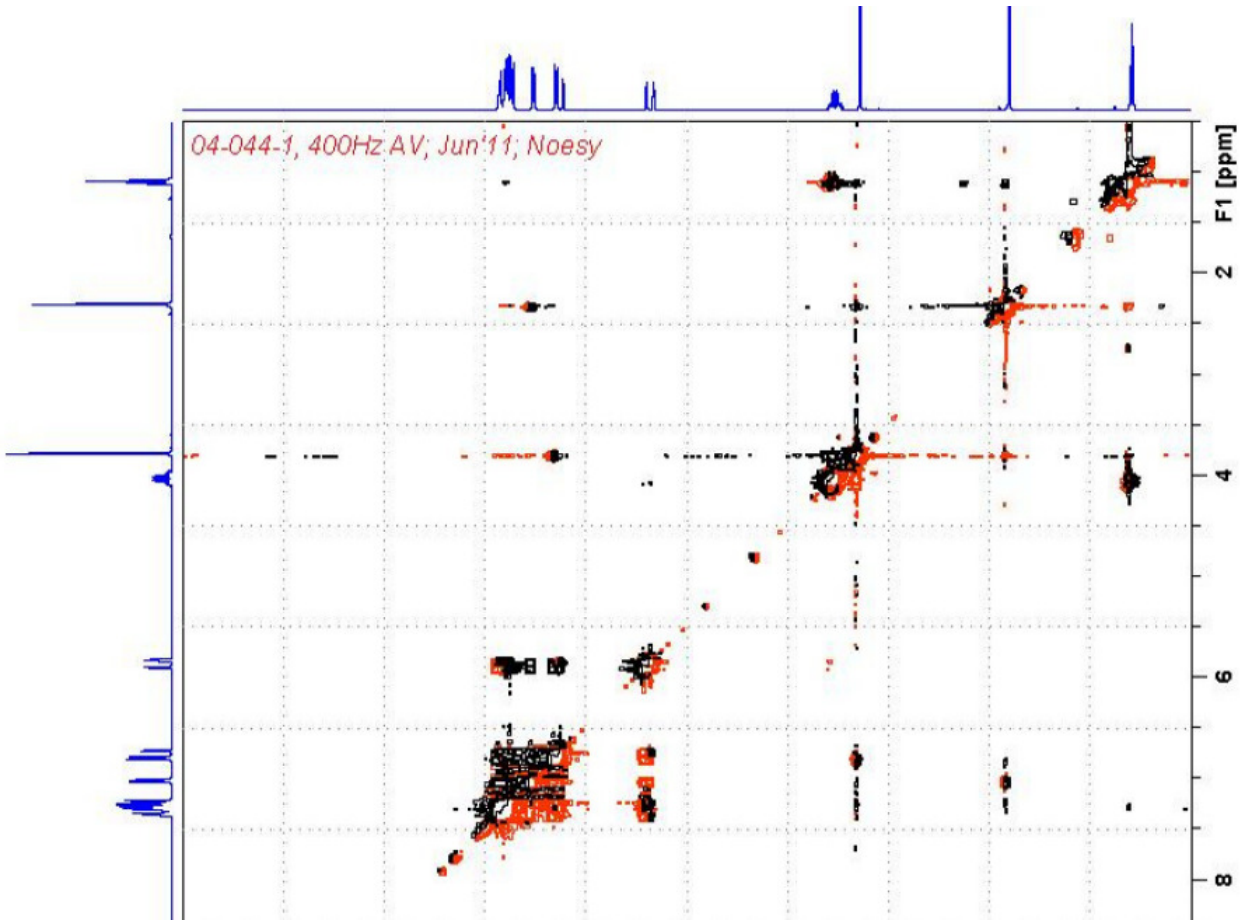
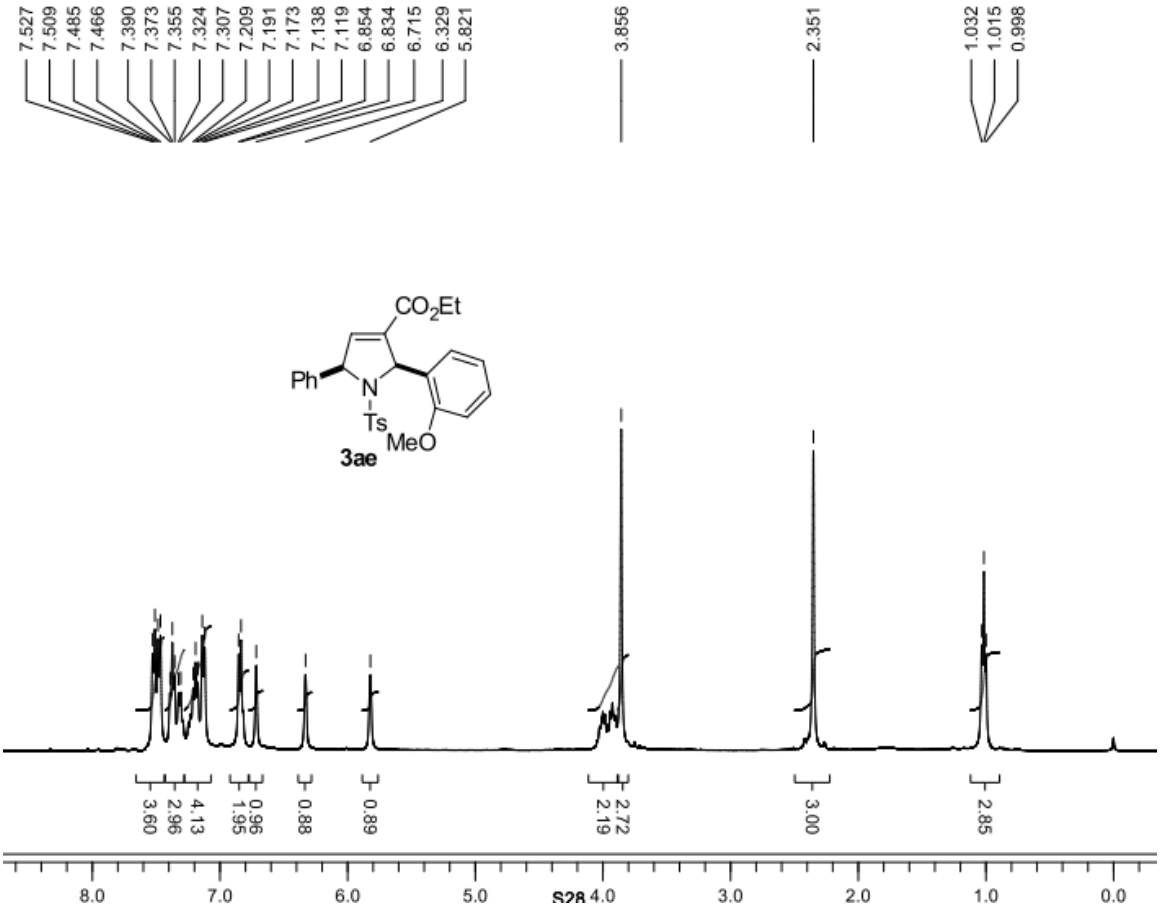


1H-1H- Noesy correlation was observed between both Ha and Hb with Hc. Also both Ha and Hb have correlation with Ha' and Hb' respectively.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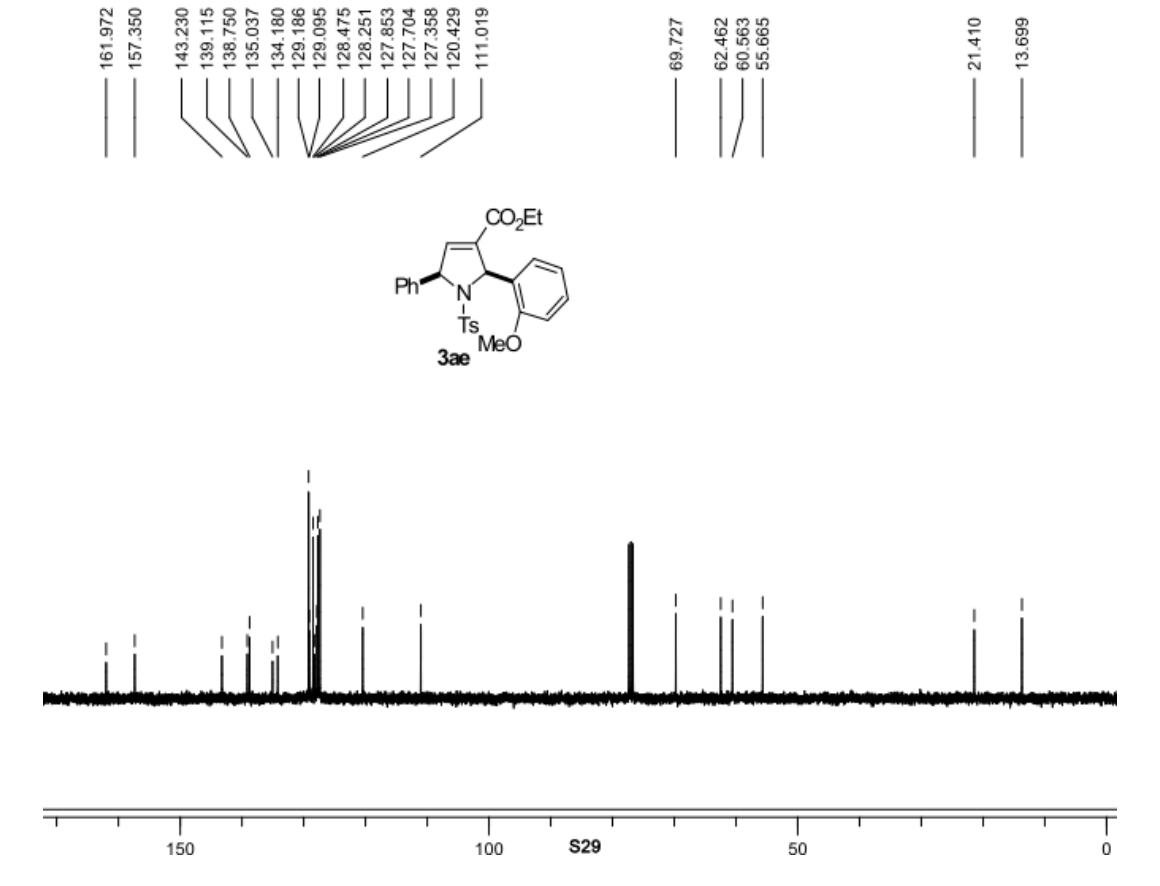
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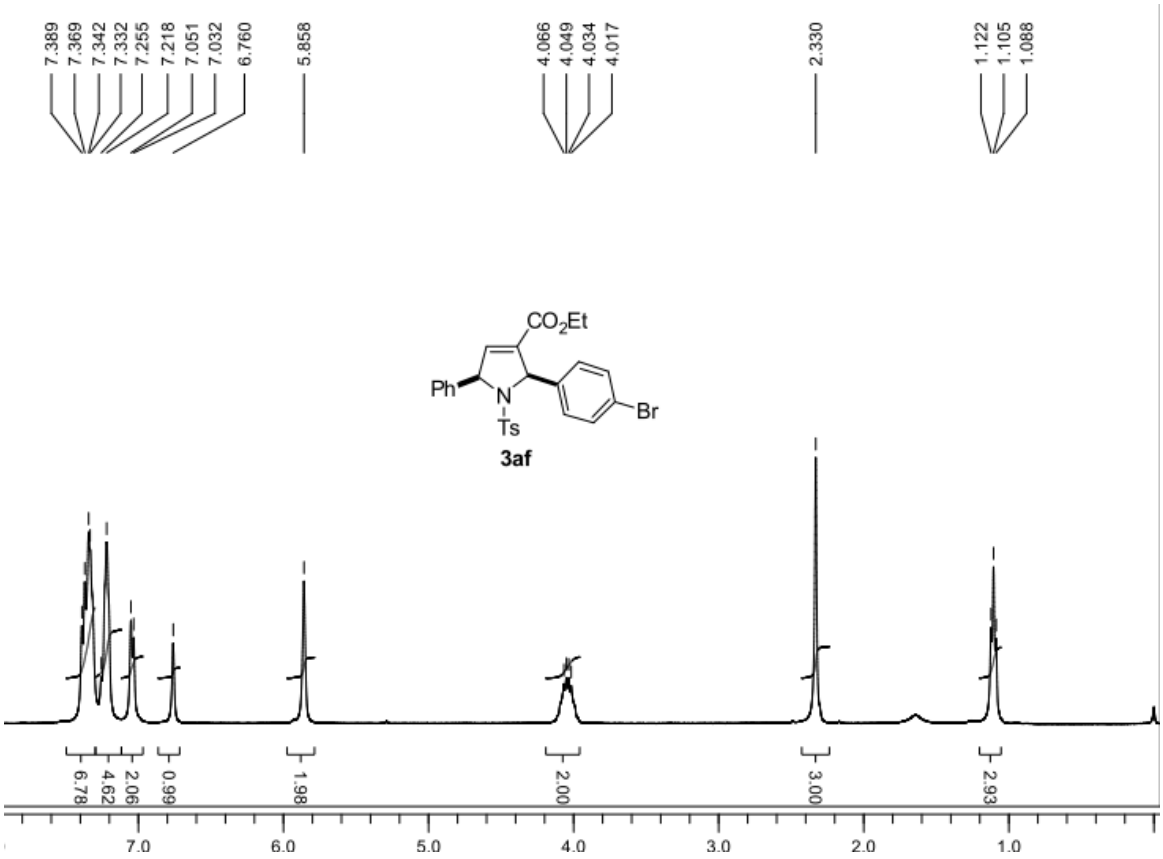
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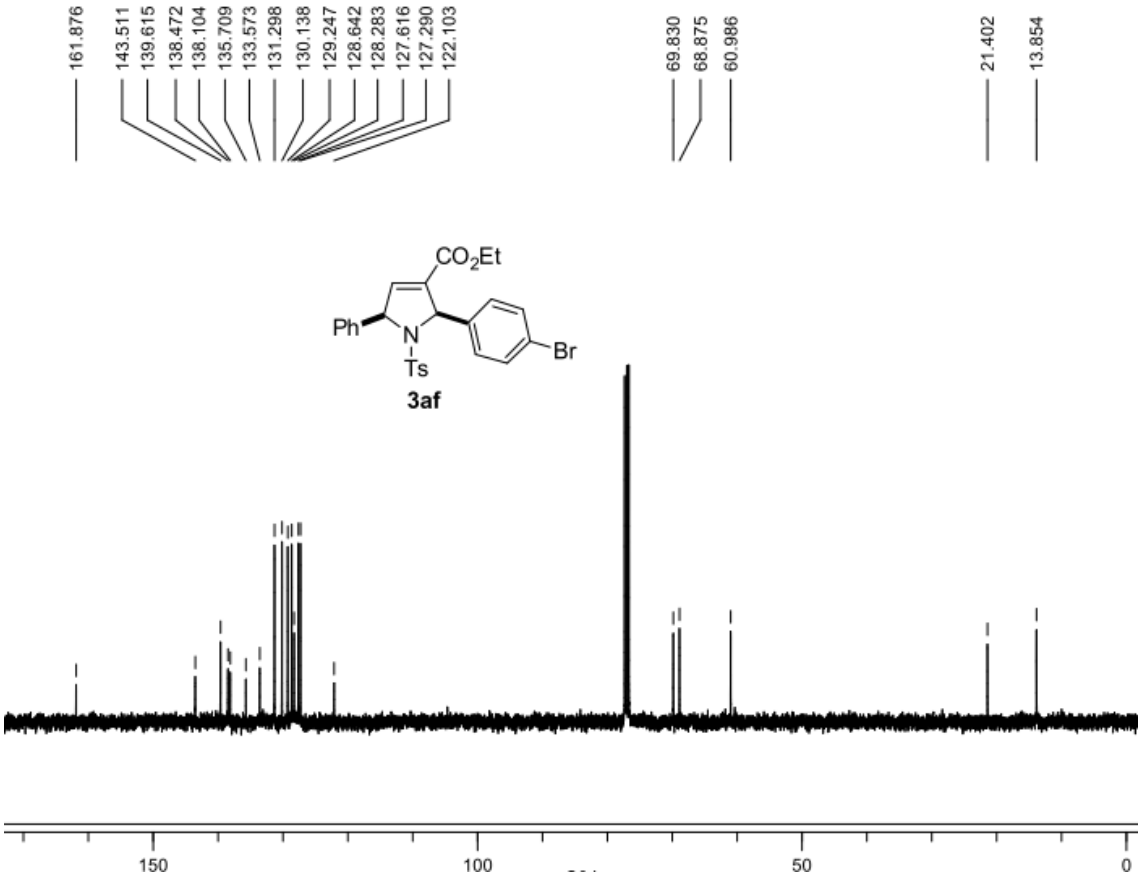
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138.472
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131.298
130.138
129.247
128.642
128.283
127.616
127.290
122.103
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60.986
21.402
13.854
CO2Et
Ph
N
Ts
Br
3af
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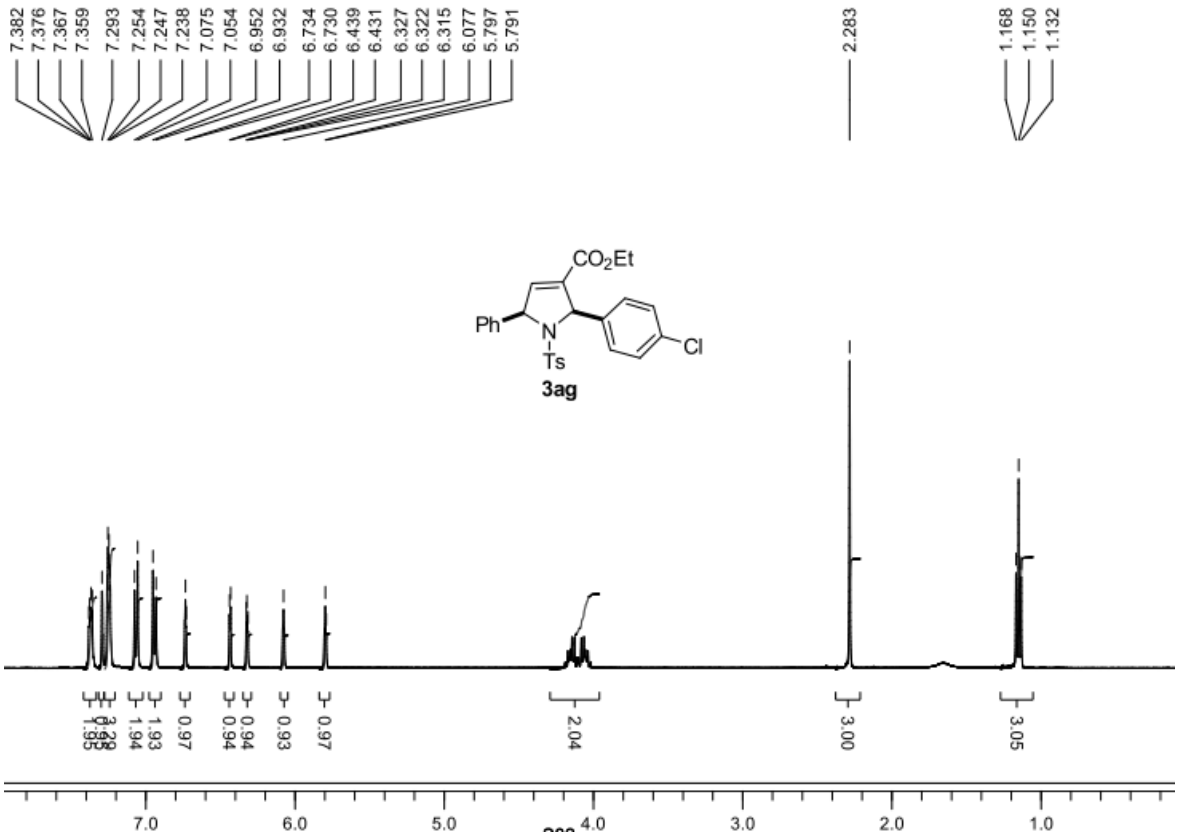
100
50
0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7.247
7.238
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6.952
6.932
6.734
6.730
6.439
6.431
6.327
6.322
6.315
6.077
5.797
5.791
2.283
1.168
1.150
1.132
CO2Et
Ph
N
Ts
Cl
3ag
1.95
1.93
1.94
0.97
0.94
0.94
0.93
0.97
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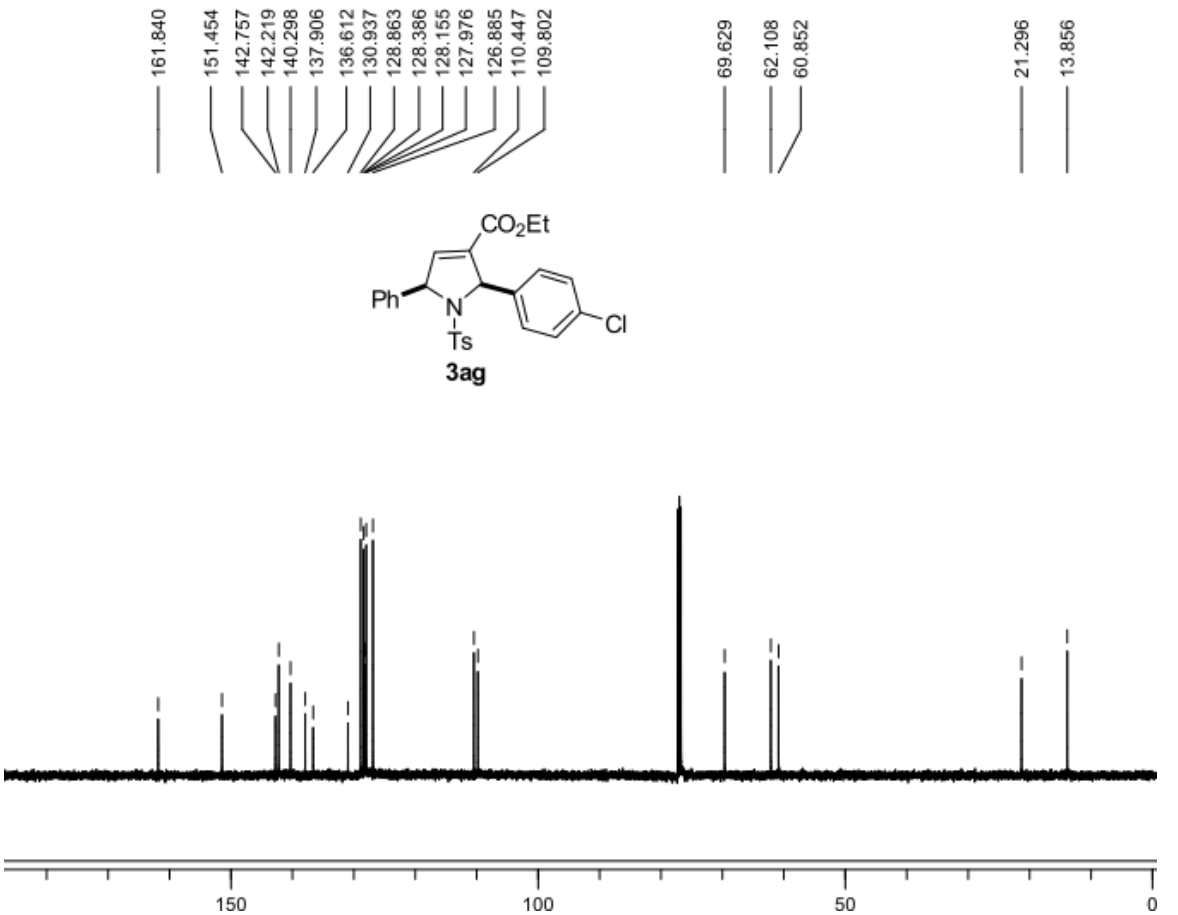
3.00
3.05
7.0
6.0
5.0
4.0
3.0
2.0
1.0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136.612
130.937
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128.386
128.155
127.976
126.885
110.447
109.802
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60.852
21.296
13.856
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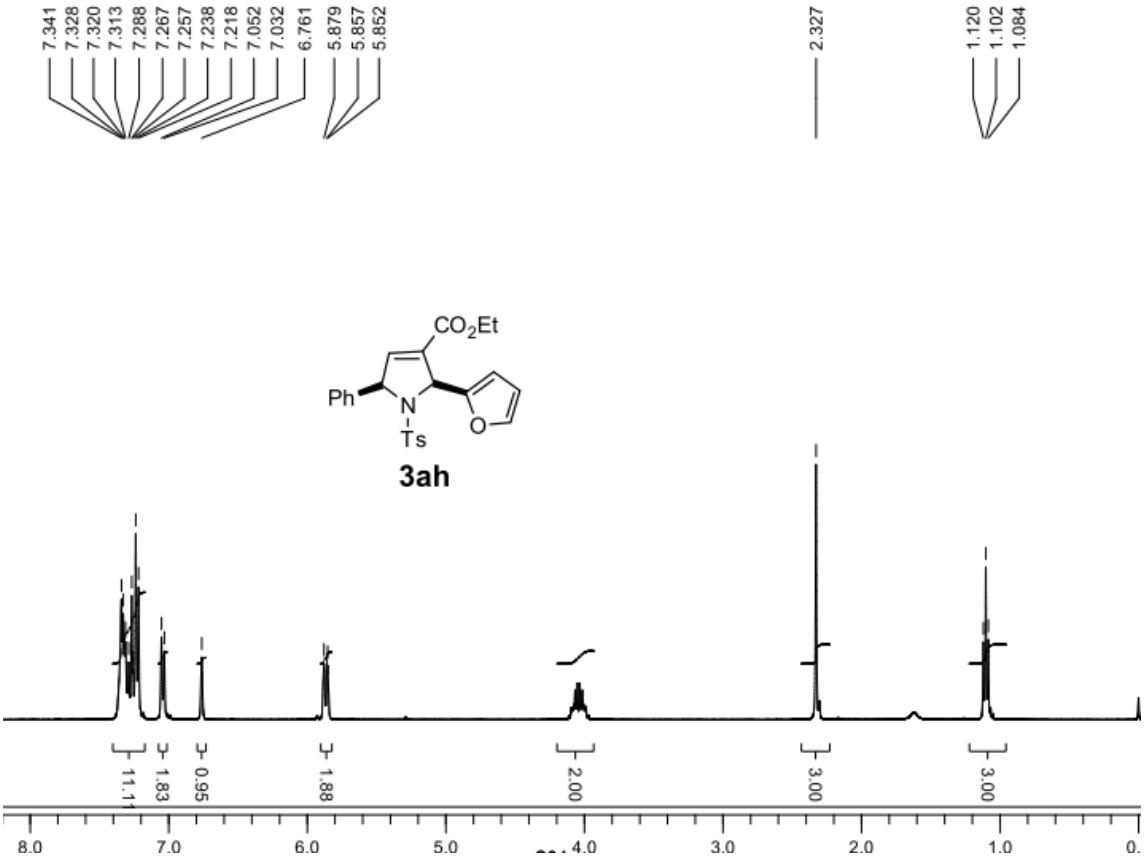
Ph
N
Ts
Cl
3ag
150
100
50
0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7.328
7.320
7.313
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7.267
7.257
7.238
7.218
7.052
7.032
6.761
5.879
5.857
5.852
2.327
1.120
1.102
1.084
CO2Et
Ph
N
Ts
O
3ah
1.11
1.83
0.95
1.88
2.00
3.00
3.00
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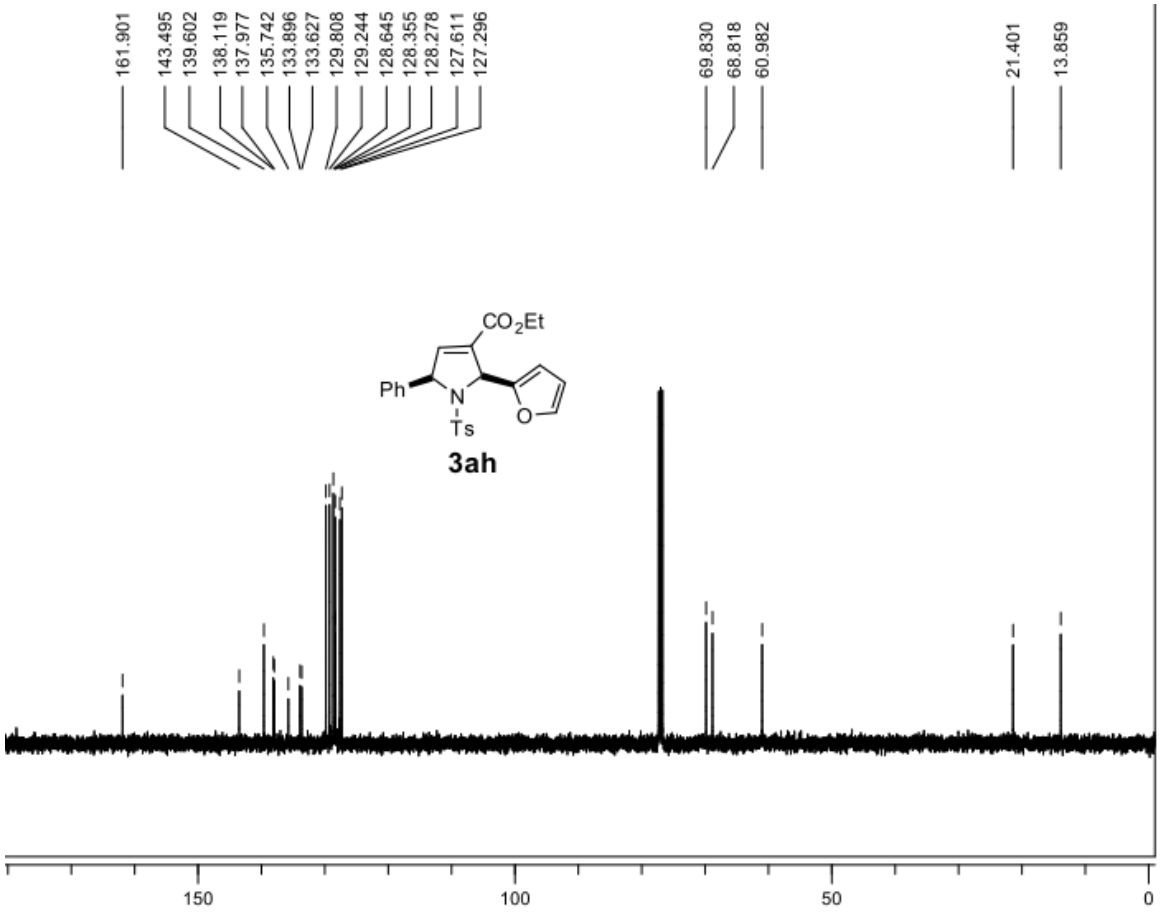
7.0
6.0
5.0
4.0
3.0
2.0
1.0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139.602
138.119
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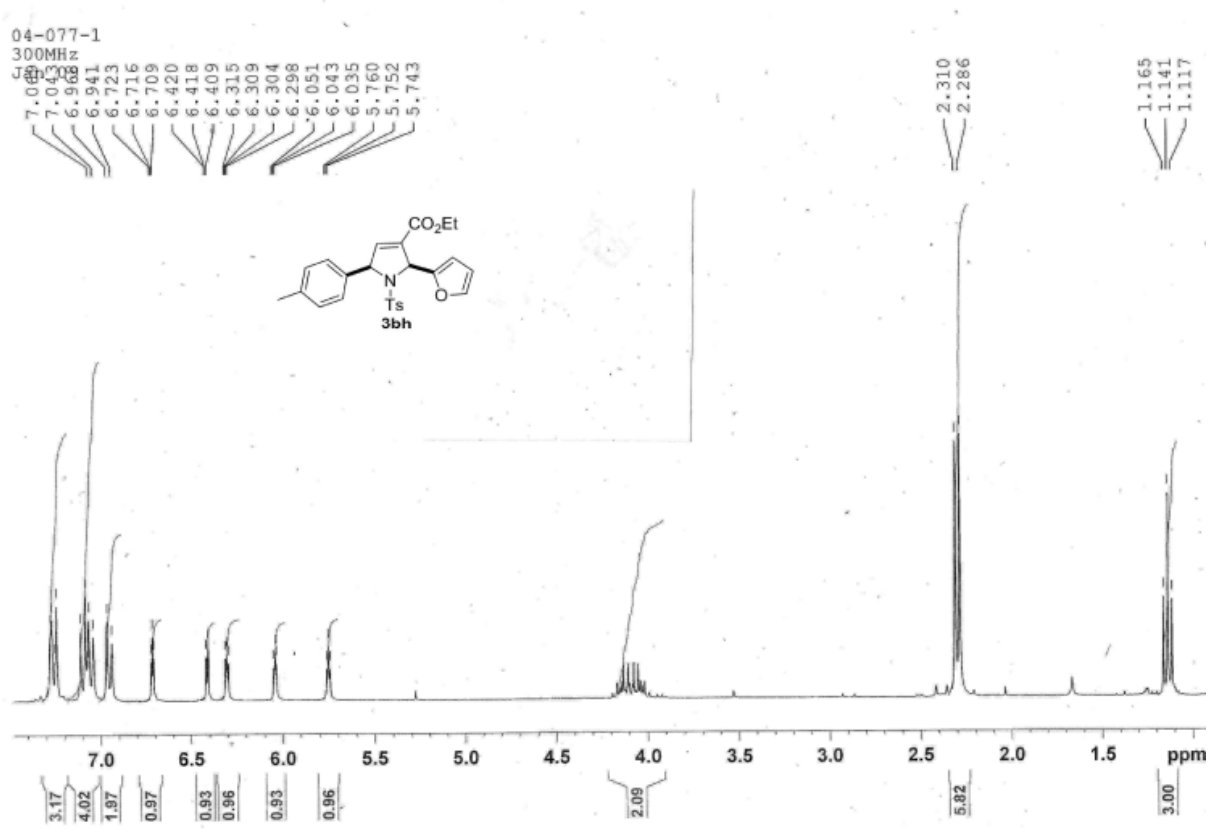
135.742
133.896
133.627
129.808
129.244
128.645
128.355
128.278
127.611
127.296
69.830
68.818
60.982
21.401
13.859
CO2Et
Ph
N
Ts
O
3ah
150
100
50
0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6.941
6.723
6.716
6.709
6.420
6.418
6.409
6.315
6.309
6.304
6.298
6.051
6.043
6.035
5.760
5.752
5.743
2.310
2.286
1.165
1.141
1.117
CO2Et
N
Ts
O
3bh
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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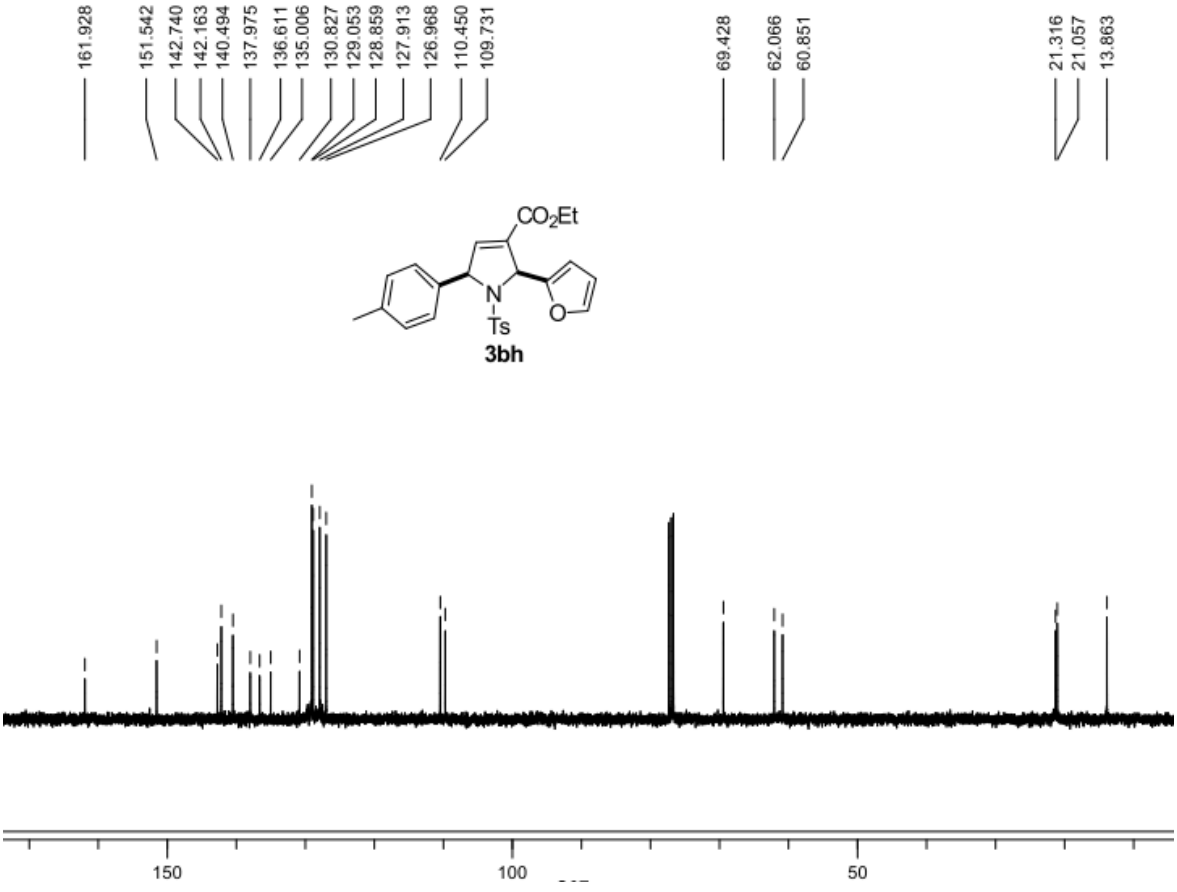
0.97
0.93
0.96
0.93
0.96
2.09
5.82
3.00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142.163
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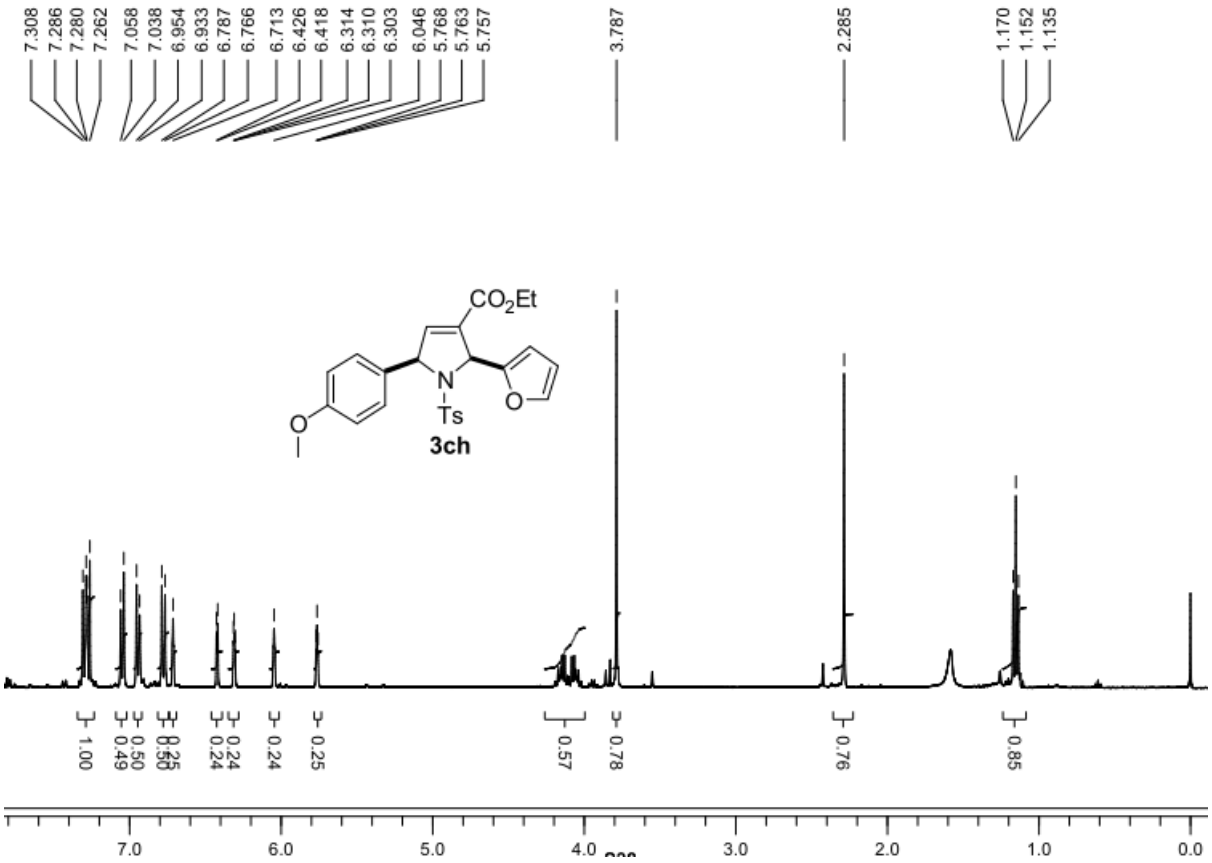
137.975
136.611
135.006
130.827
129.053
128.859
127.913
126.968
110.450
109.731
69.428
62.066
60.851
21.316
21.057
13.863
CO2Et
N
Ts
O
3bh
150
100
50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7.280
7.262
7.058
7.038
6.954
6.933
6.787
6.766
6.713
6.426
6.418
6.314
6.310
6.303
6.046
5.768
5.763
5.757
3.787
2.285
1.170
1.152
1.135
CO2Et
N
Ts
O
O
3ch
1.00
0.49
0.50
0.50
0.25
0.24
0.24
0.25
0.57
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0.76
0.85
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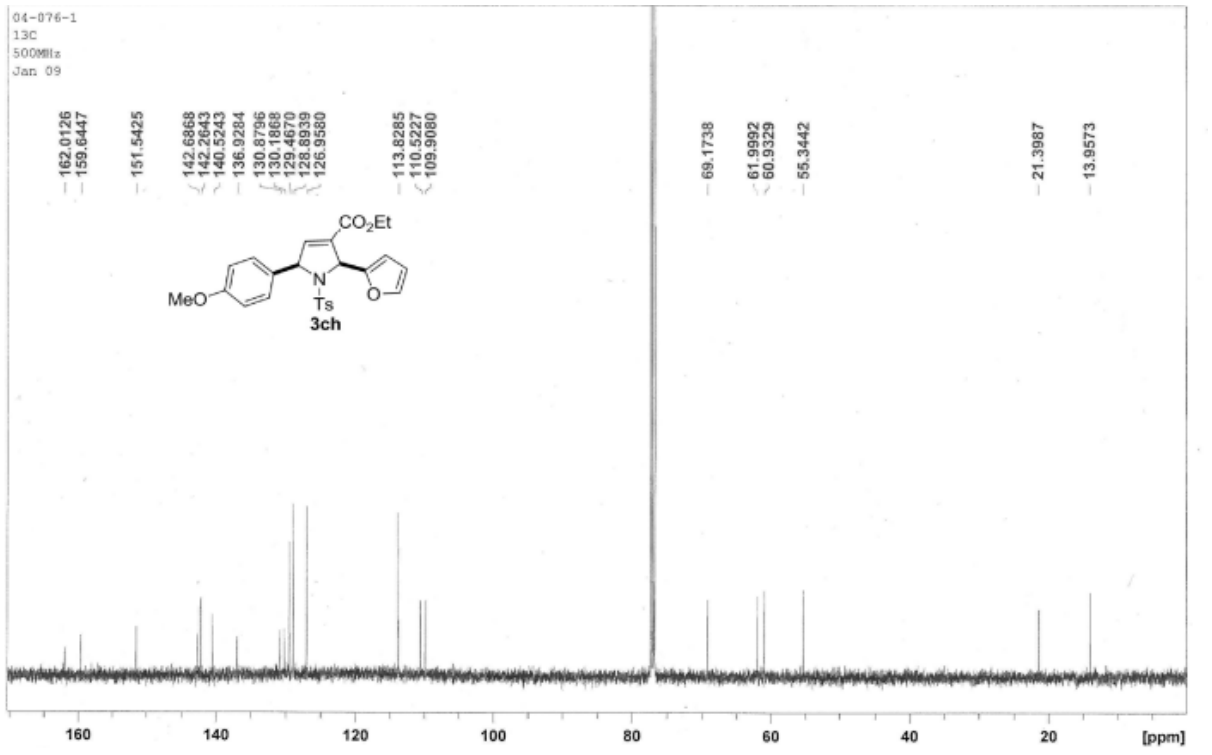
6.0
5.0
4.0
3.0
2.0
1.0
0.0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500MHz
Jan 09
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151.5425
142.6868
142.2643
140.5243
136.0284
130.8796
130.1868
129.4670
128.8939
126.9580
113.8285
110.5227
109.9080
69.1738
61.9992
60.9329
55.3442
21.3987
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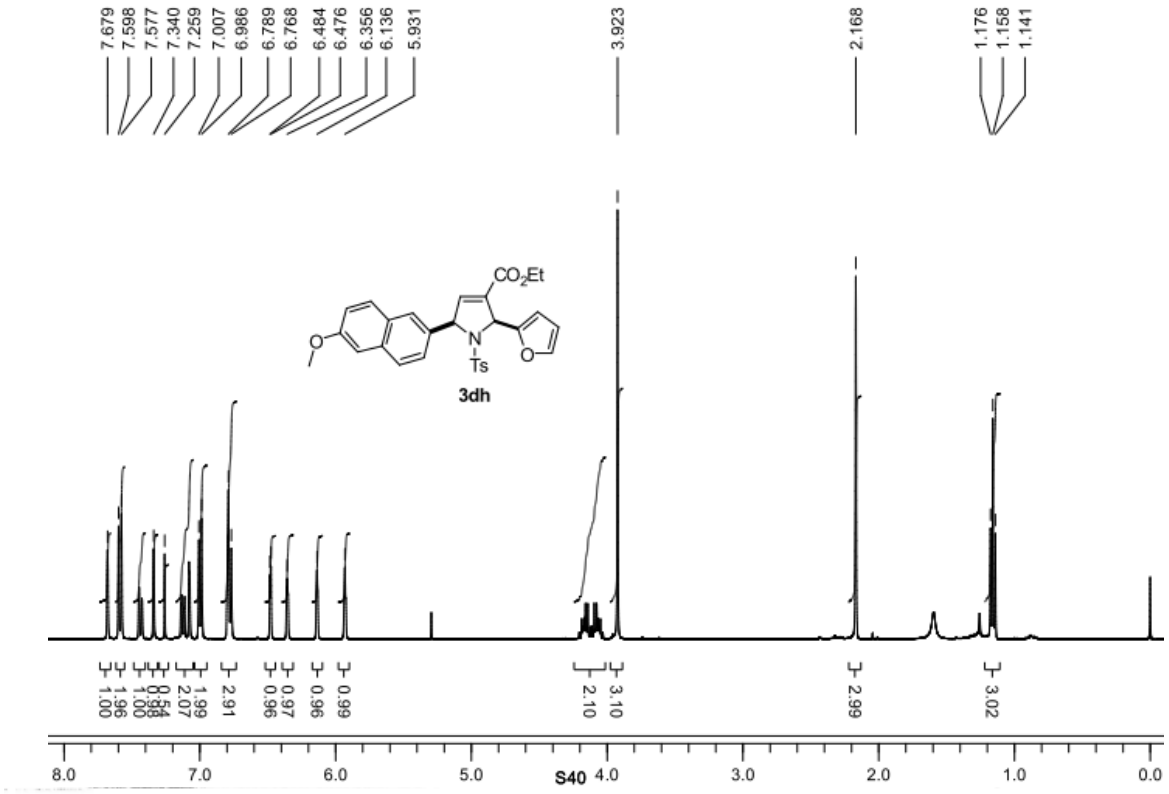
CO2Et
N
Ts
O
MeO
3ch
160
140
120
100
80
60
40
20
[ppm]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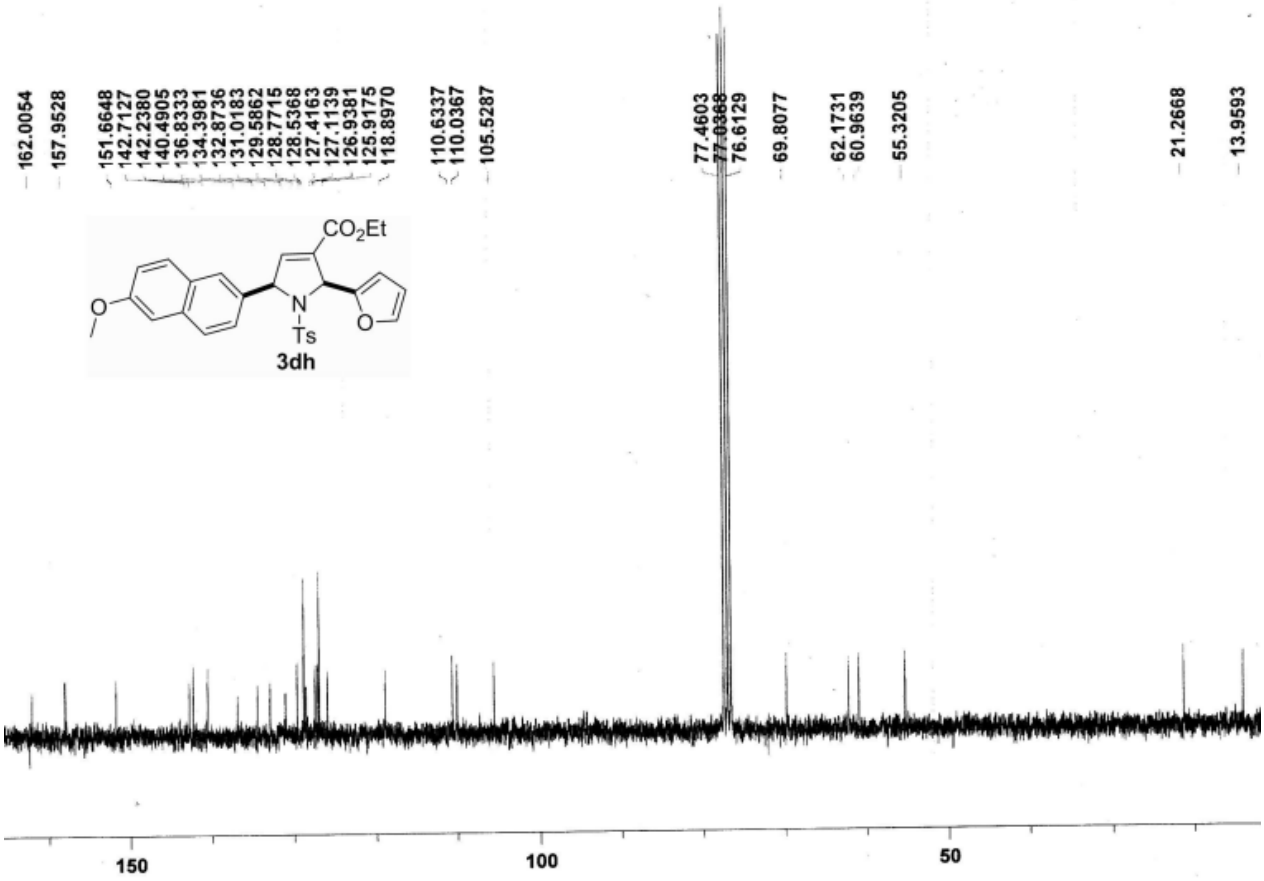
7.577
7.340
7.259
7.007
6.986
6.789
6.768
6.484
6.476
6.356
6.136
5.931
3.923
2.168
1.176
1.158
1.141
CO2Et
N
Ts
O
O
3dh
1.00
1.96
1.96
1.00
0.88
0.44
2.07
1.99
2.91
0.97
0.96
0.96
0.99
2.10
3.10
2.99
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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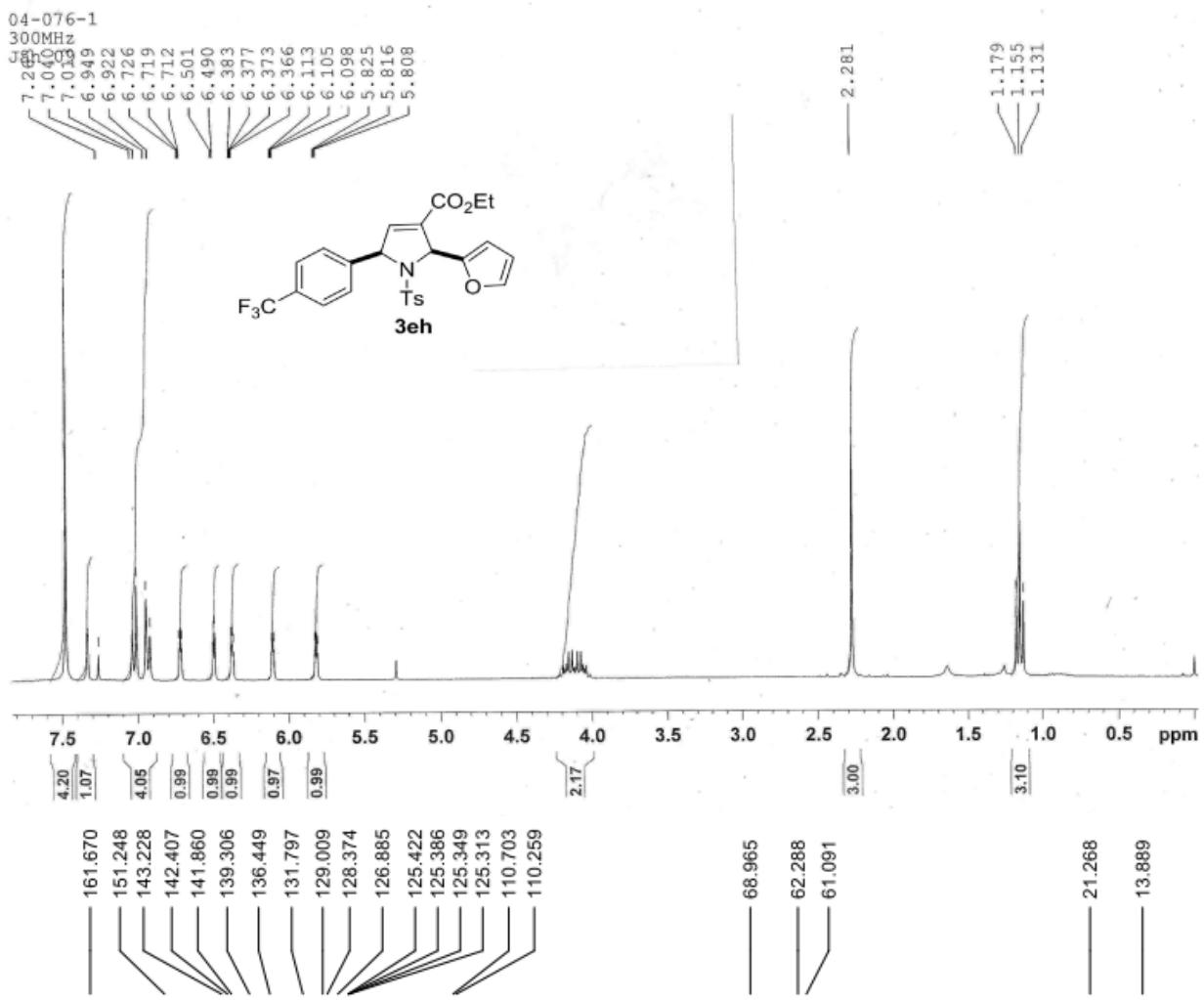
142.2380
140.4905
136.8333
134.3981
132.8736
131.0183
129.5862
128.7715
128.5368
127.4163
127.1139
126.9381
125.9175
118.8970
110.6337
110.0367
105.5287
77.4603
77.0388
76.6129
69.8077
62.1731
60.9639
55.3205
21.2668
13.9593
CO2Et
N
Ts
O
O
3dh
150
100
50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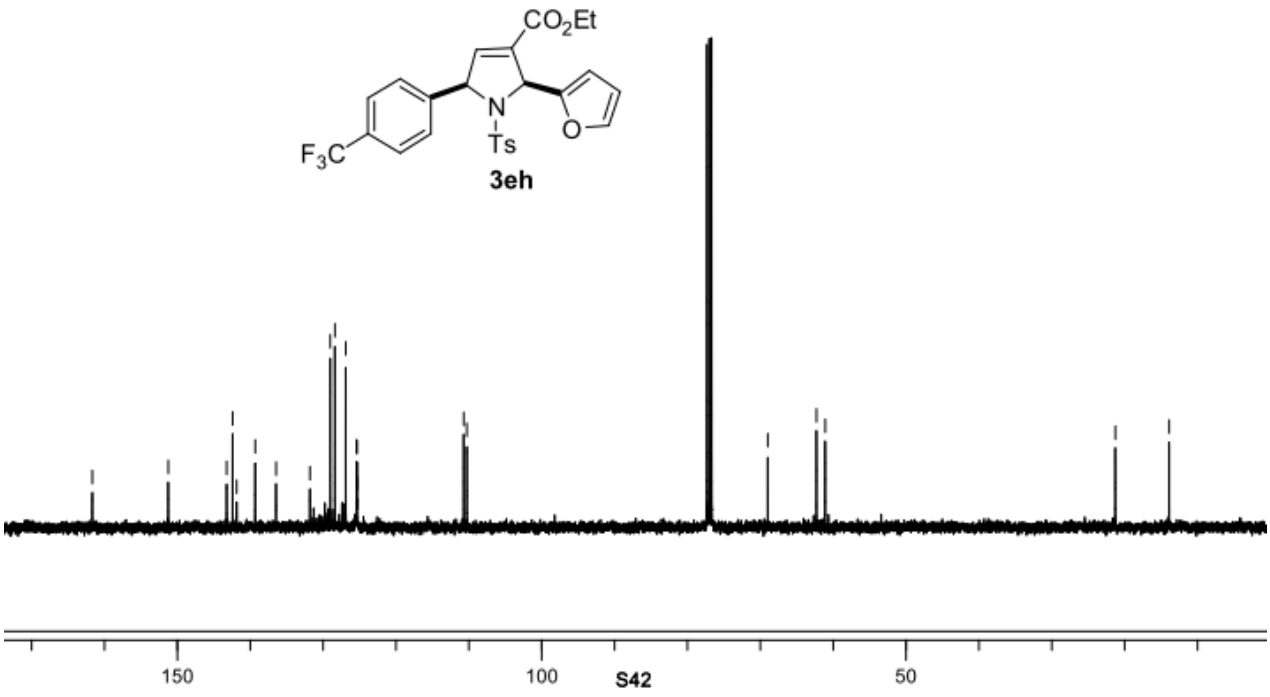
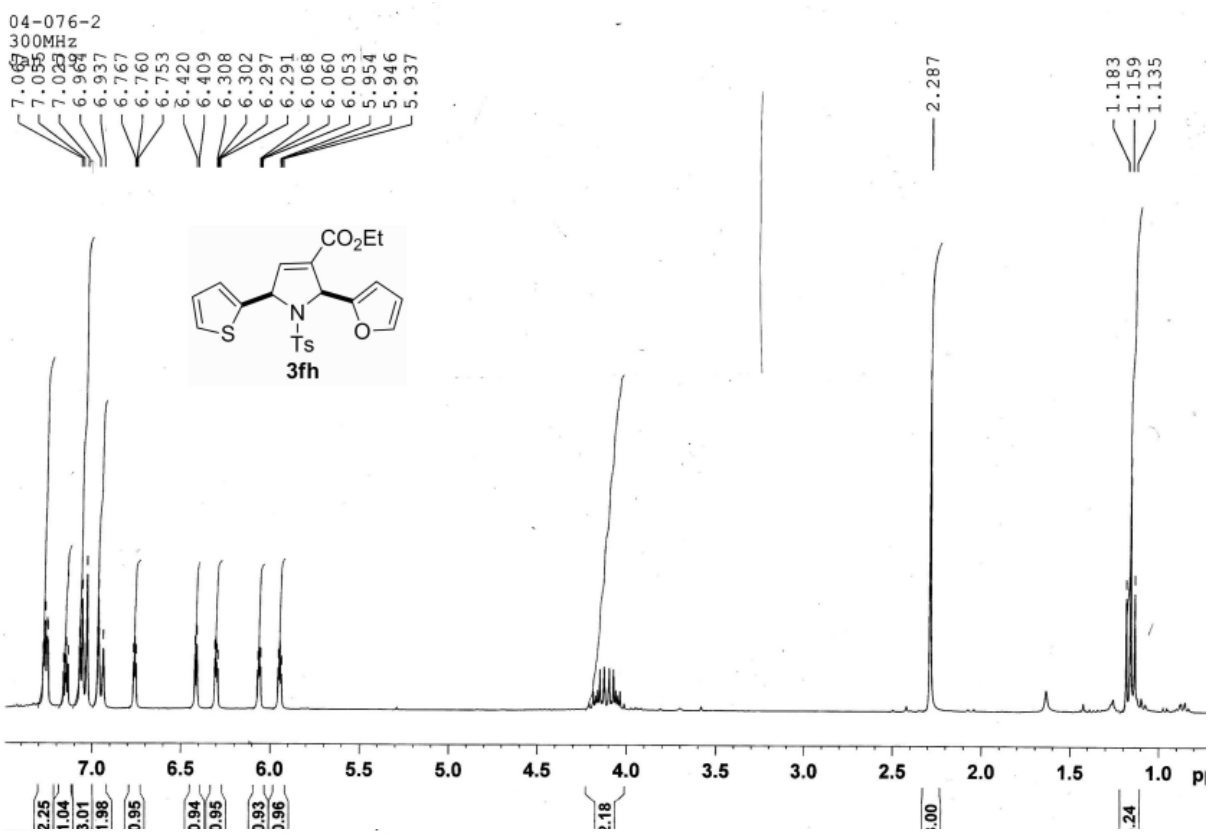
6.922
6.726
6.719
6.712
6.501
6.490
6.383
6.377
6.373
6.366
6.113
6.105
6.098
5.825
5.816
5.808
2.281
1.179
1.155
1.131
CO2Et
N
Ts
O
F3C
3eh
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.20
1.07
4.05
0.99
0.99
0.99
0.97
0.99
2.17
3.00
3.10
161.670
151.248
143.228
142.407
141.860
139.306
136.449
131.797
129.009
128.374
126.885
125.422
125.386
125.349
125.313
110.703
110.259
68.965
62.288
61.091
21.268
13.889


CO2Et
N
Ts
O
F3C
3eh
150
100
50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6.767
6.760
6.753
6.420
6.409
6.308
6.302
6.297
6.291
6.068
6.060
6.053
5.954
5.946
5.937
2.287
1.183
1.159
1.135
CO2Et
N
Ts
S
O
3fh
7.0
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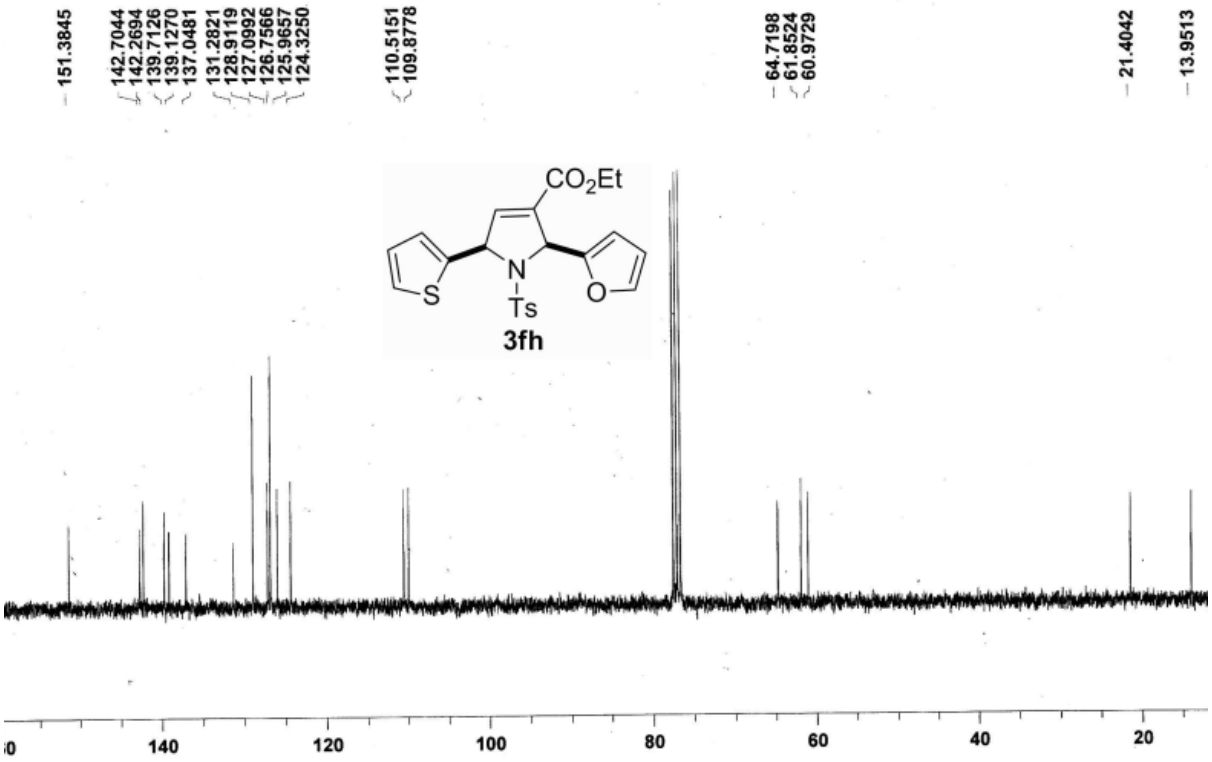
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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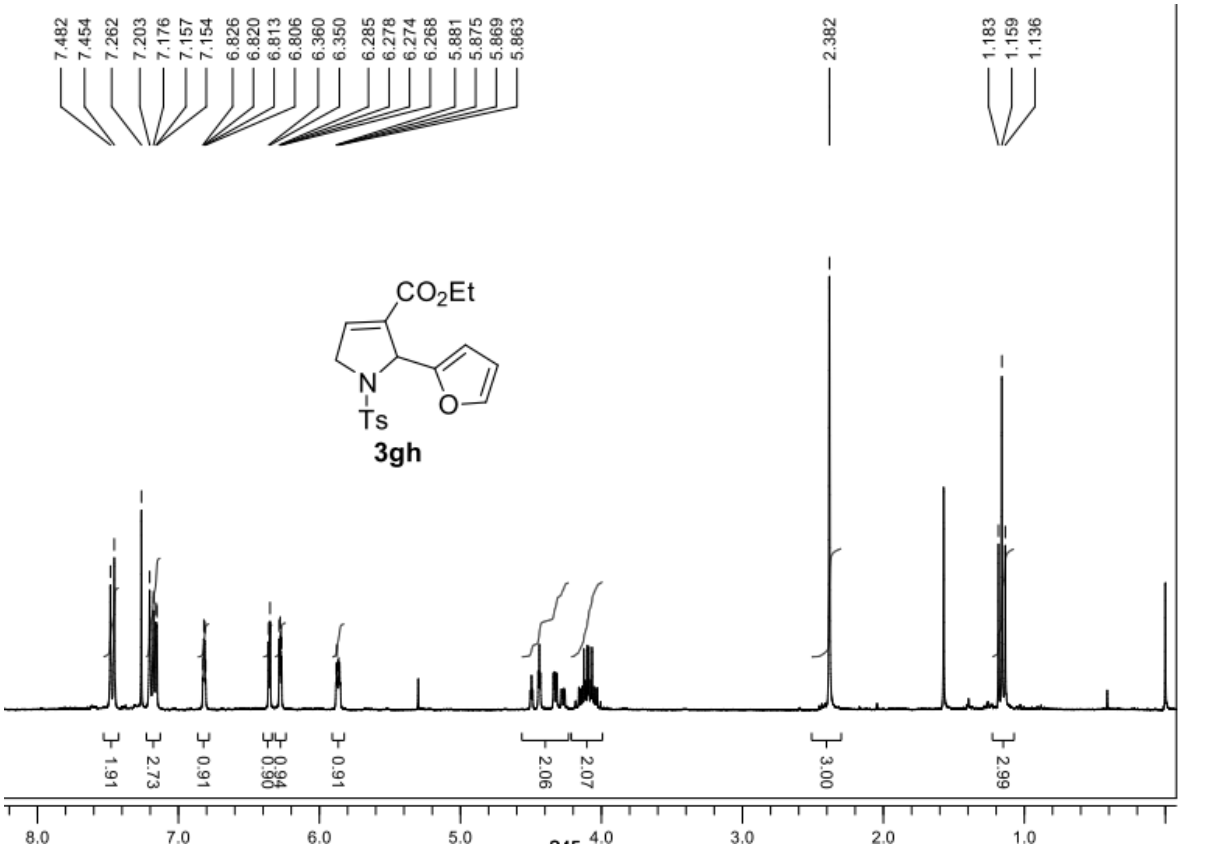
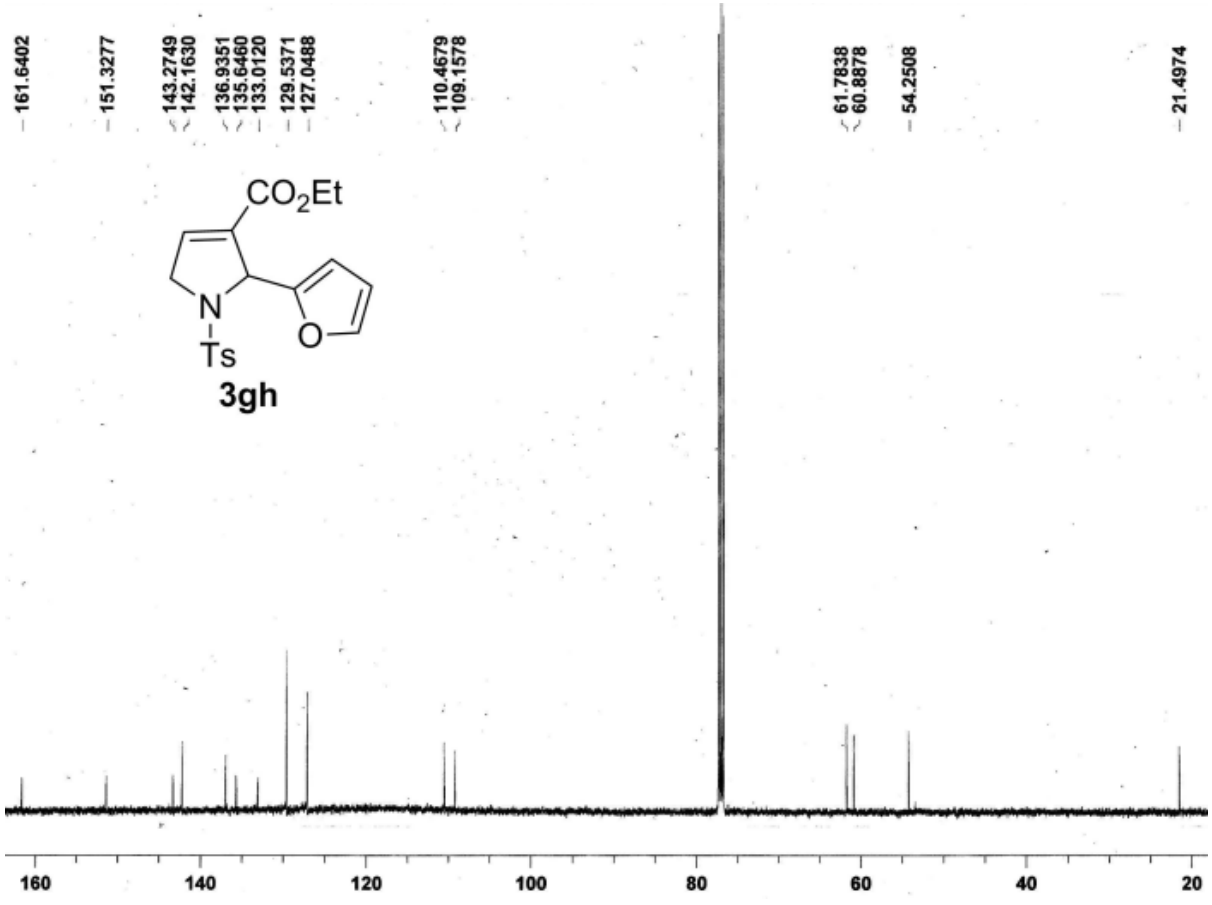
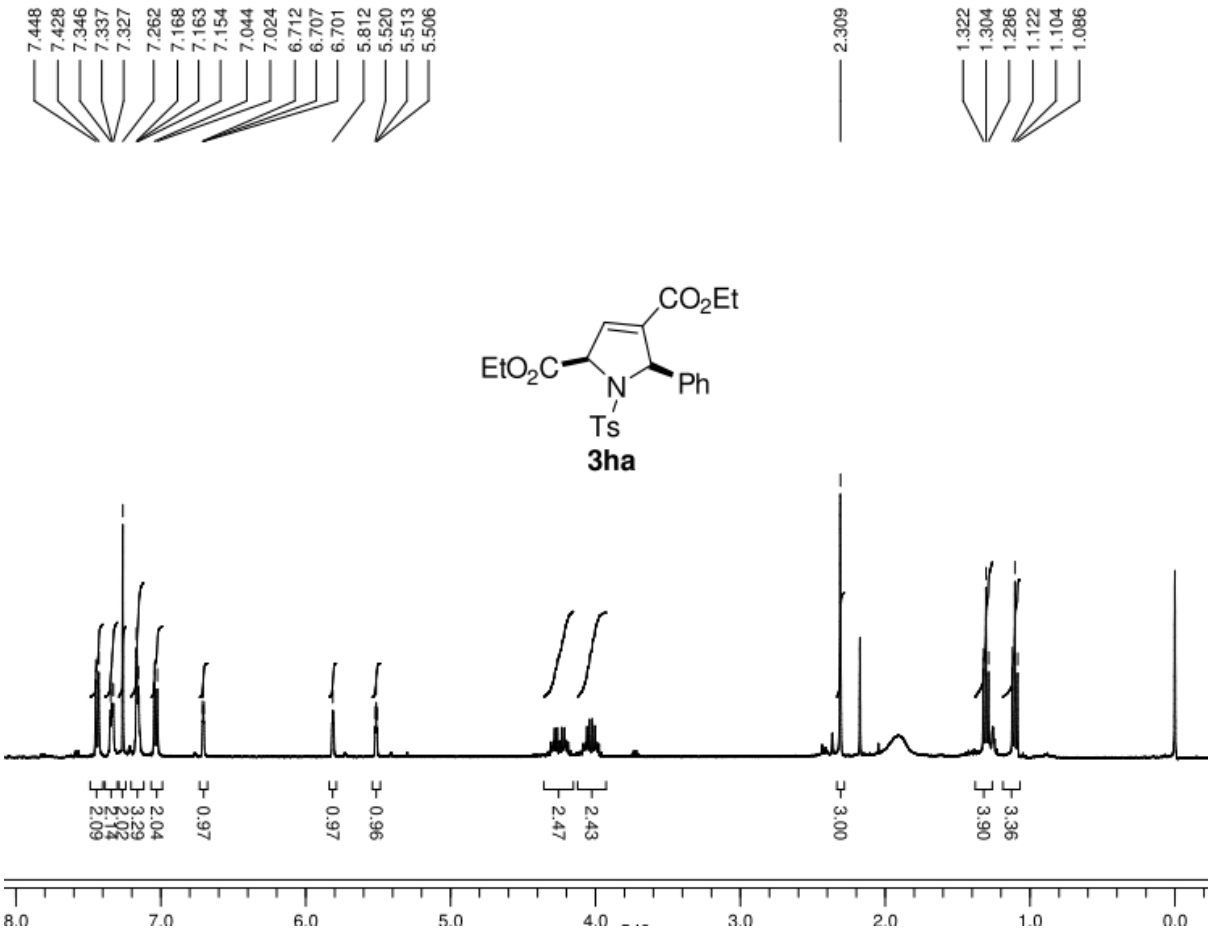
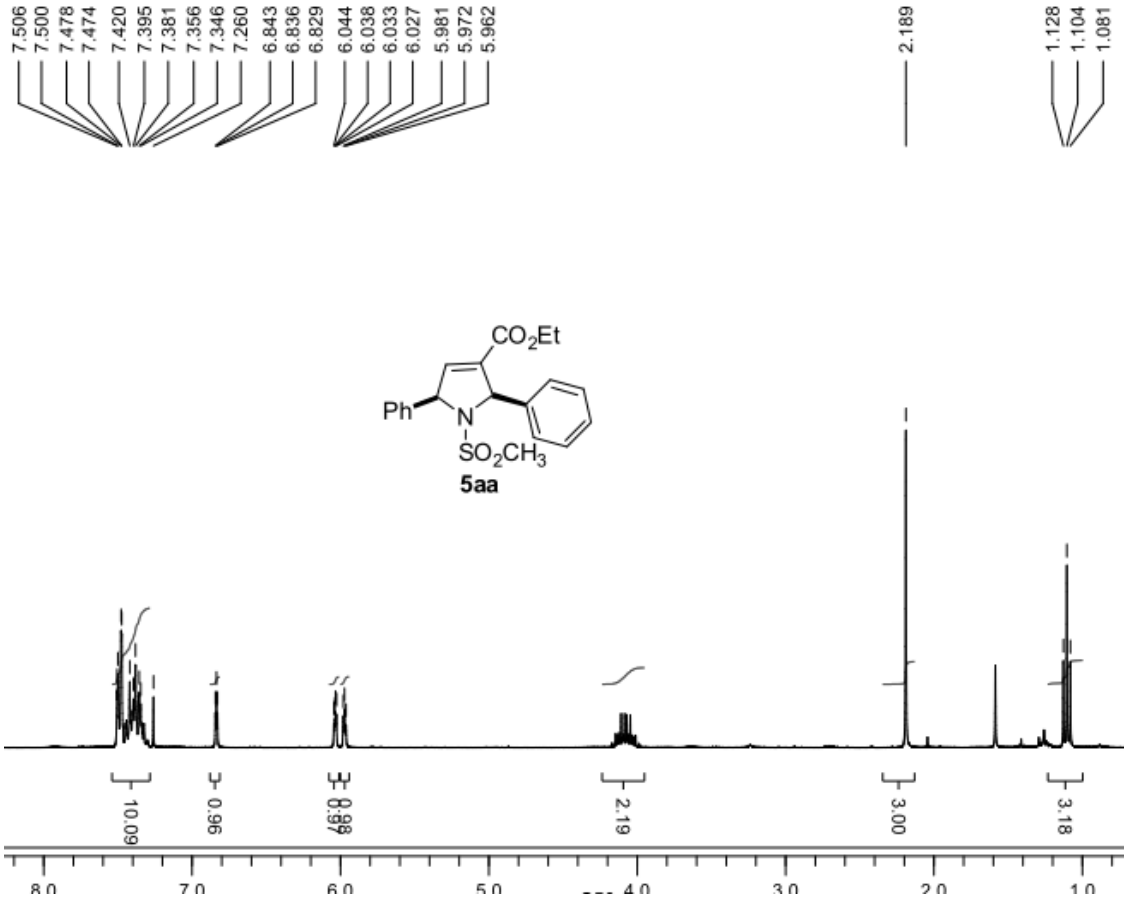
137.0481
131.2821
128.9119
127.0992
126.7566
125.9657
124.3250
110.5151
109.8778
64.7198
61.8524
60.9729
21.4042
13.9513
CO2Et
N
Ts
S
O
3fh
140
120
100
80
60
40
20





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7.356
7.346
7.260
6.843
6.836
6.829
6.044
6.038
6.033
6.027
5.981
5.972
5.962
2.189
1.128
1.104
1.081
CO2Et
Ph
N
SO2CH3
5aa
10.09
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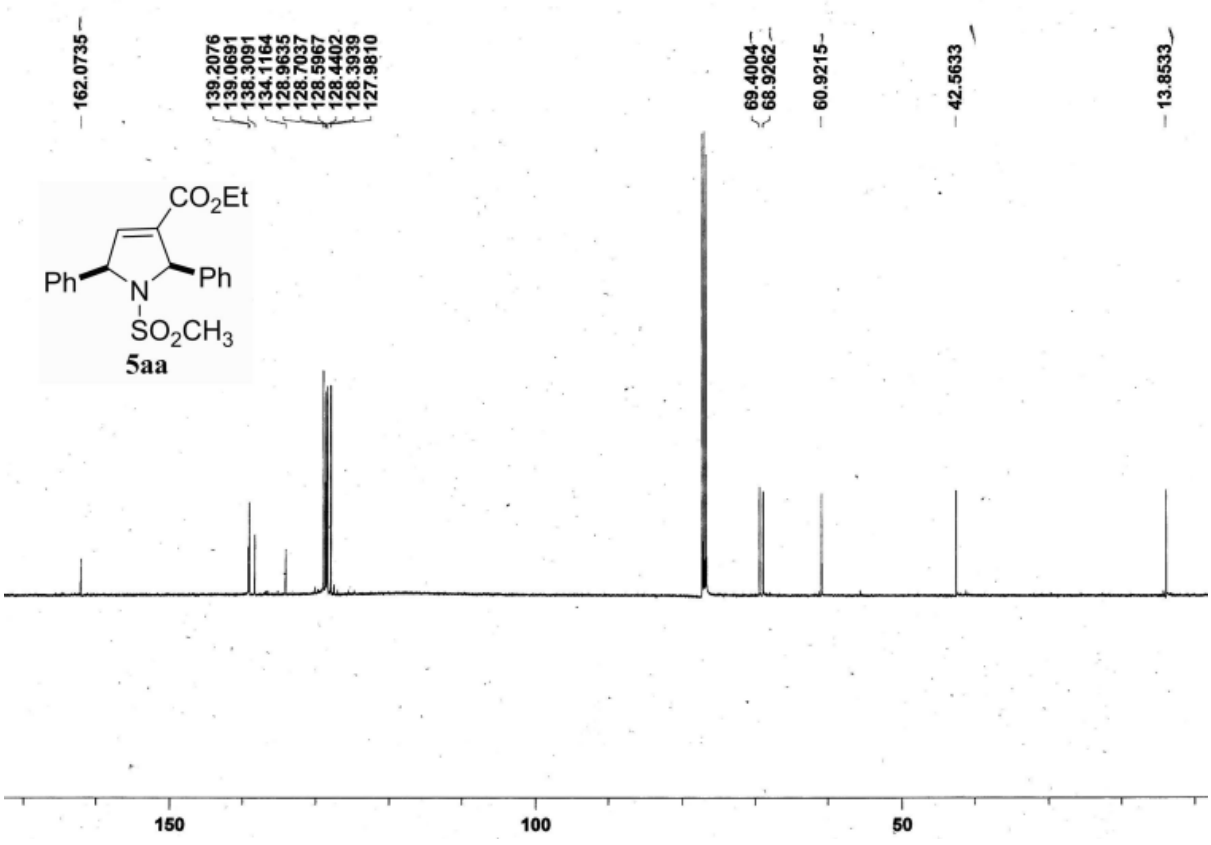
0.98
0.99
2.19
3.00
3.18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128.7037
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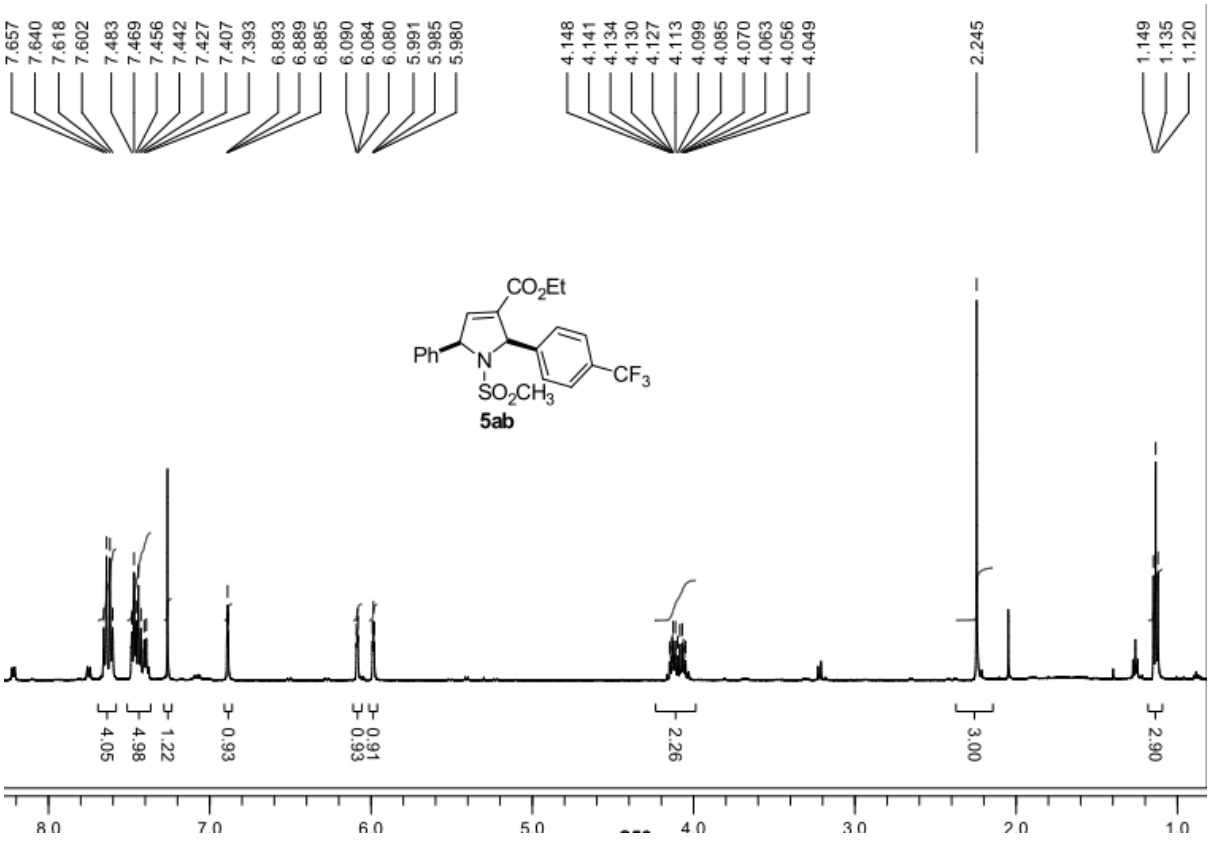
128.4402
128.3939
127.9810
69.4004
68.9262
60.9215
42.5633
13.8533
CO2Et
Ph
Ph
N
SO2CH3
5aa
150
100
50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7.442
7.427
7.407
7.393
6.893
6.889
6.885
6.090
6.084
6.080
5.991
5.985
5.980
4.148
4.141
4.134
4.130
4.127
4.113
4.099
4.085
4.070
4.063
4.056
4.049
2.245
1.149
1.135
1.120
CO2Et
Ph
N
SO2CH3
CF3
5ab
4.05
4.98
1.22
0.93
0.91
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2.90
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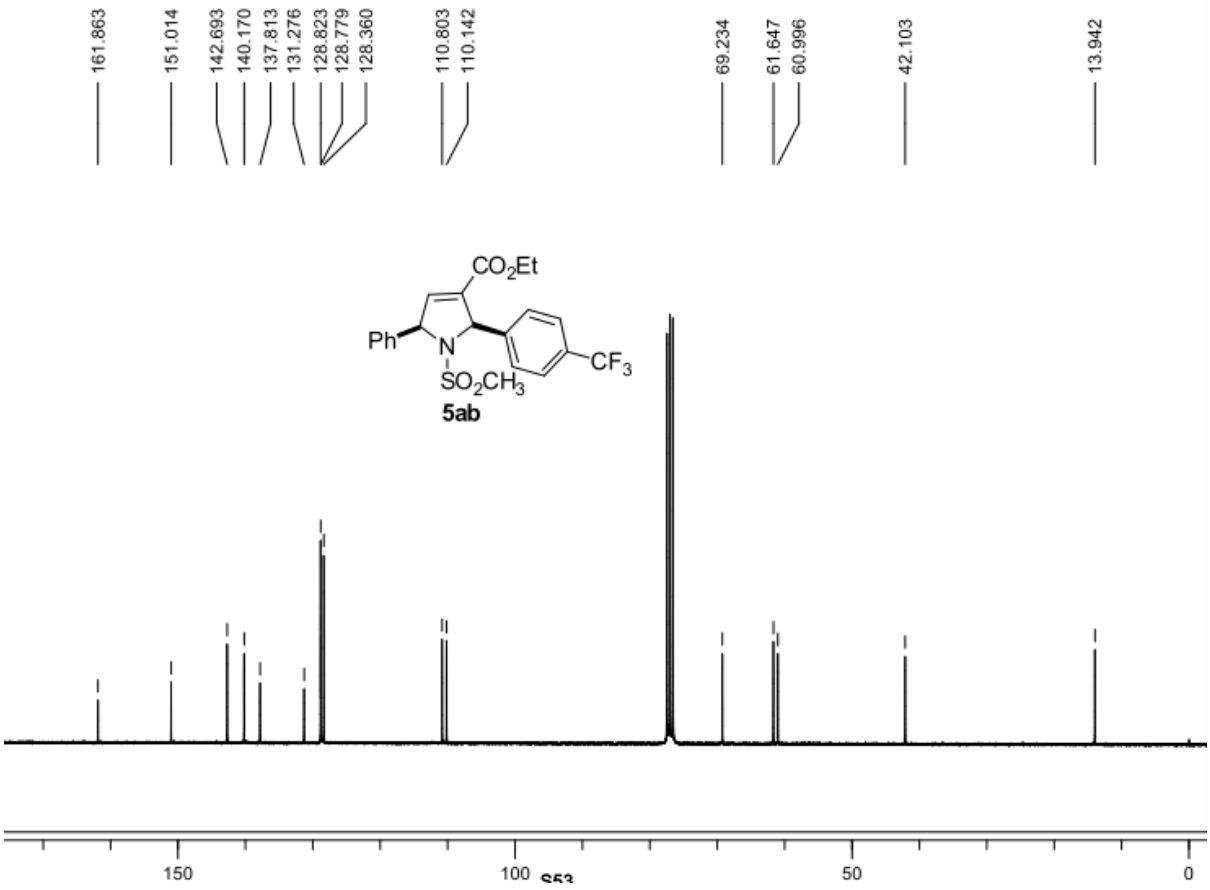
5.0
4.0
3.0
2.0
1.0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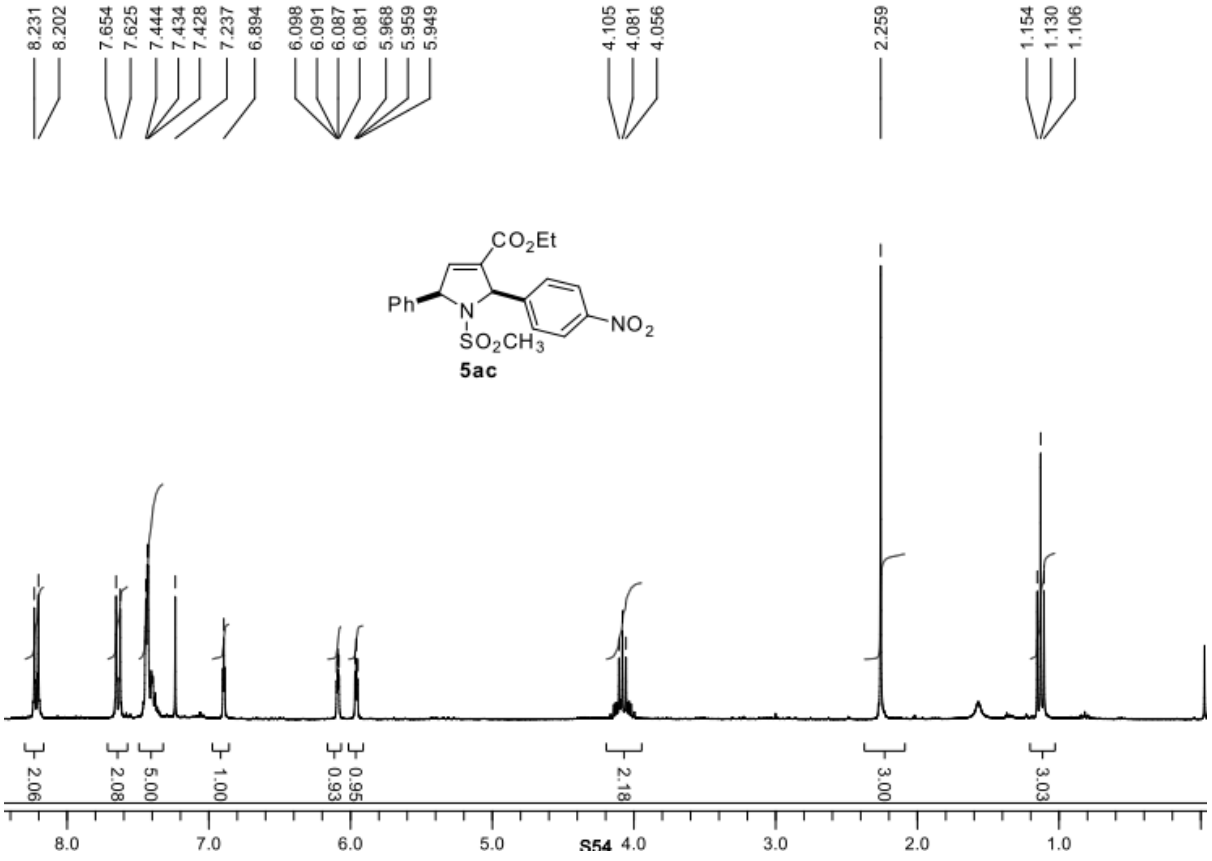
131.276
128.823
128.779
128.360
110.803
110.142
69.234
61.647
60.996
42.103
13.942
CO2Et
Ph
N
SO2CH3
CF3
5ab
150
100
50
0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7.434
7.428
7.237
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6.098
6.091
6.087
6.081
5.968
5.959
5.949
4.105
4.081
4.056
2.259
1.154
1.130
1.106
CO2Et
Ph
N
SO2CH3
NO2
5ac
2.06
2.08
5.00
1.00
0.93
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3.00
3.03
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7.0
6.0
5.0
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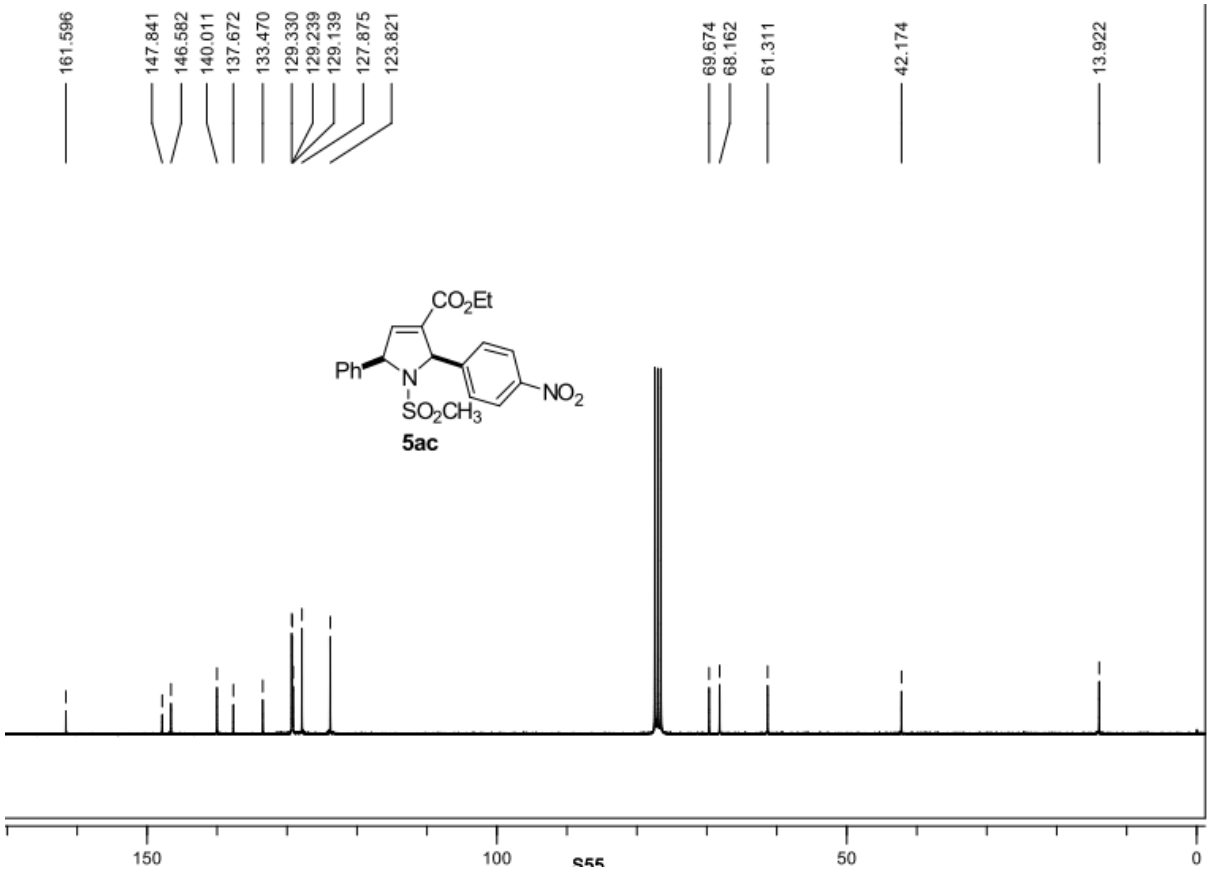
3.0
2.0
1.0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129.330
129.239
129.139
127.875
123.821
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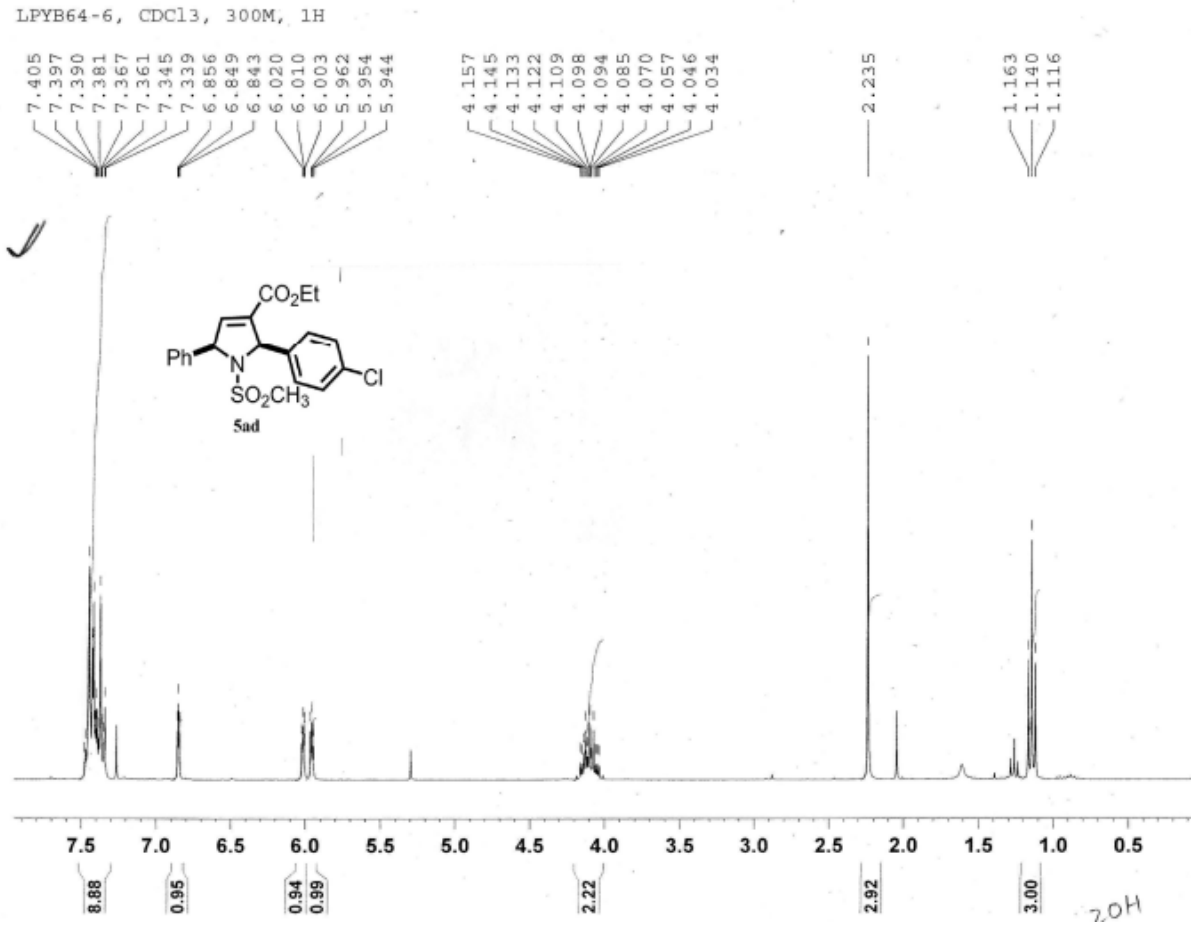
42.174
13.922
CO2Et
Ph
N
SO2CH3
NO2
5ac
150
100
50
0


LPYB64-6, CDCl3, 300M, 1H
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7.361
7.345
7.339
6.856
6.849
6.843
6.020
6.010
6.003
5.962
5.954
5.944
4.157
4.145
4.133
4.122
4.109
4.098
4.094
4.085
4.070
4.057
4.046
4.034
2.235
1.163
1.140
1.116
CO2Et
Ph
N
SO2CH3
Cl
5ad
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
0.5
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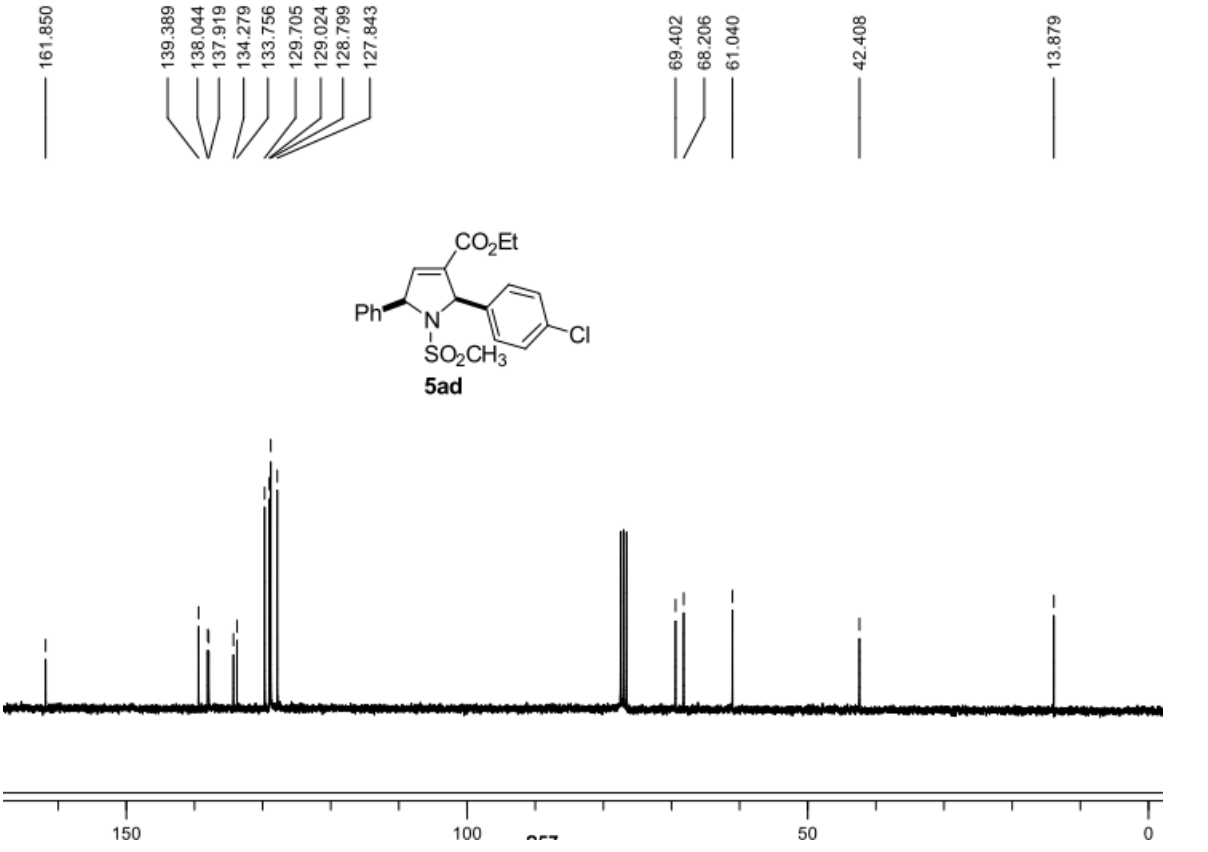
0.95
0.94
0.99
2.22
2.92
3.00
2.0H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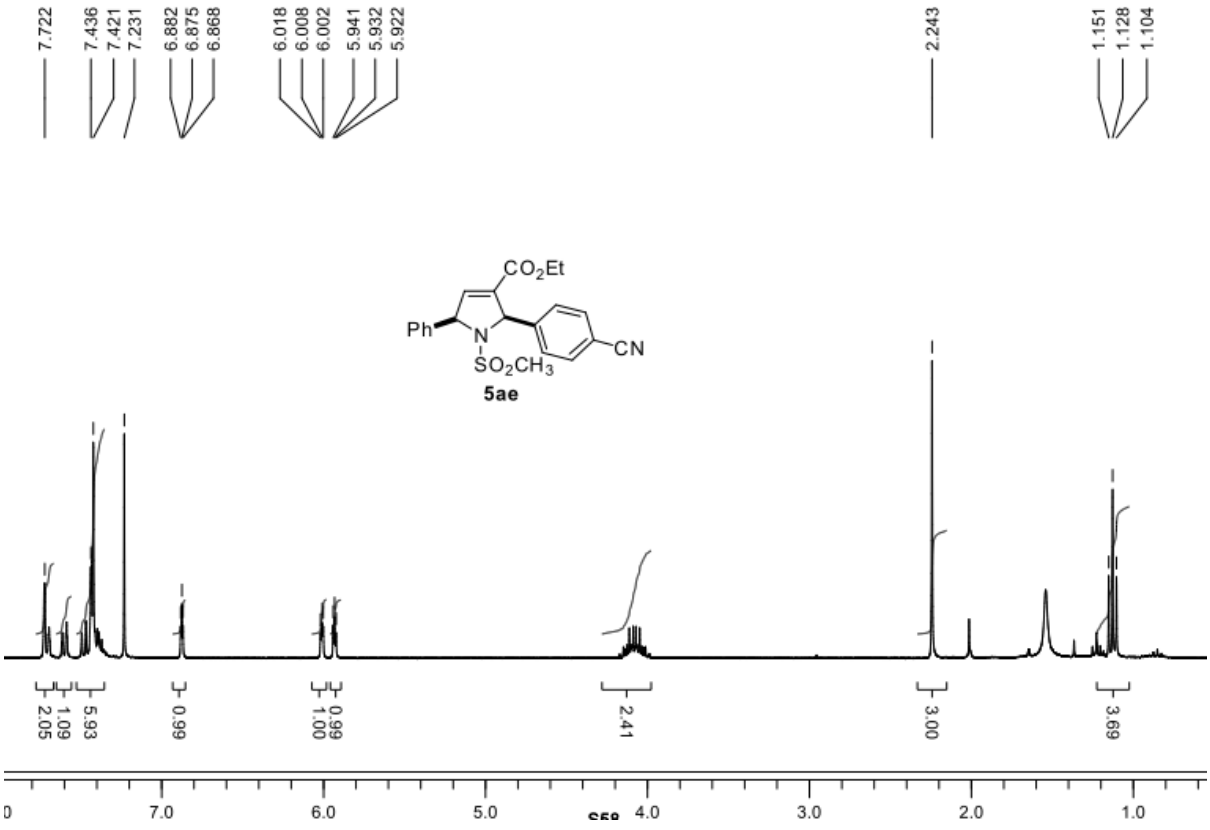
138.044
137.919
134.279
133.756
129.705
129.024
128.799
127.843
69.402
68.206
61.040
42.408
13.879
CO2Et
Ph
N
SO2CH3
Cl
5ad
150
100
50
0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6.875
6.868
6.018
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6.002
5.941
5.932
5.922
2.243
1.151
1.128
1.104
CO2Et
Ph
N
SO2CH3
CN
5ae
2.06
1.09
5.93
0.99
1.00
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2.41
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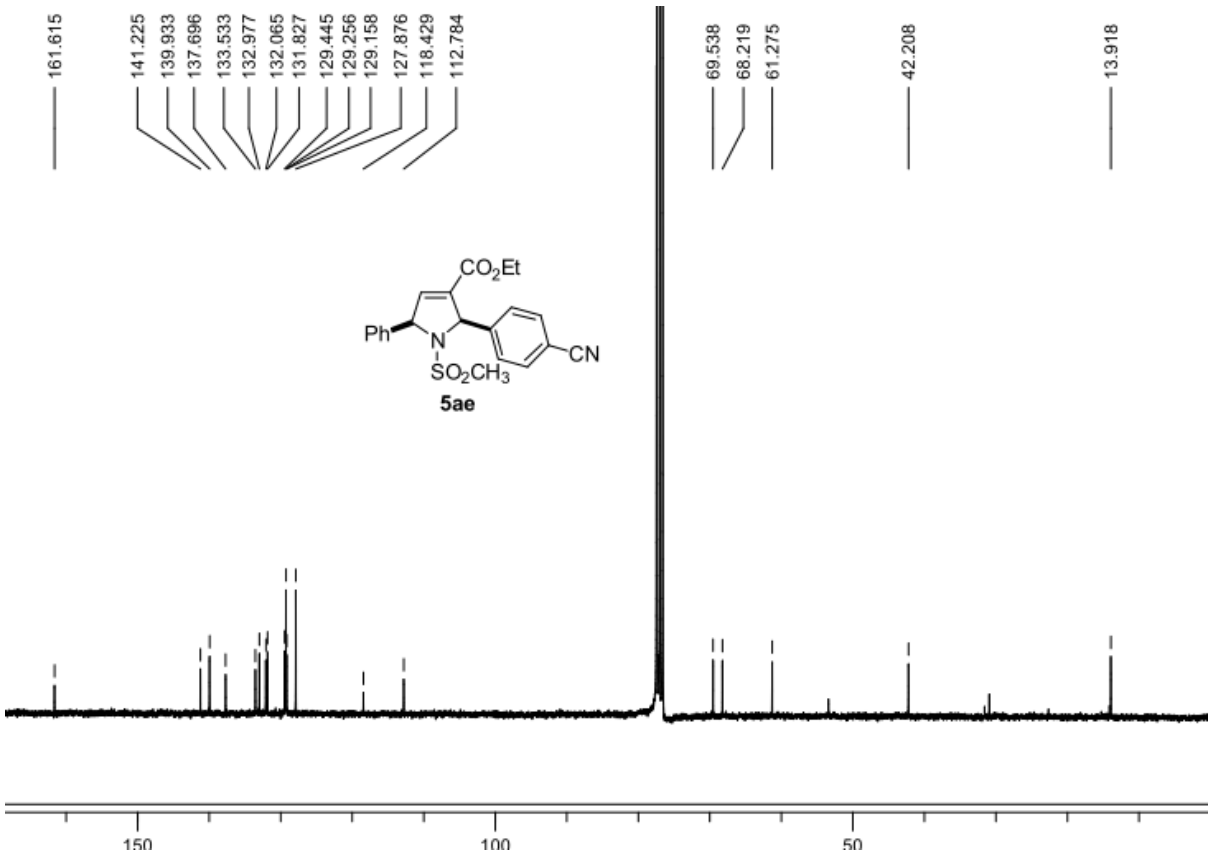
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Ph
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SO2CH3
CN
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100
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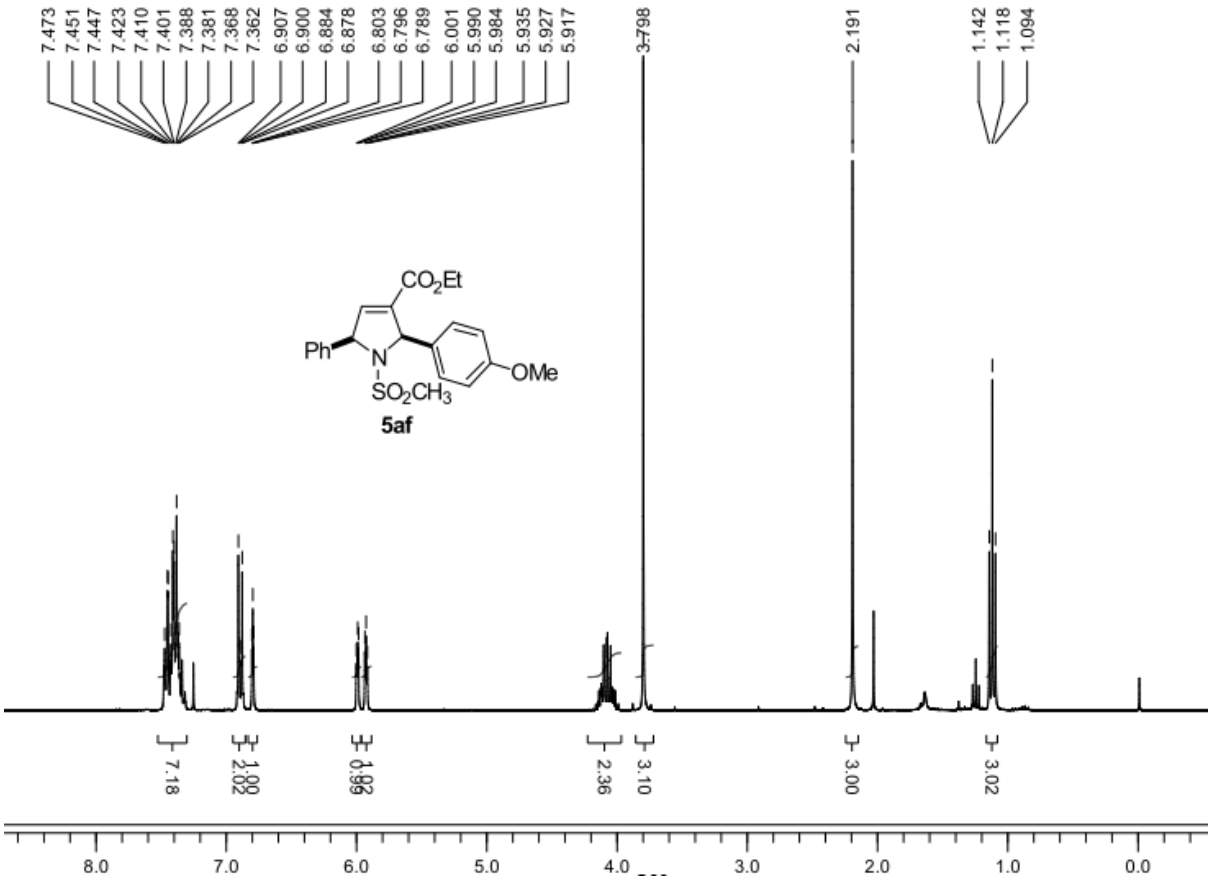

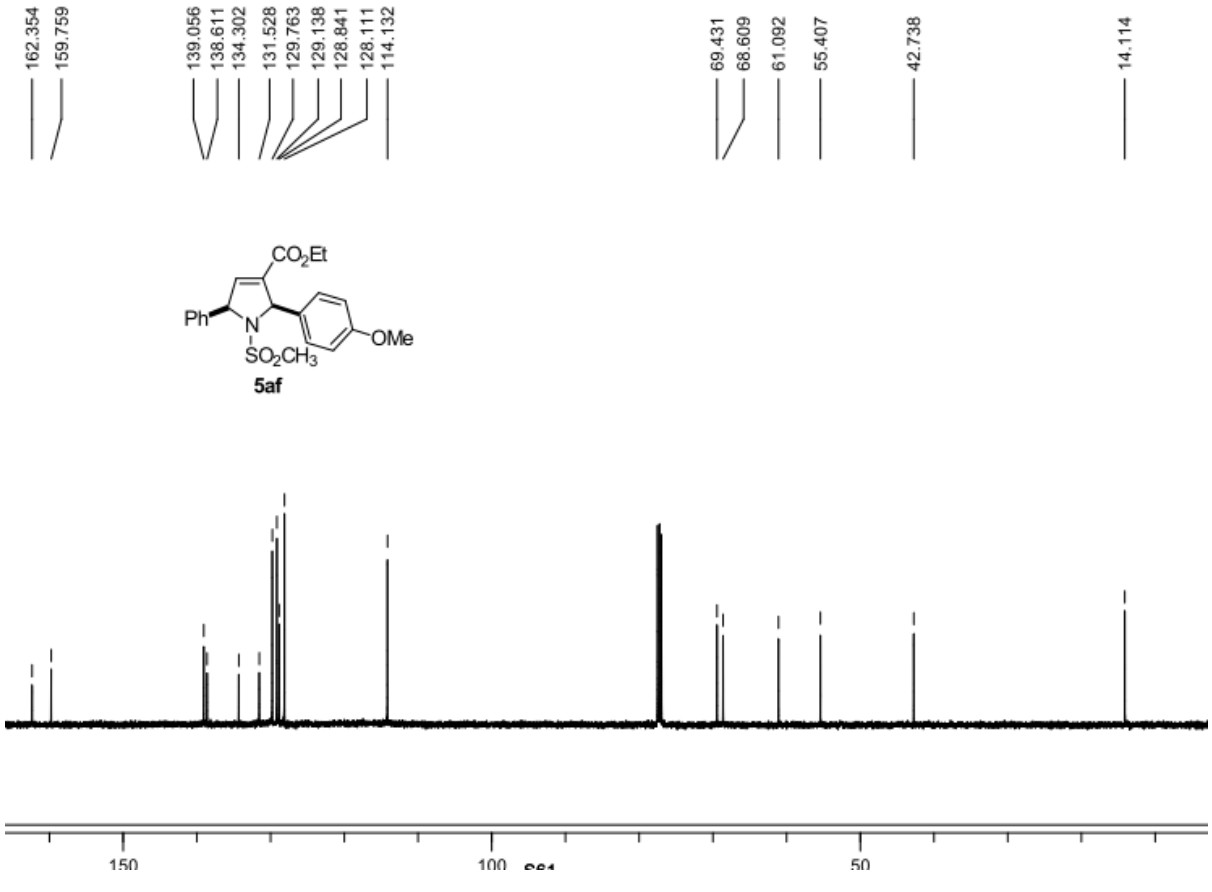

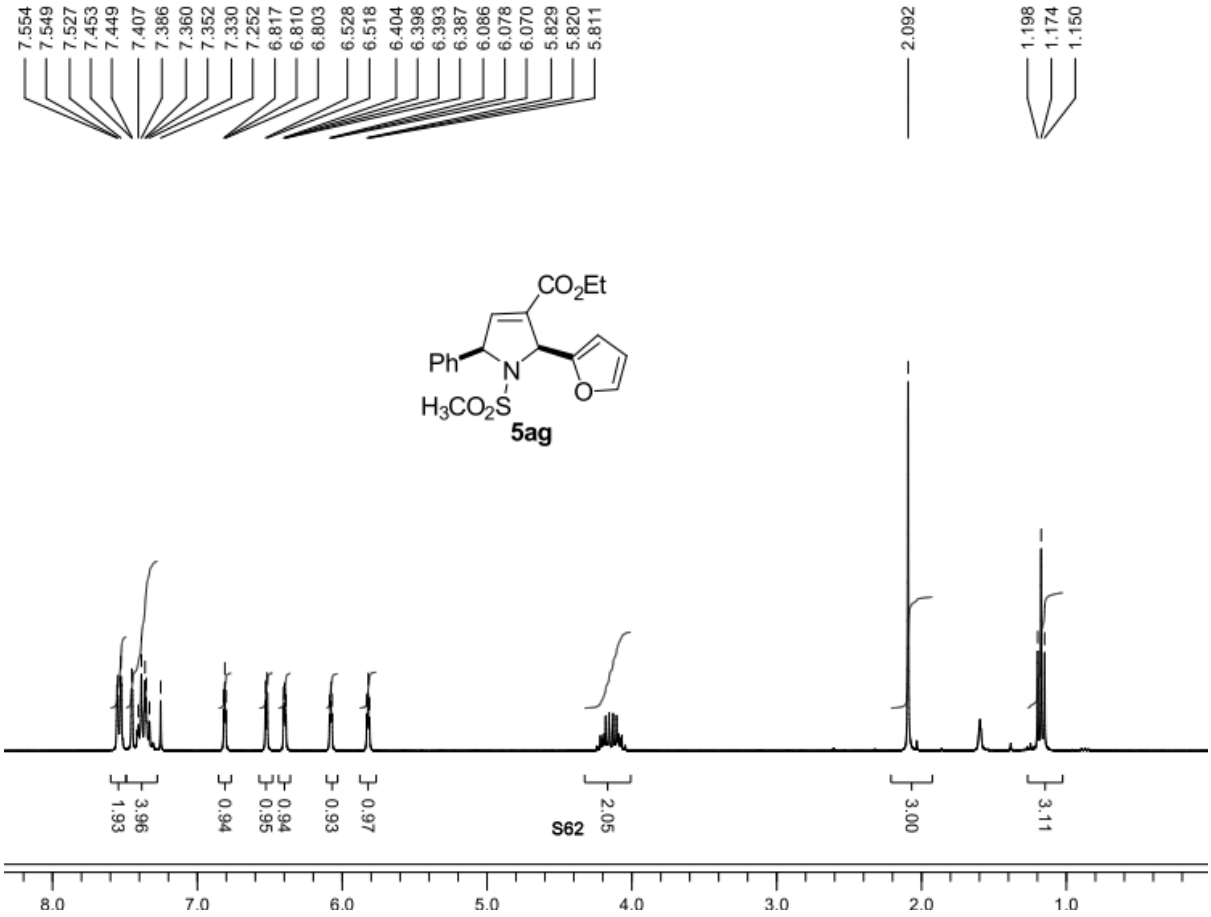
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6.810
6.803
6.528
6.518
6.404
6.398
6.393
6.387
6.086
6.078
6.070
5.829
5.820
5.811
2.092
1.198
1.174
1.150
CO2Et
Ph
N
O
H3CO2S
5ag
1.93
3.96
0.94
0.95
0.94
0.93
0.97
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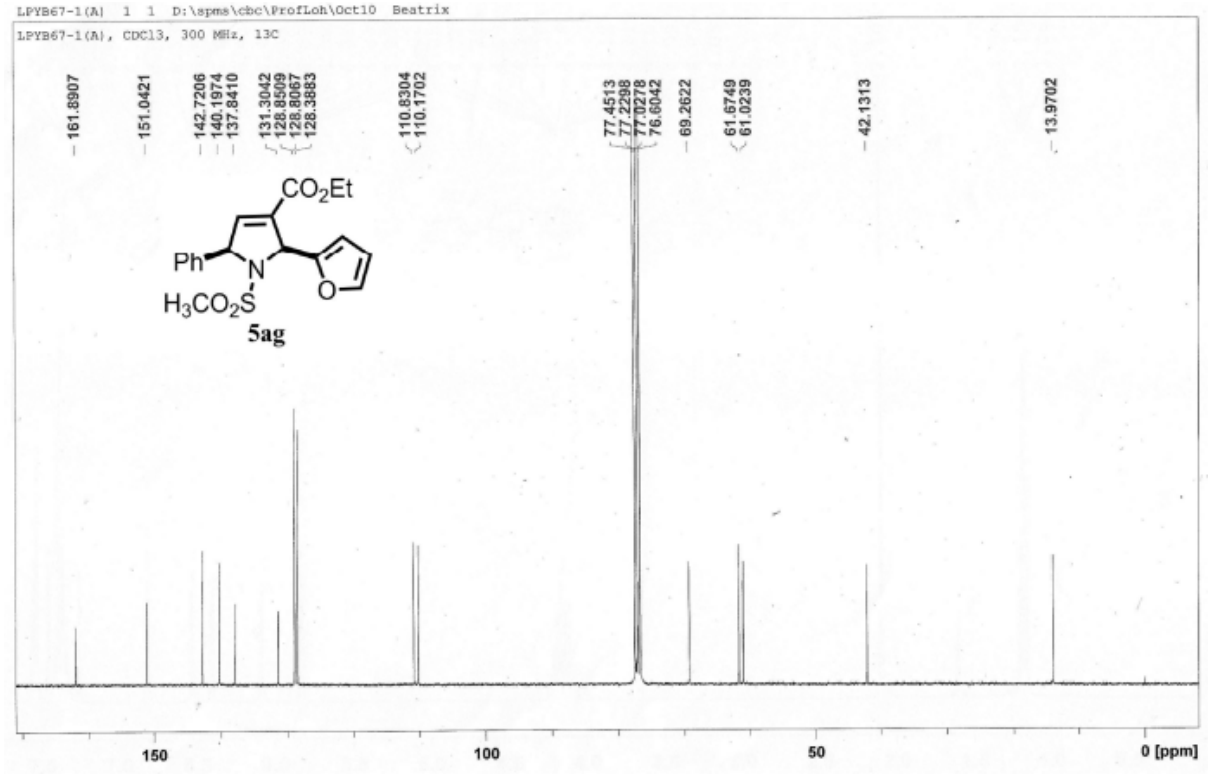
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LPYB67-1(A), CDCl3, 300 MHz, 13C
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110.1702
77.4513
77.2298
77.0278
76.6042
69.2622
61.6749
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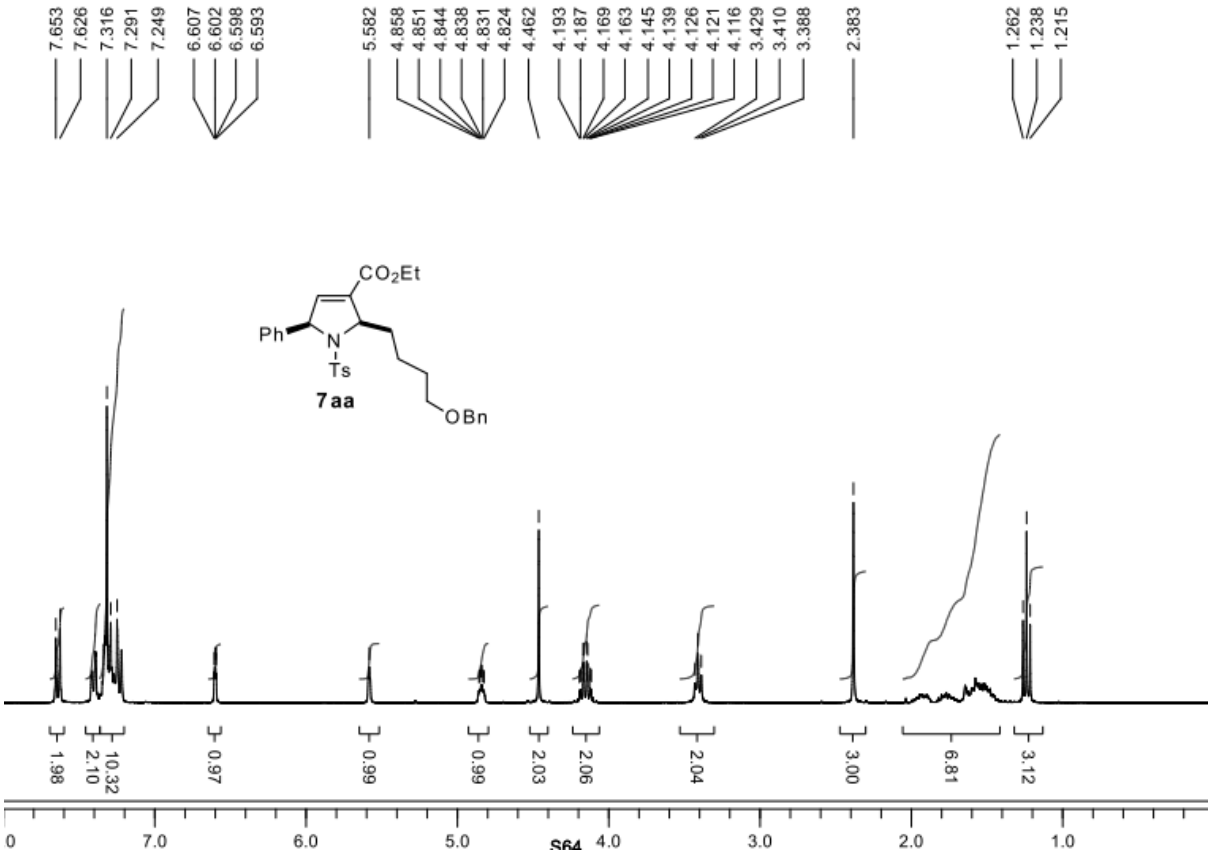
13.9702
CO2Et
Ph
N
O
H3CO2S
5ag
150
100
50
0 [ppm]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4.838
4.831
4.824
4.462
4.193
4.187
4.169
4.163
4.145
4.139
4.126
4.121
4.116
3.429
3.410
3.388
2.383
1.262
1.238
1.215
CO2Et
Ph
N
Ts
OBn
7aa
1.98
2.10
10.32
0.97
0.99
0.99
2.03
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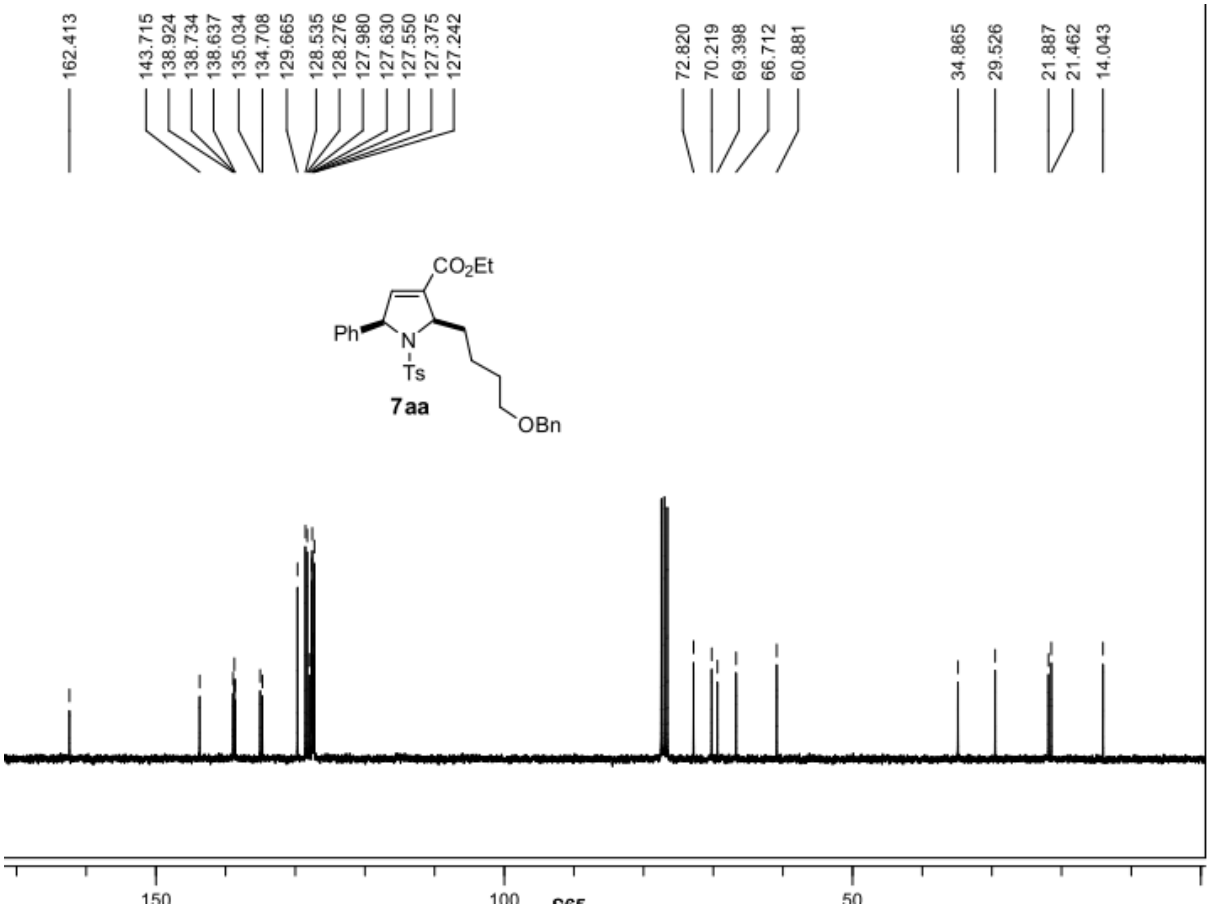
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66.712
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Ph
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Ts
OBn
7aa
150
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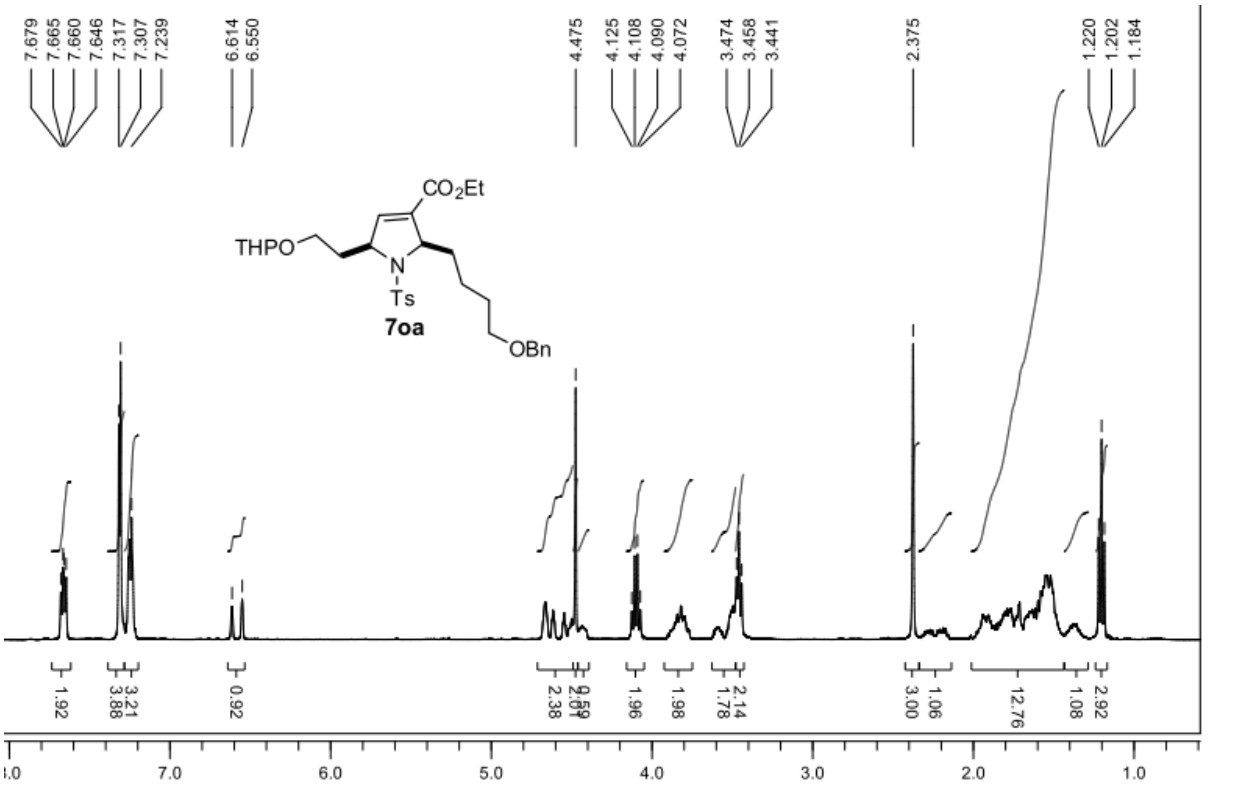
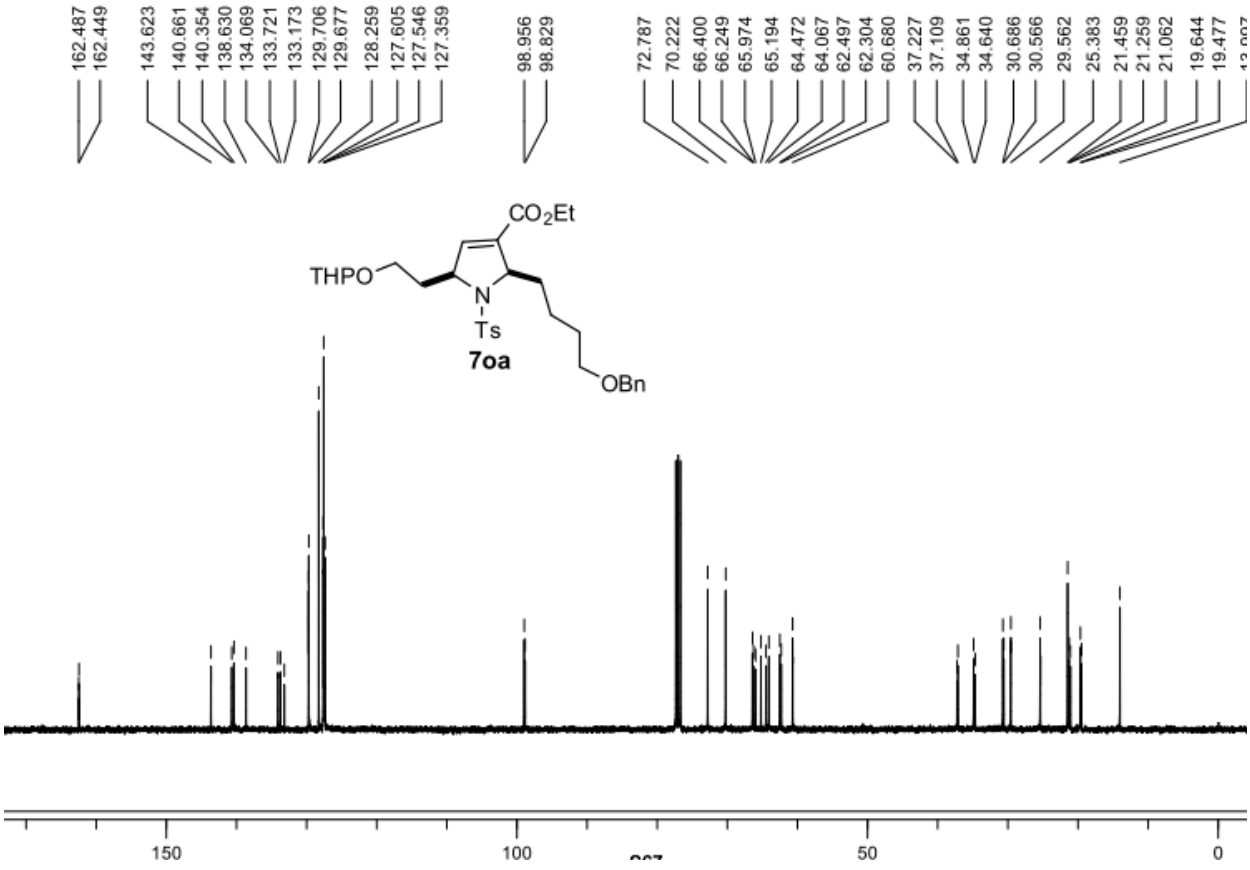
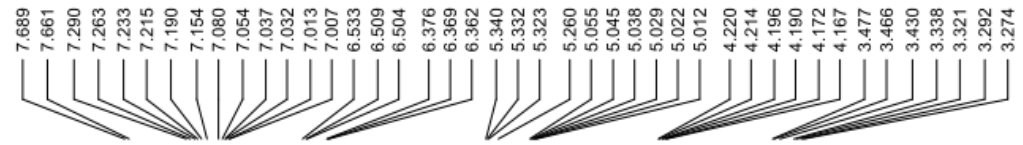
50



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7.054
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7.013
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6.533
6.509
6.504
6.376
6.369
6.362
5.340
5.332
5.323
5.260
5.055
5.045
5.038
5.029
5.022
5.012
4.220
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3.430
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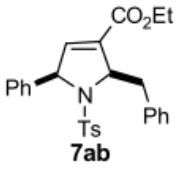
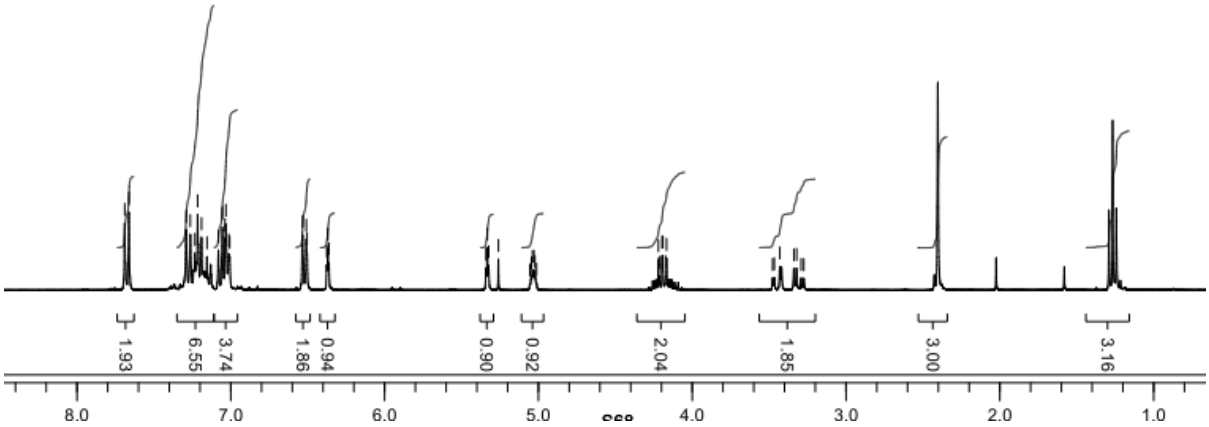
3.321
3.292
3.274


CO2Et
Ph
N
Ts
Ph

7ab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3.00
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7.0
6.0
5.0
4.0
3.0
2.0
1.0


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139.617
138.612
136.364
134.231
133.068
130.945
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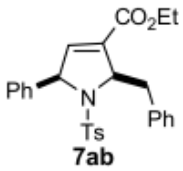
61.006
39.503
21.490
14.089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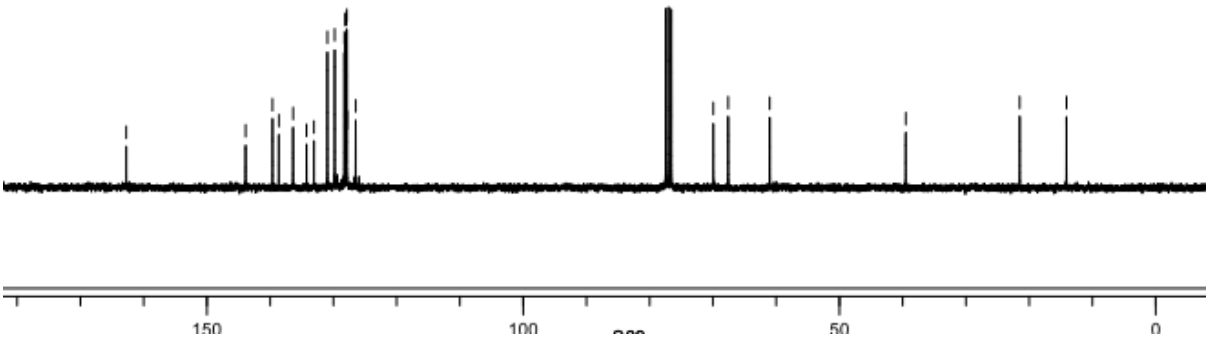
Ph
N
Ts
Ph

7ab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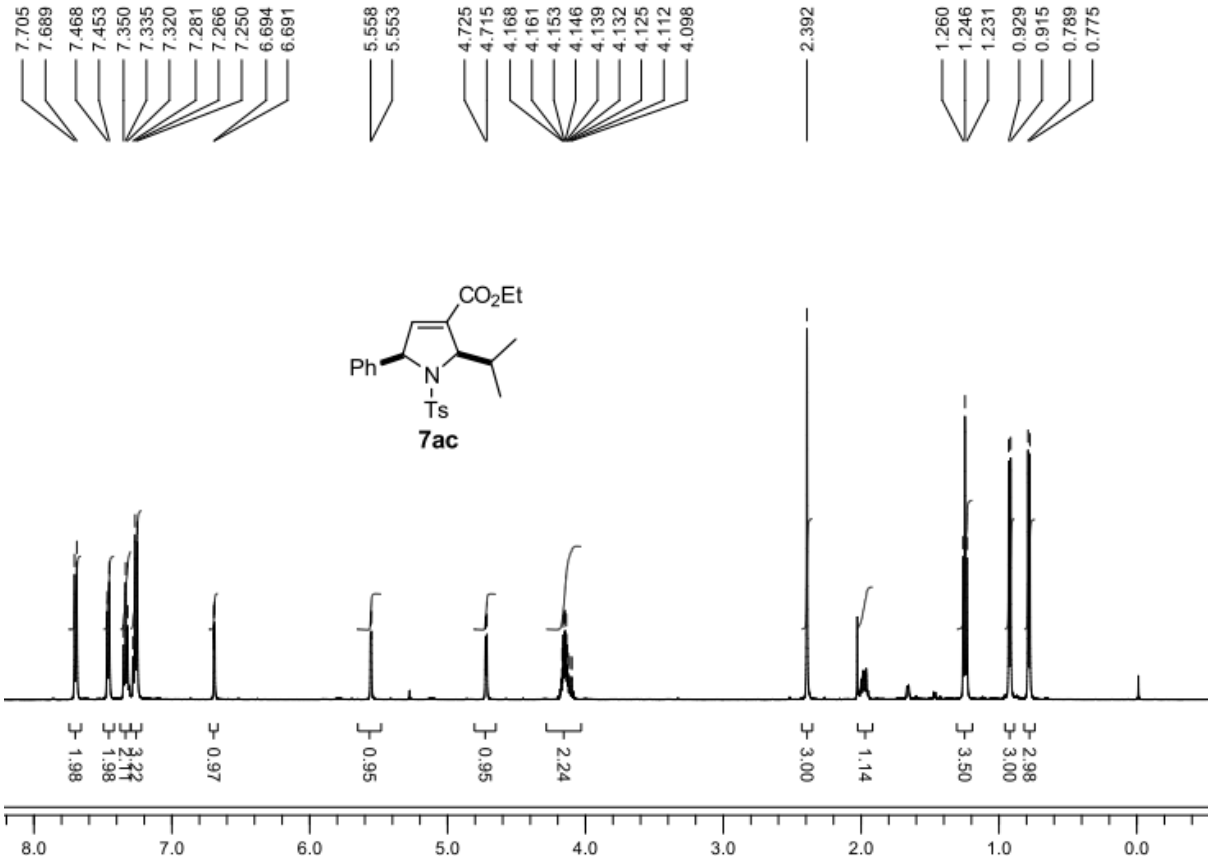
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5.553
4.725
4.715
4.168
4.161
4.153
4.146
4.139
4.132
4.125
4.112
4.098
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1.246
1.231
0.929
0.915
0.789
0.775
CO2Et
Ph
N
Ts
7ac
1.98
1.98
2.11
2.22
0.97
0.96
0.95
2.24
3.00
1.14
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4.0
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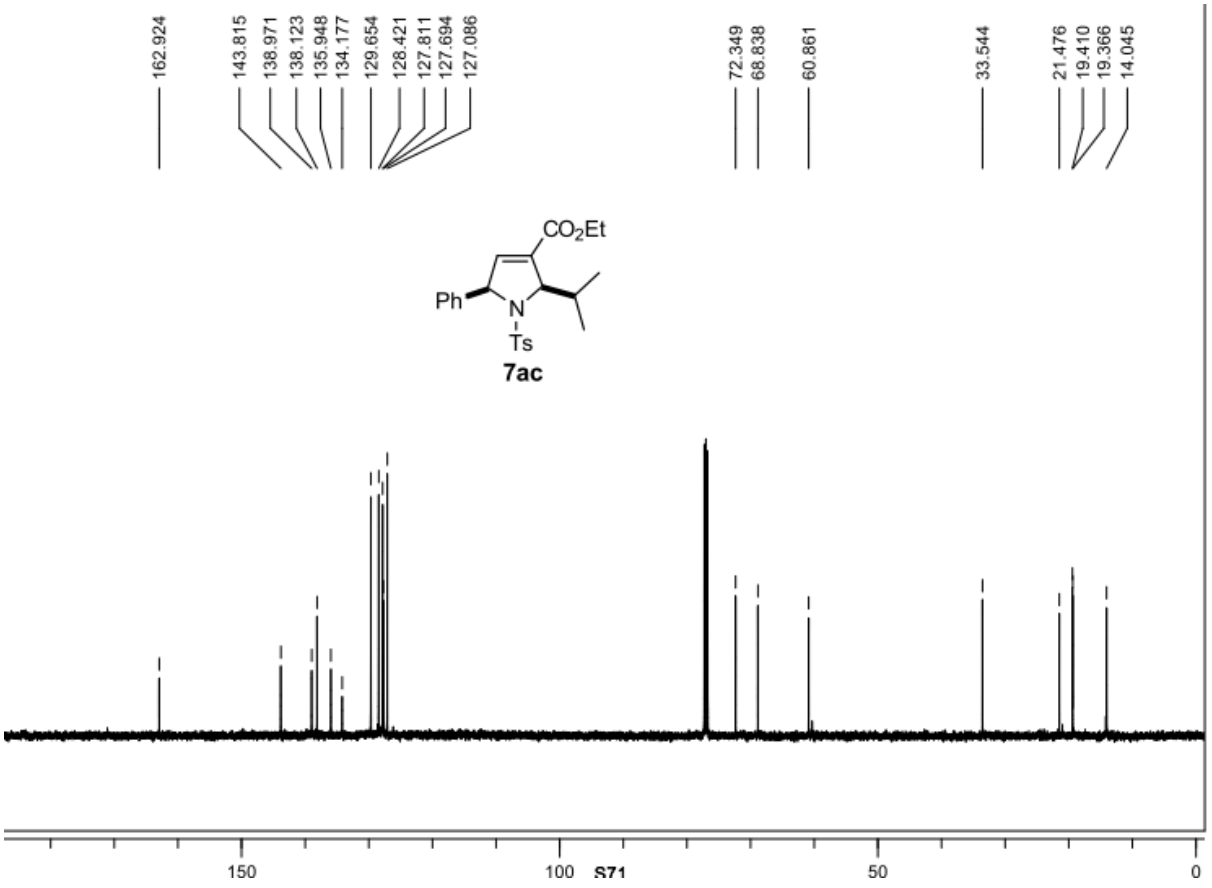
2.0
1.0
0.0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Ph
N
Ts
7ac
150
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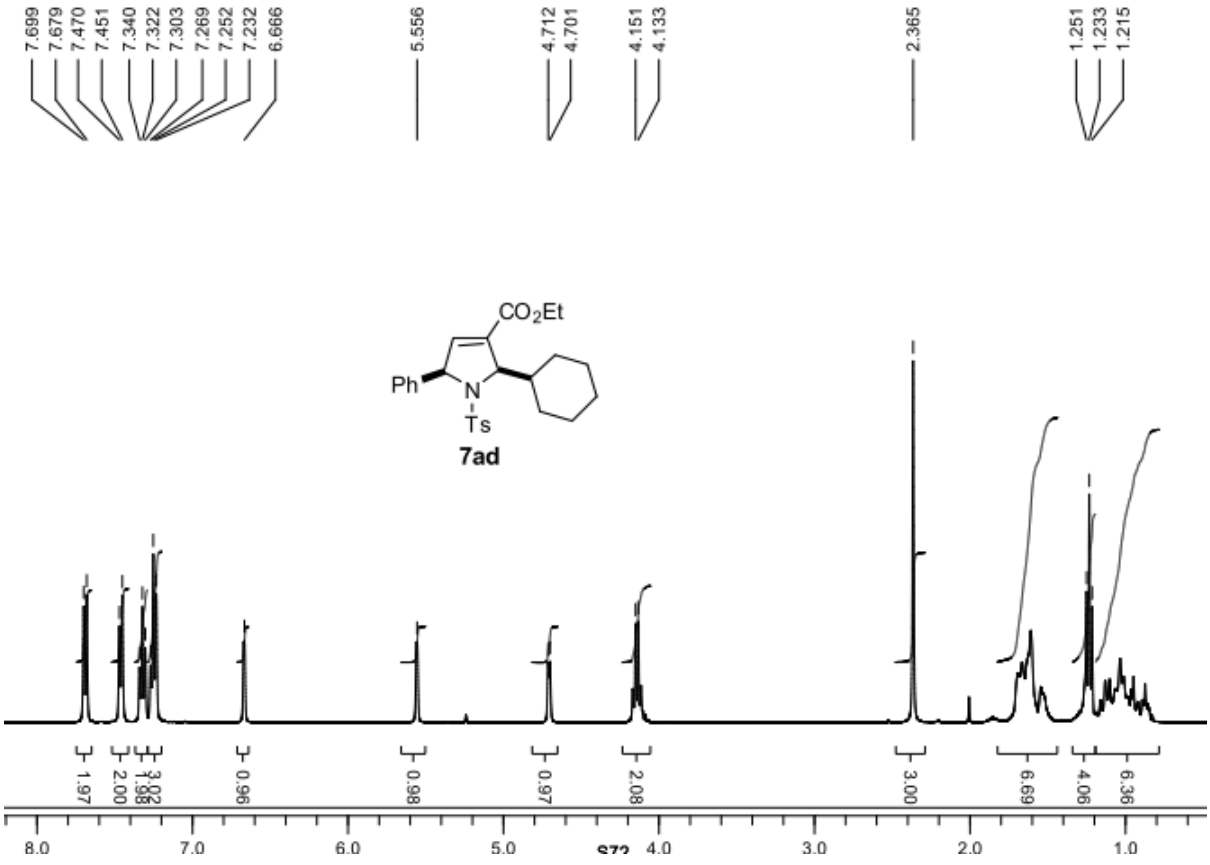
50
0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7.232
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4.701
4.151
4.133
2.365
1.251
1.233
1.215
CO2Et
Ph
N
Ts
7ad
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3.02
1.98
1.00
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0.97
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5.0
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3.0
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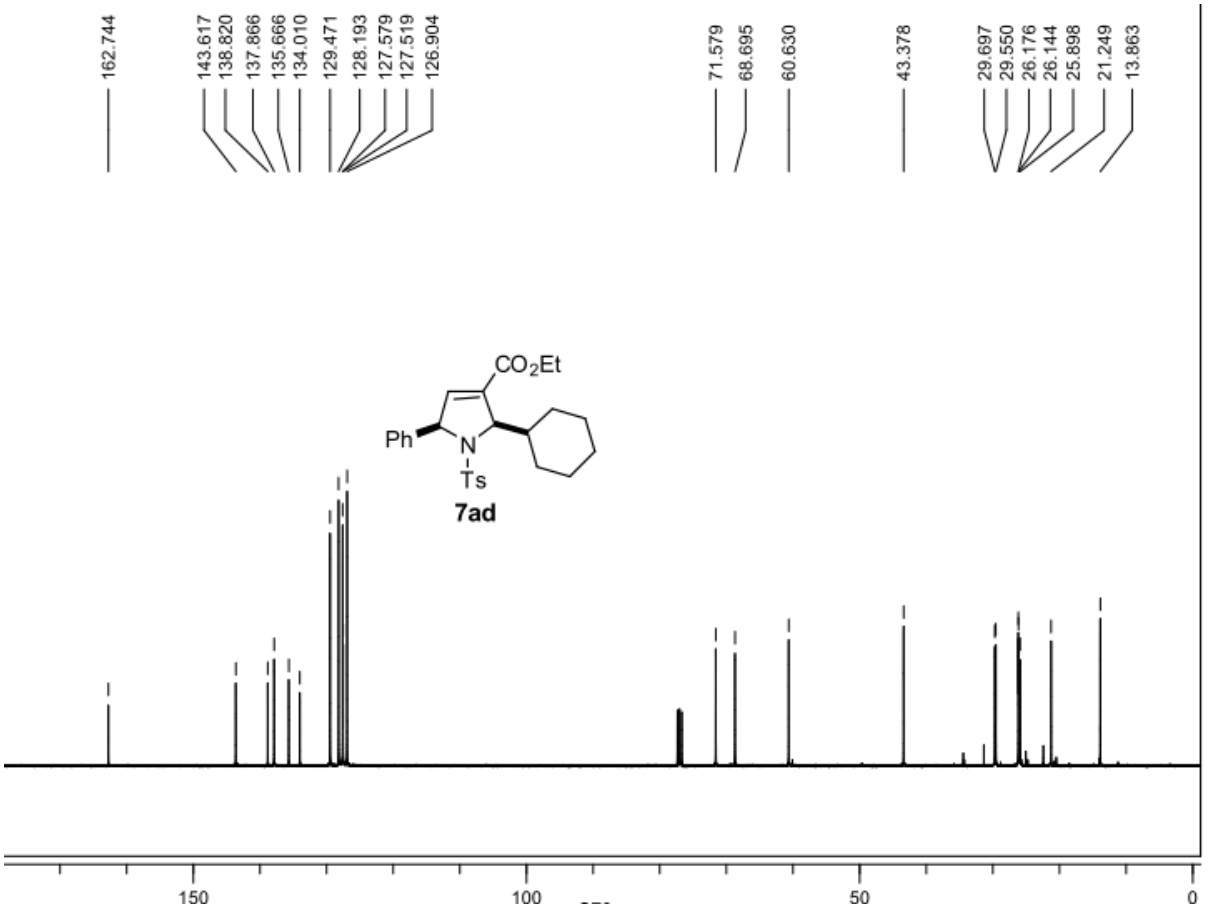
1.0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29.697
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25.898
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Ph
N
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7ad
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50
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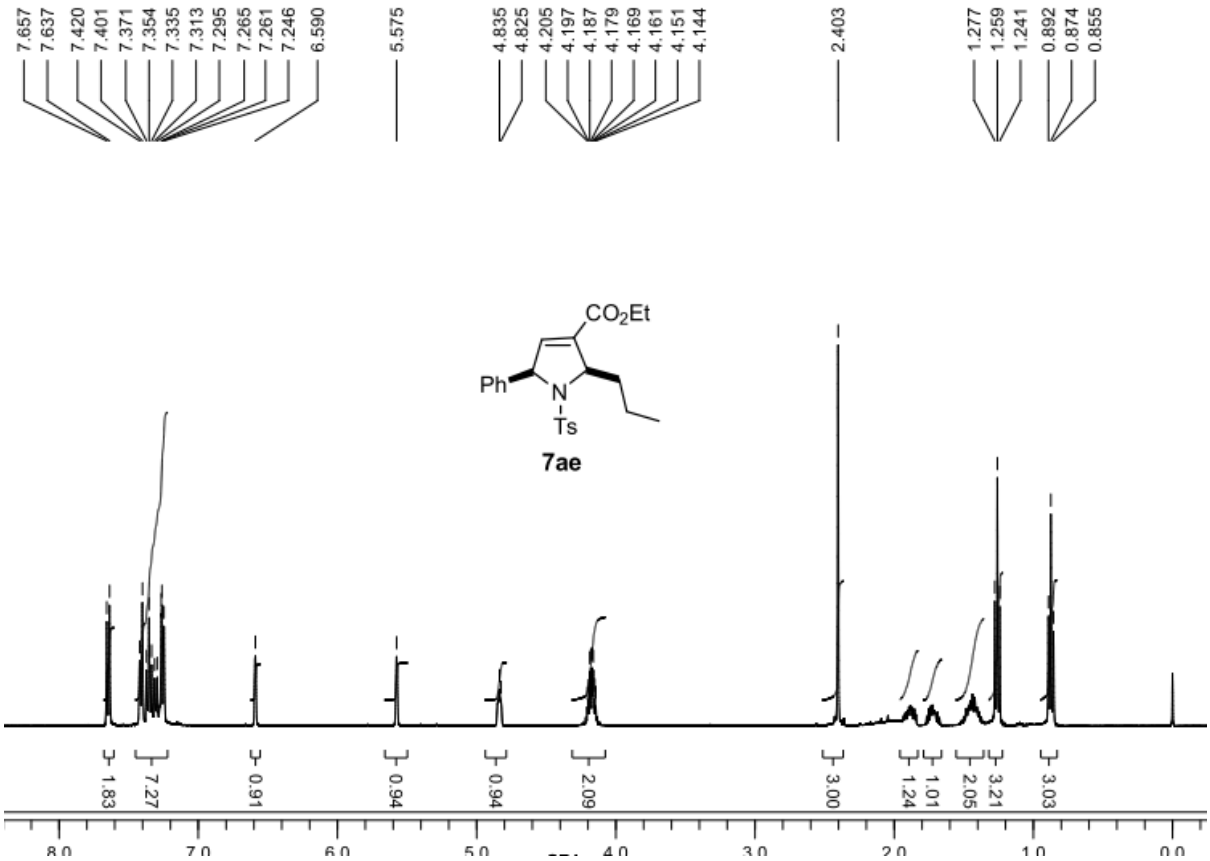
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7.261
7.246
6.590
5.575
4.835
4.825
4.205
4.197
4.187
4.179
4.169
4.161
4.151
4.144
2.403
1.277
1.259
1.241
0.892
0.874
0.855
CO2Et
Ph
N
Ts
7ae
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0.94
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1.24
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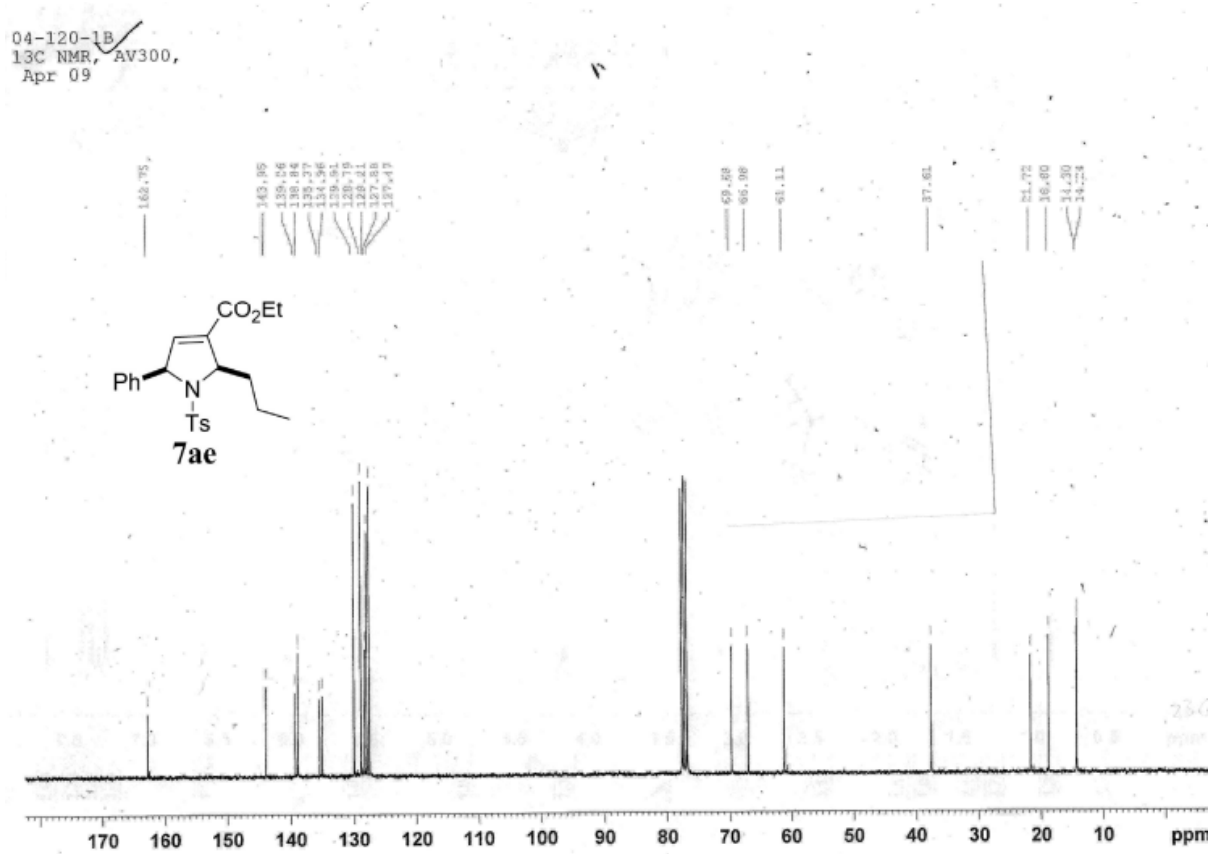
3.21
3.03


04-120-1B
13C NMR, AV300,
Apr 09
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Ph
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Ts
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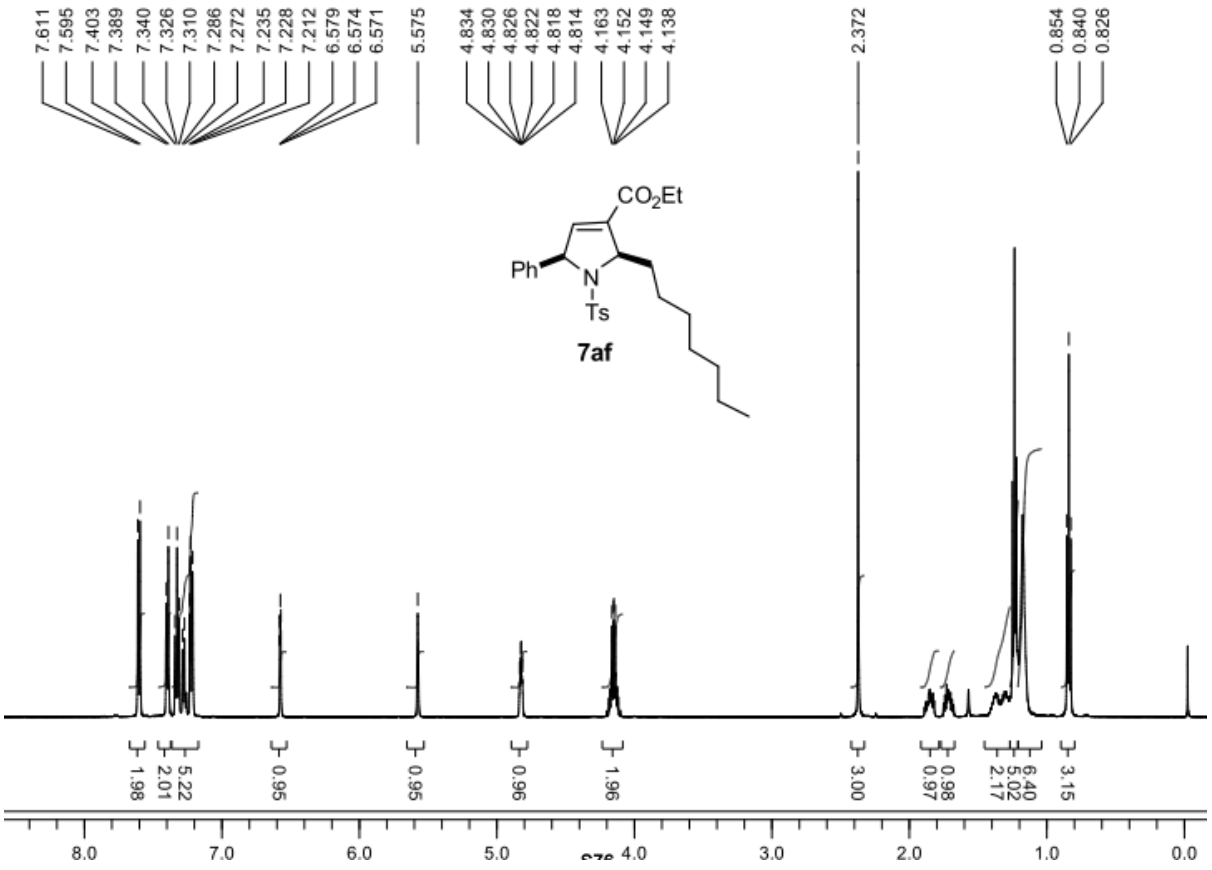
30
20
10
ppm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5.575
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4.152
4.149
4.138
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0.840
0.826
CO2Et
Ph
N
Ts
7af
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2.01
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0.95
0.96
1.96
3.00
0.97
0.98
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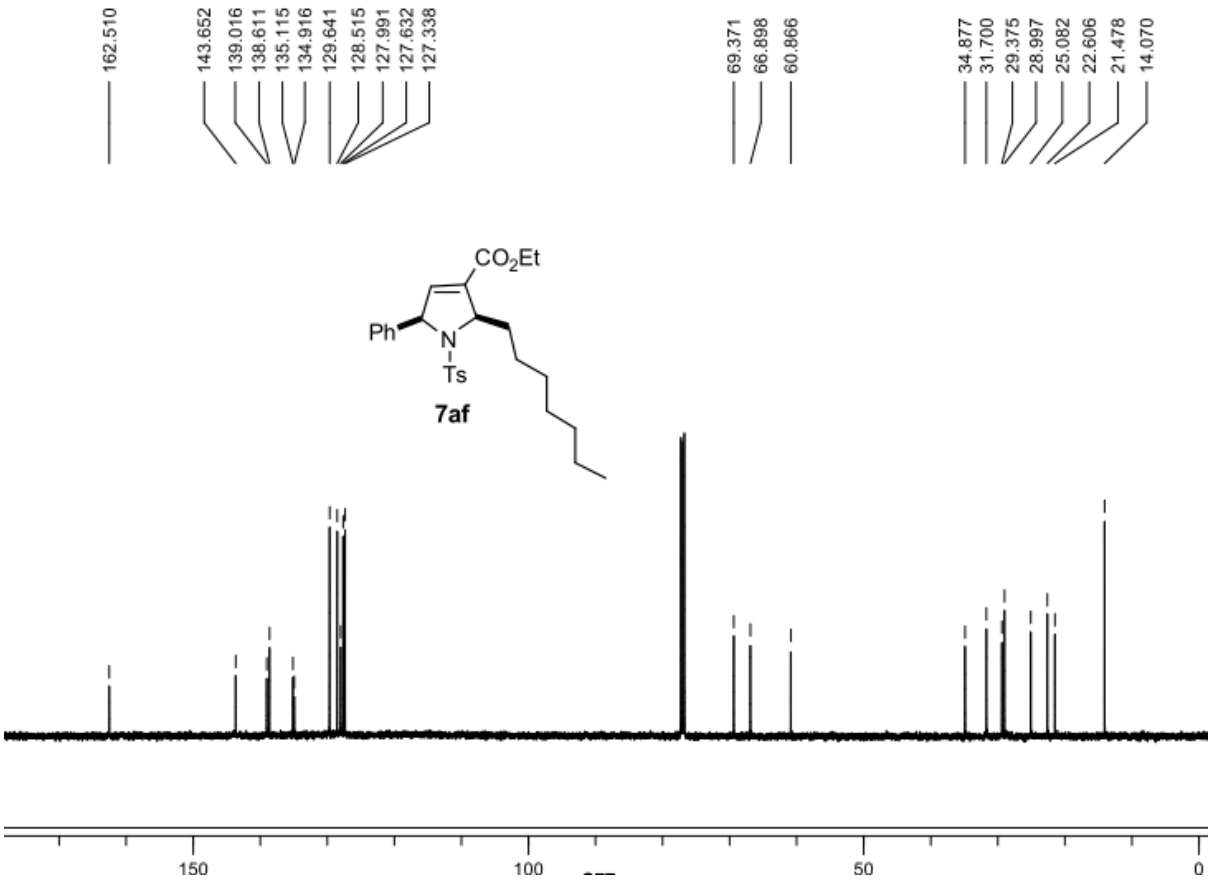
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69.371
66.898
60.866
34.877
31.700
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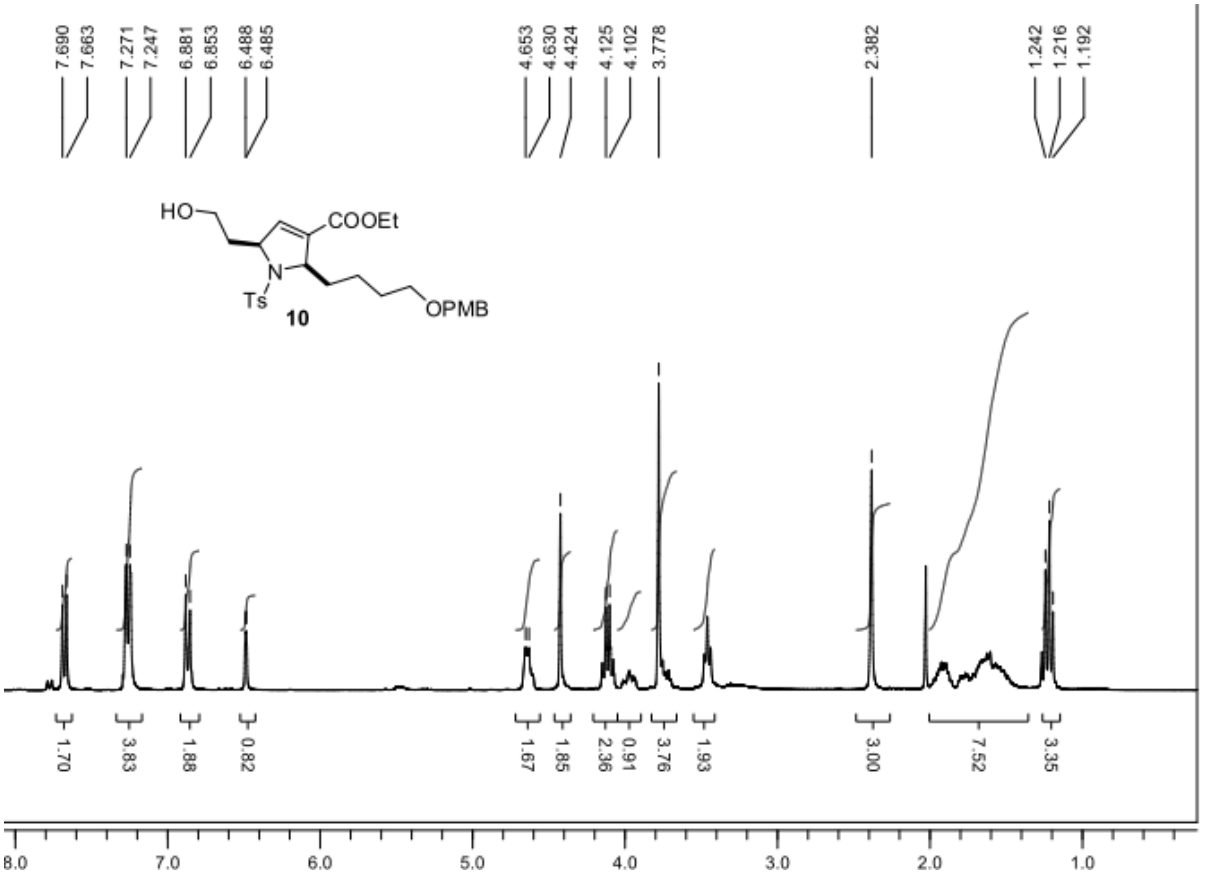
22.606
21.478
14.070
CO2Et
Ph
N
Ts
7af
150
100
50
0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2.382
1.242
1.216
1.192
HO
COOEt
N
Ts
OPMB
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1.88
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1.85
2.36
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3.78
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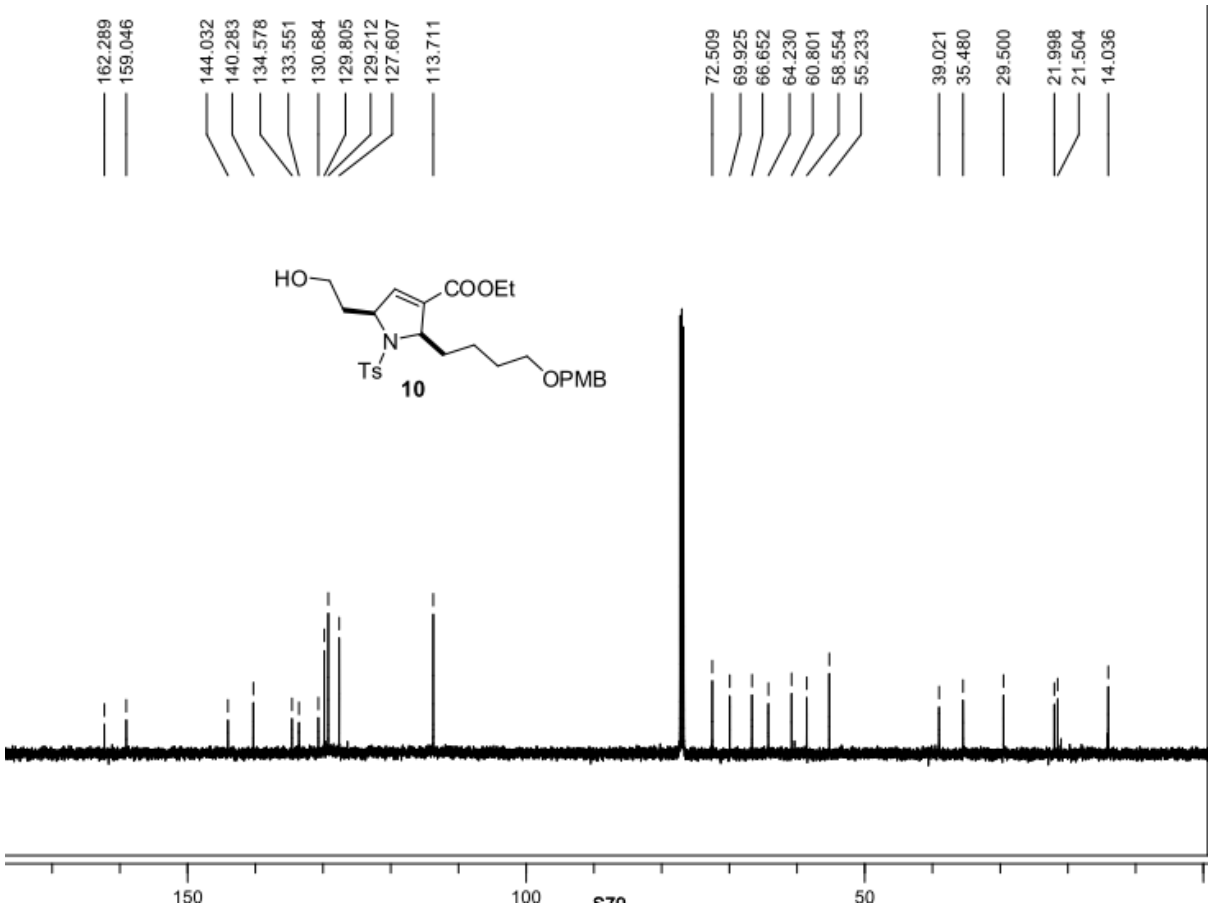
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64.230
60.801
58.554
55.233
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21.998
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14.036
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COOEt
N
Ts
OPMB
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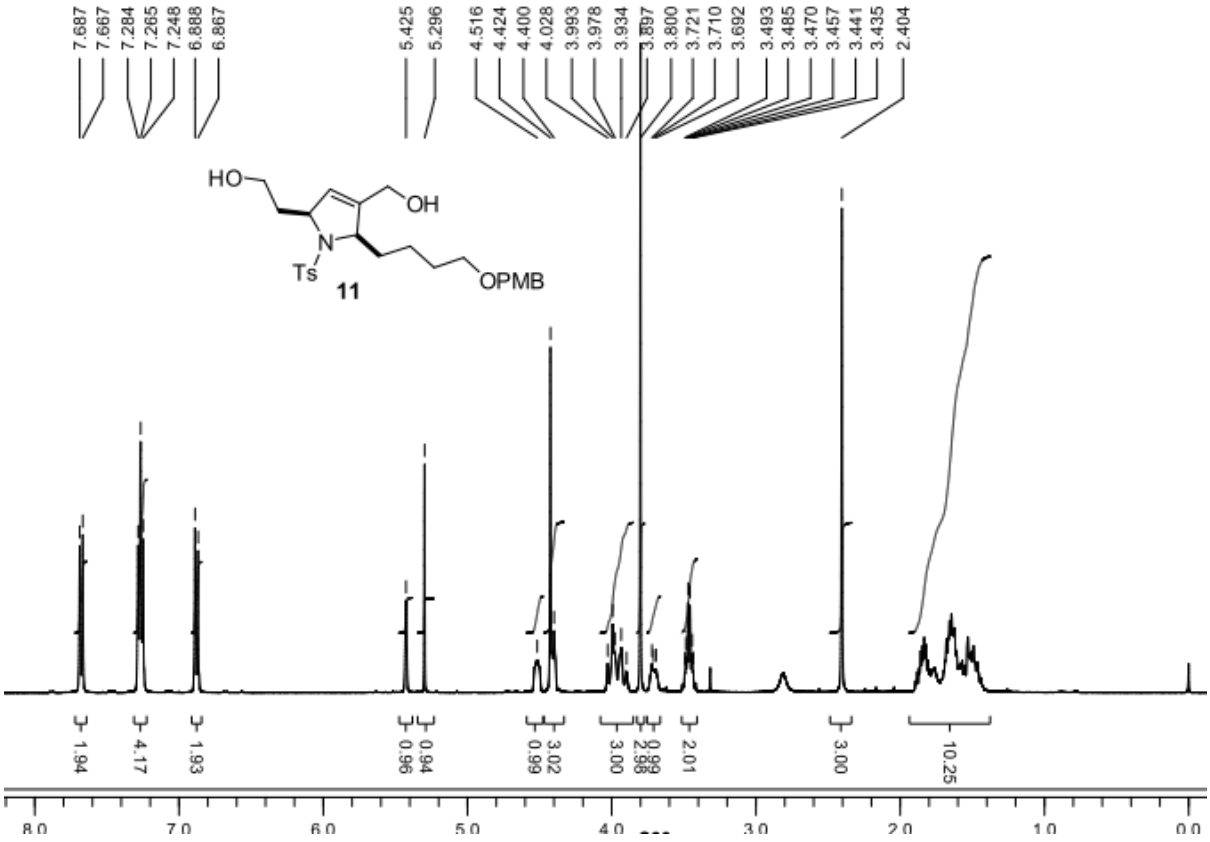
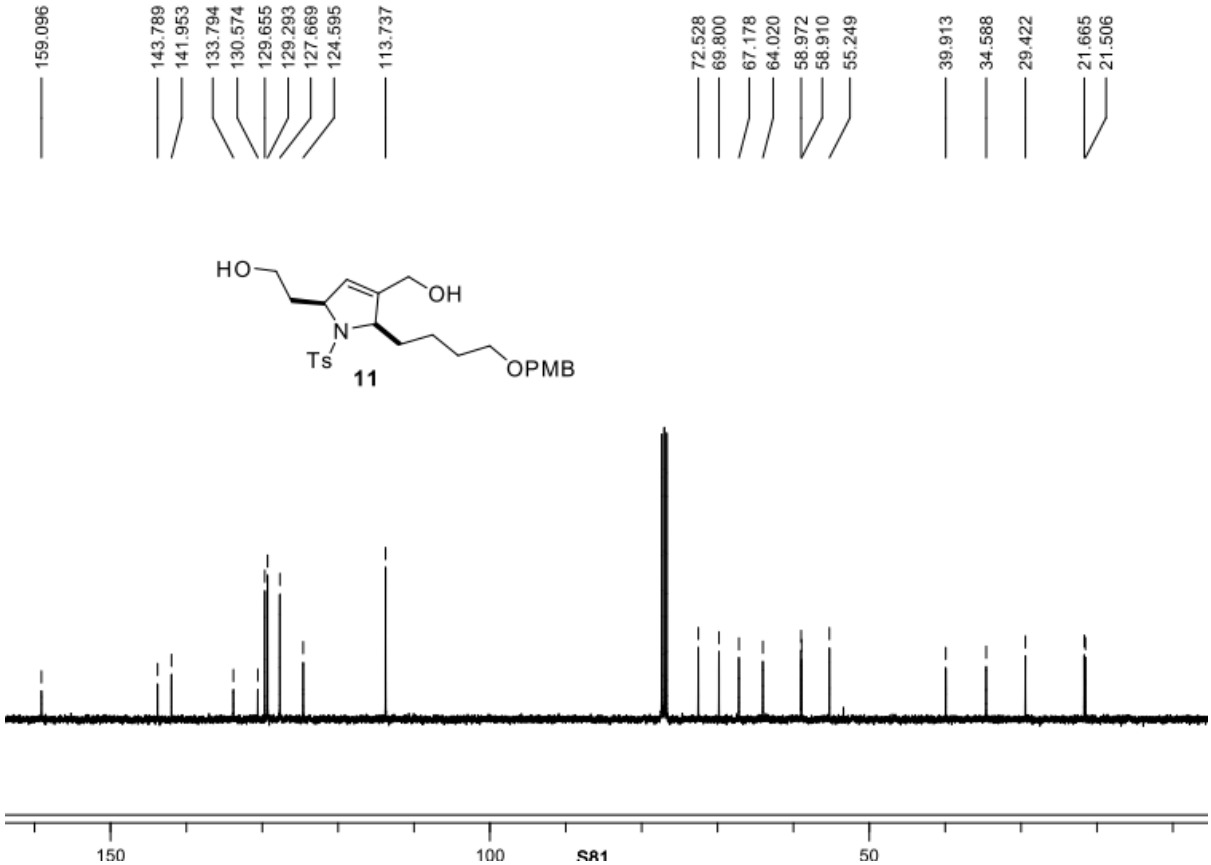
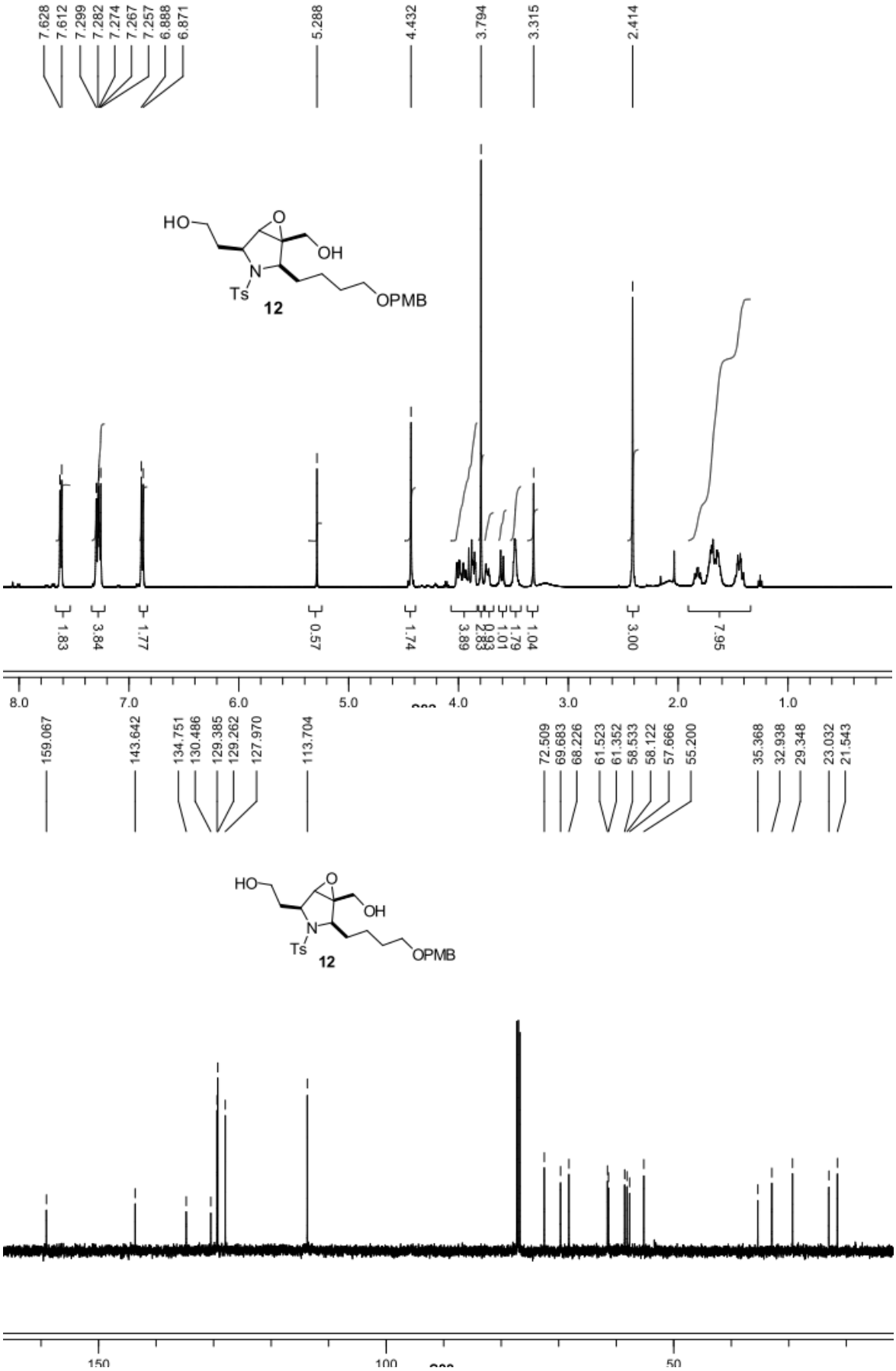
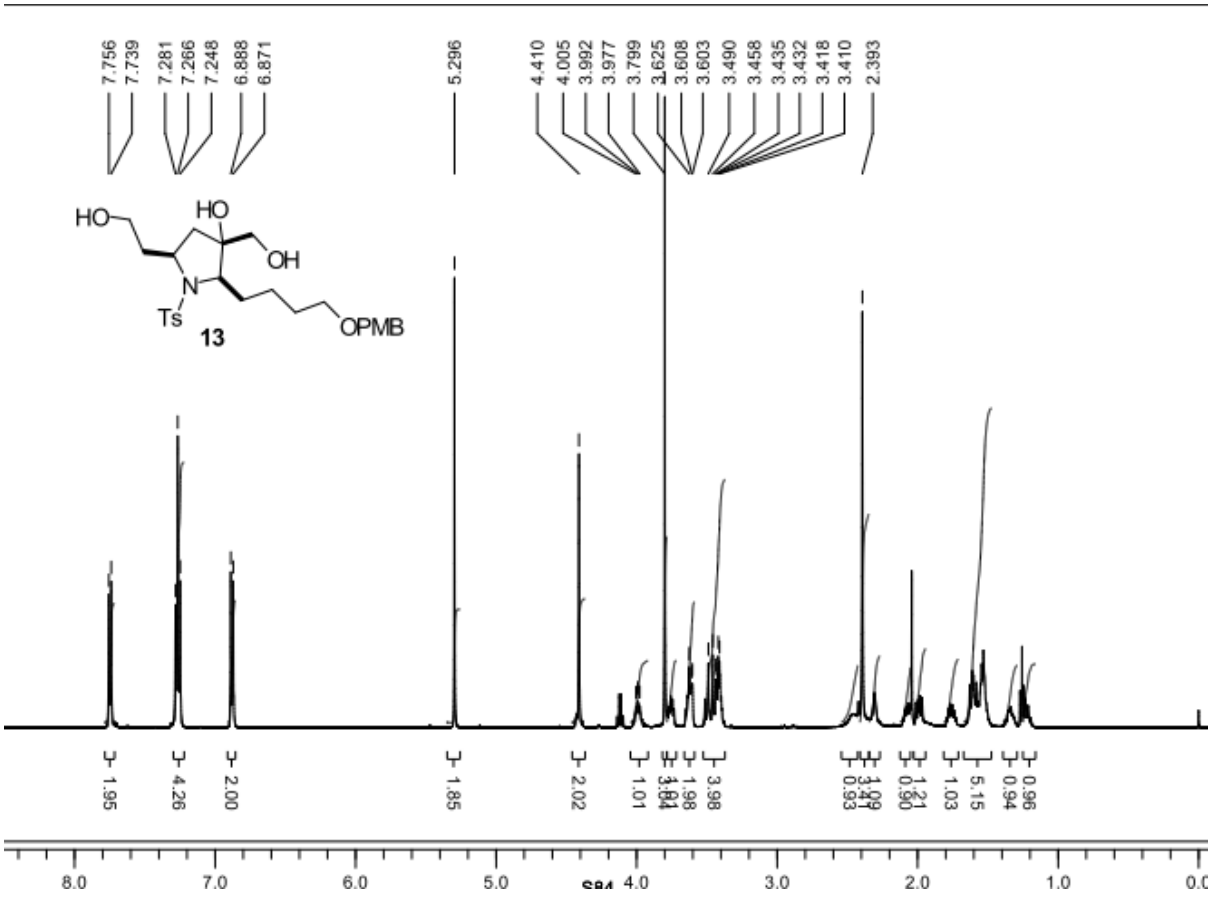
150
100
50





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3.490
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3.435
3.432
3.418
3.410
2.393
HO
HO
OH
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Ts
OPMB
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1.01
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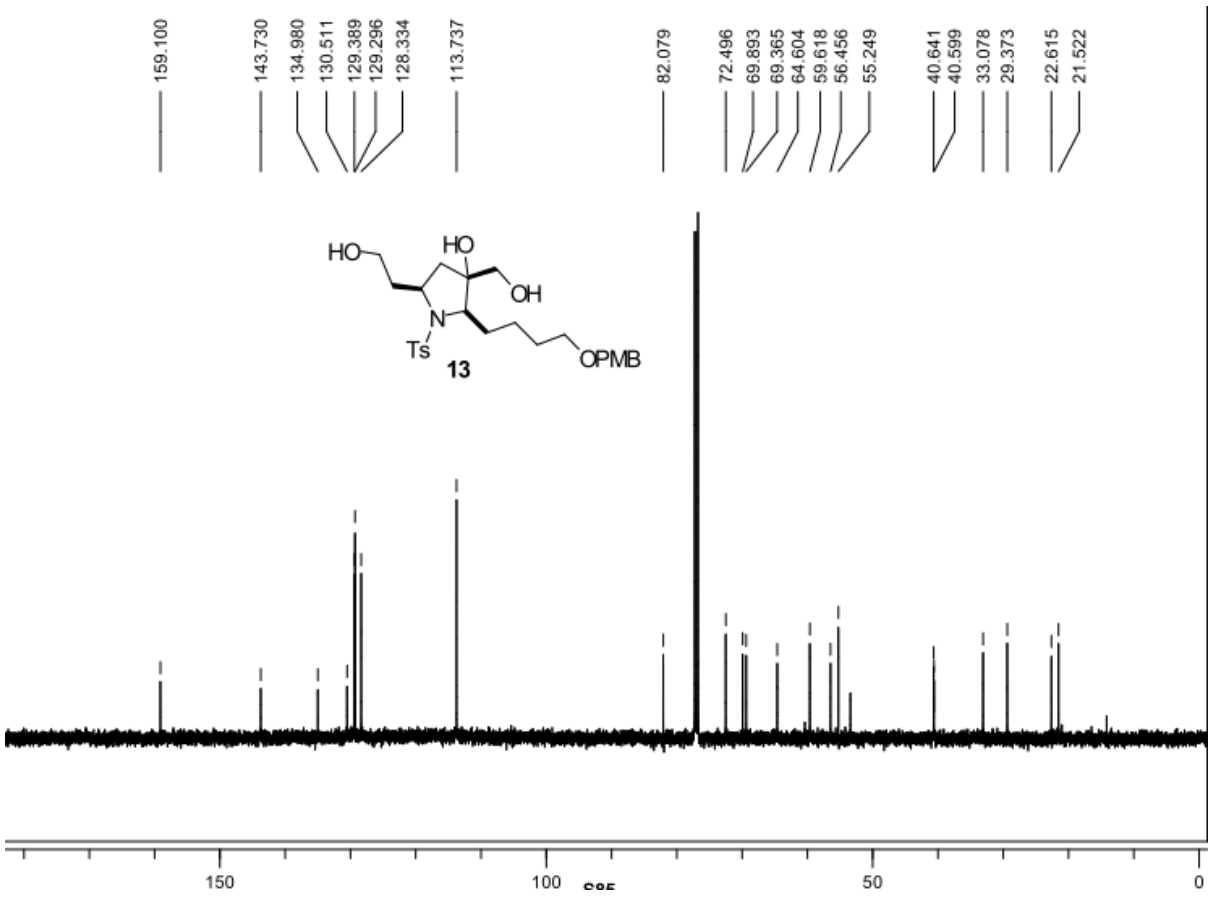
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29.373
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HO
HO
OH
N
Ts
OPMB
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50
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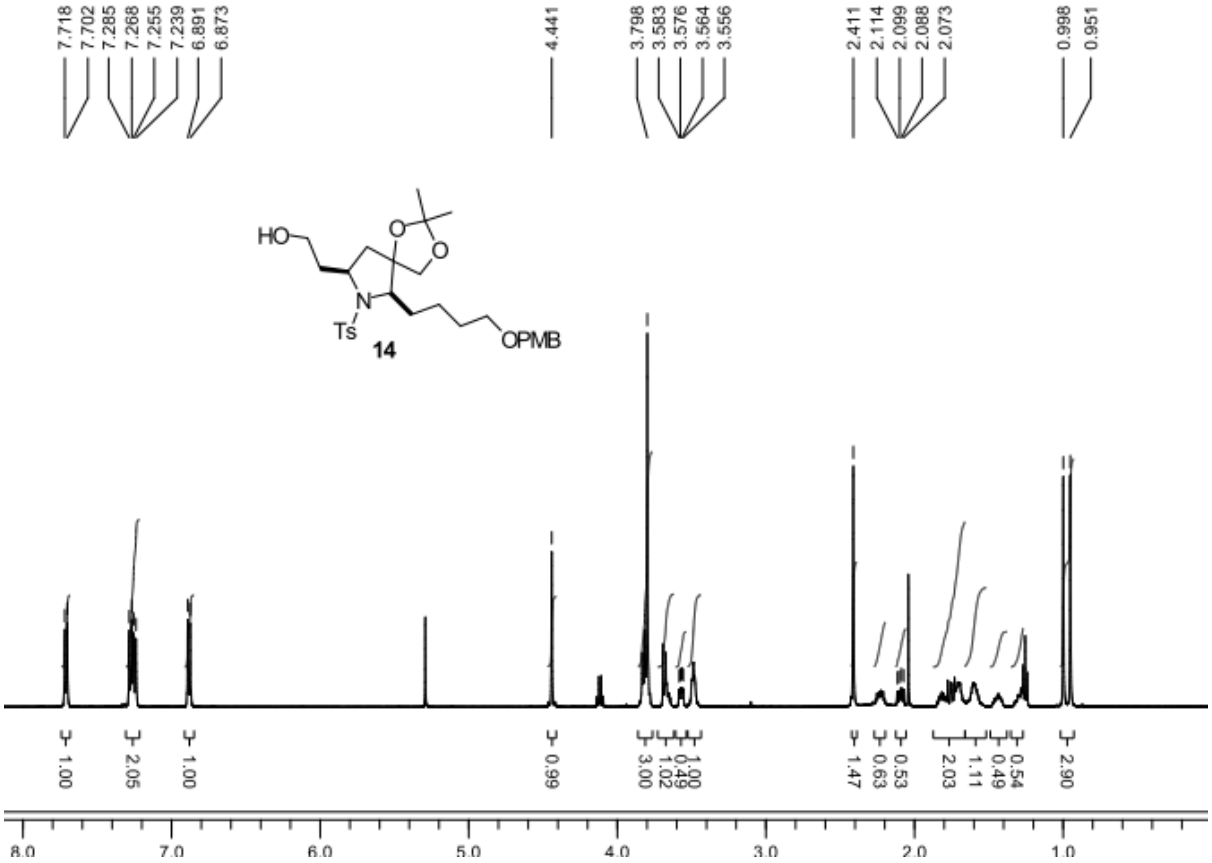
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2.073
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O
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Ts
OPMB
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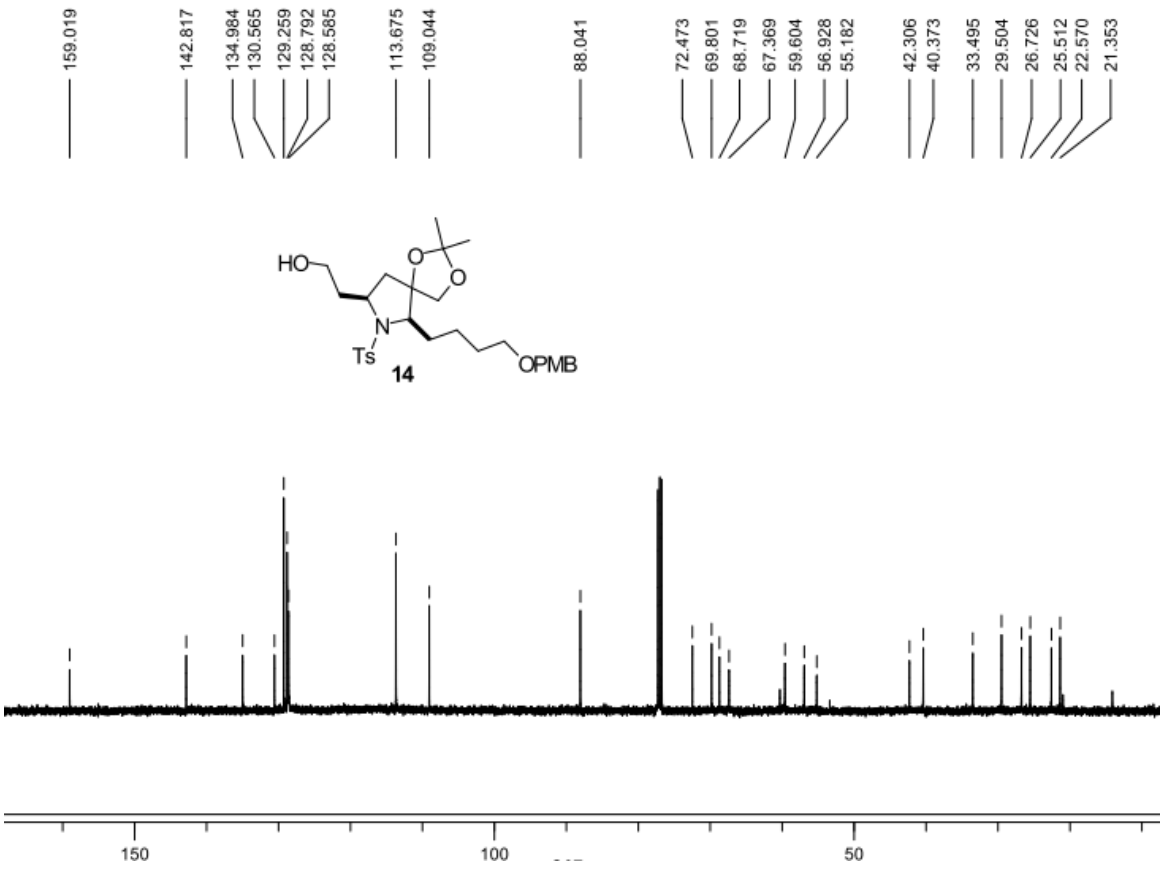
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88.041
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68.719
67.369
59.604
56.928
55.182
42.306
40.373
33.495
29.504
26.726
25.512
22.570
21.353
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O
N
Ts
OPMB
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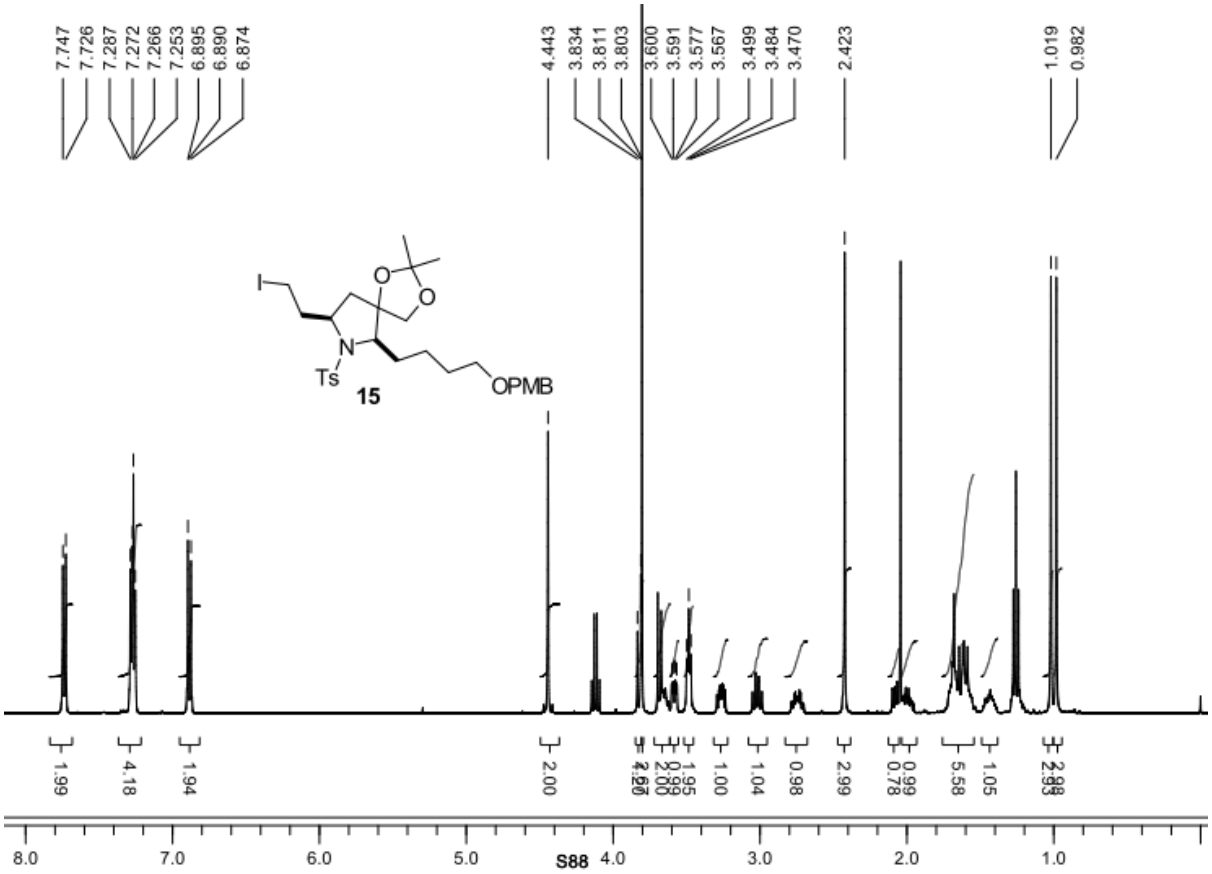
100
50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3.811
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3.567
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Ts
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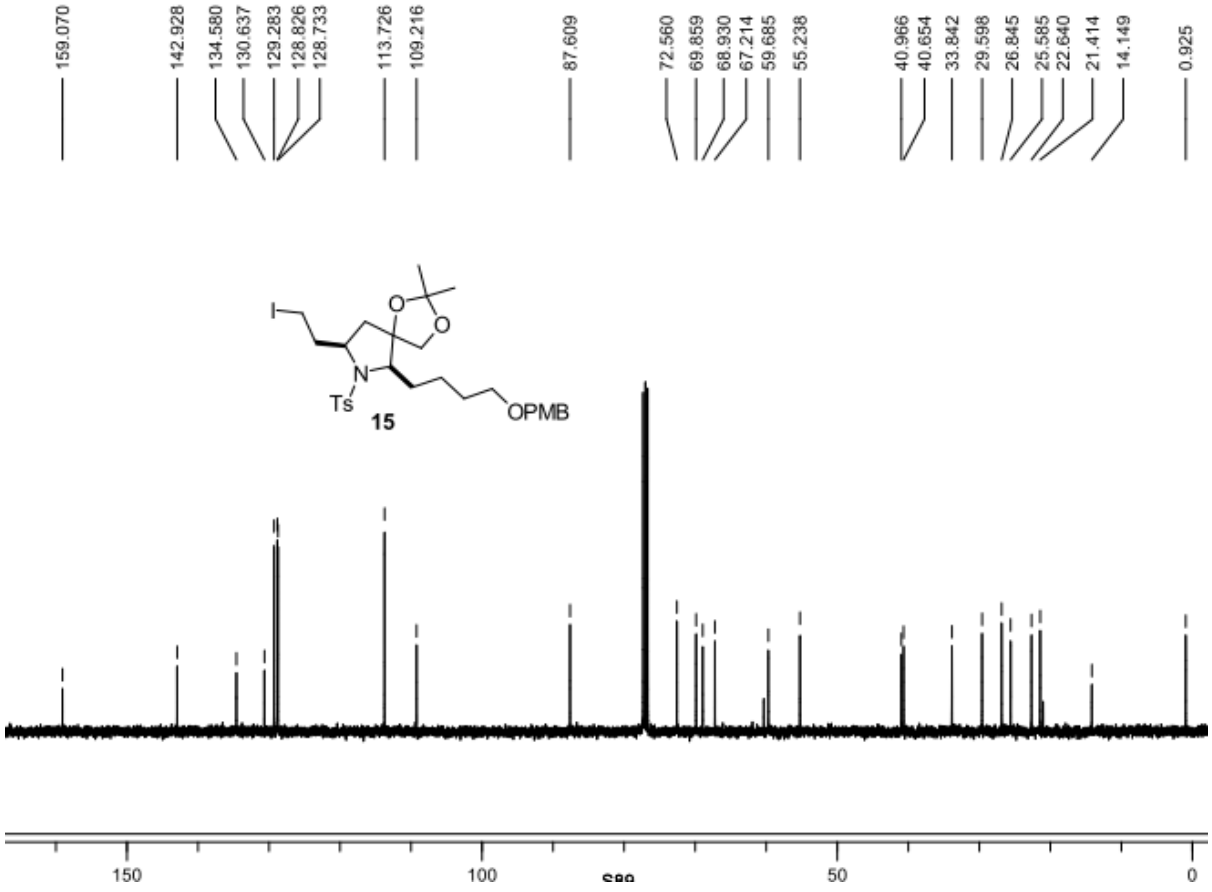
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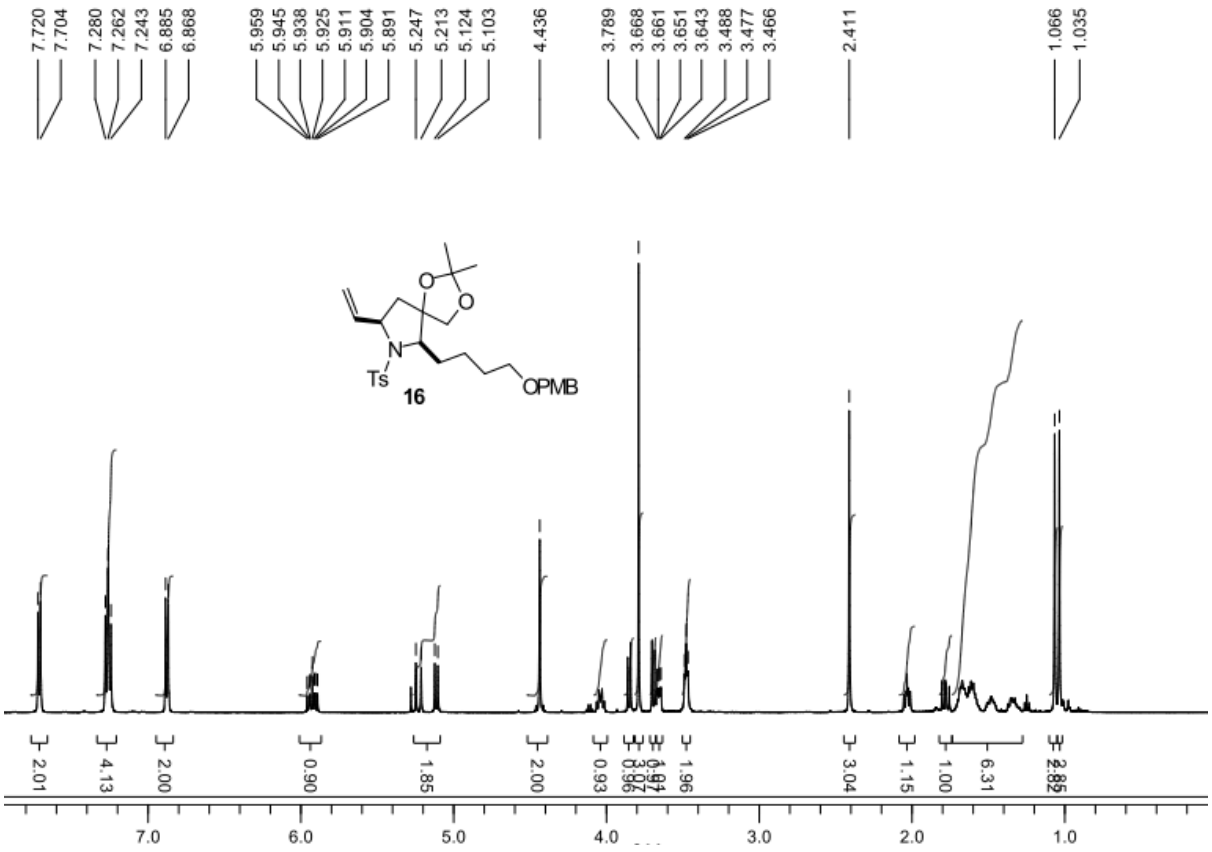

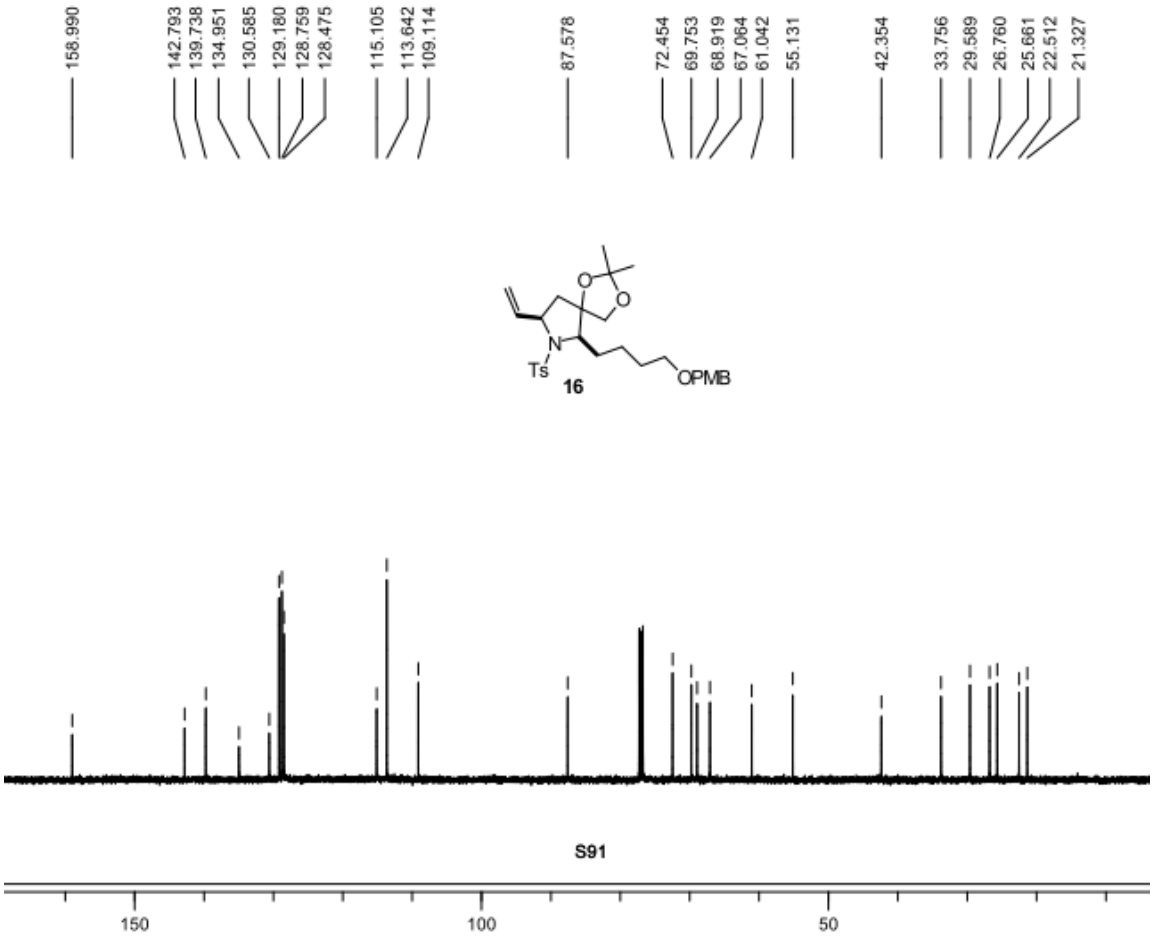

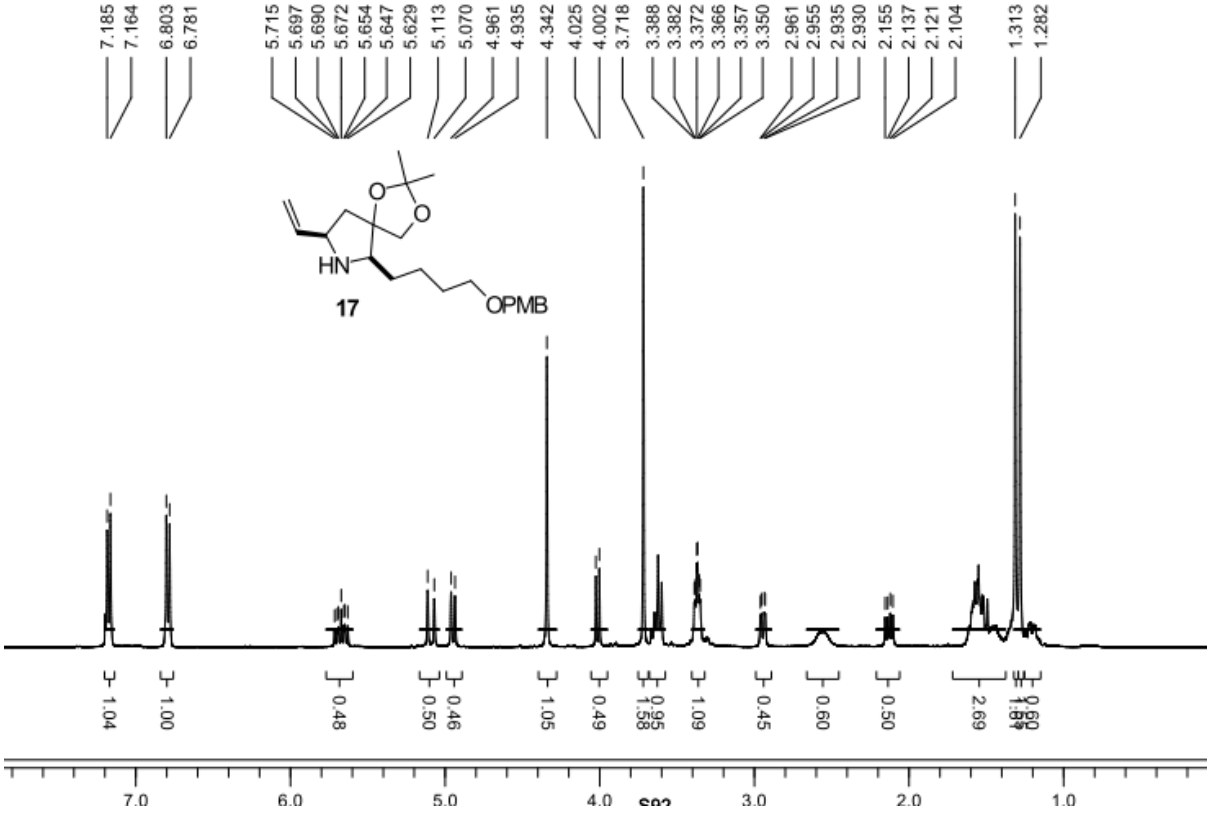
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4.961
4.935
4.342
4.025
4.002
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3.382
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3.357
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O
HN
17
OPMB
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0.95
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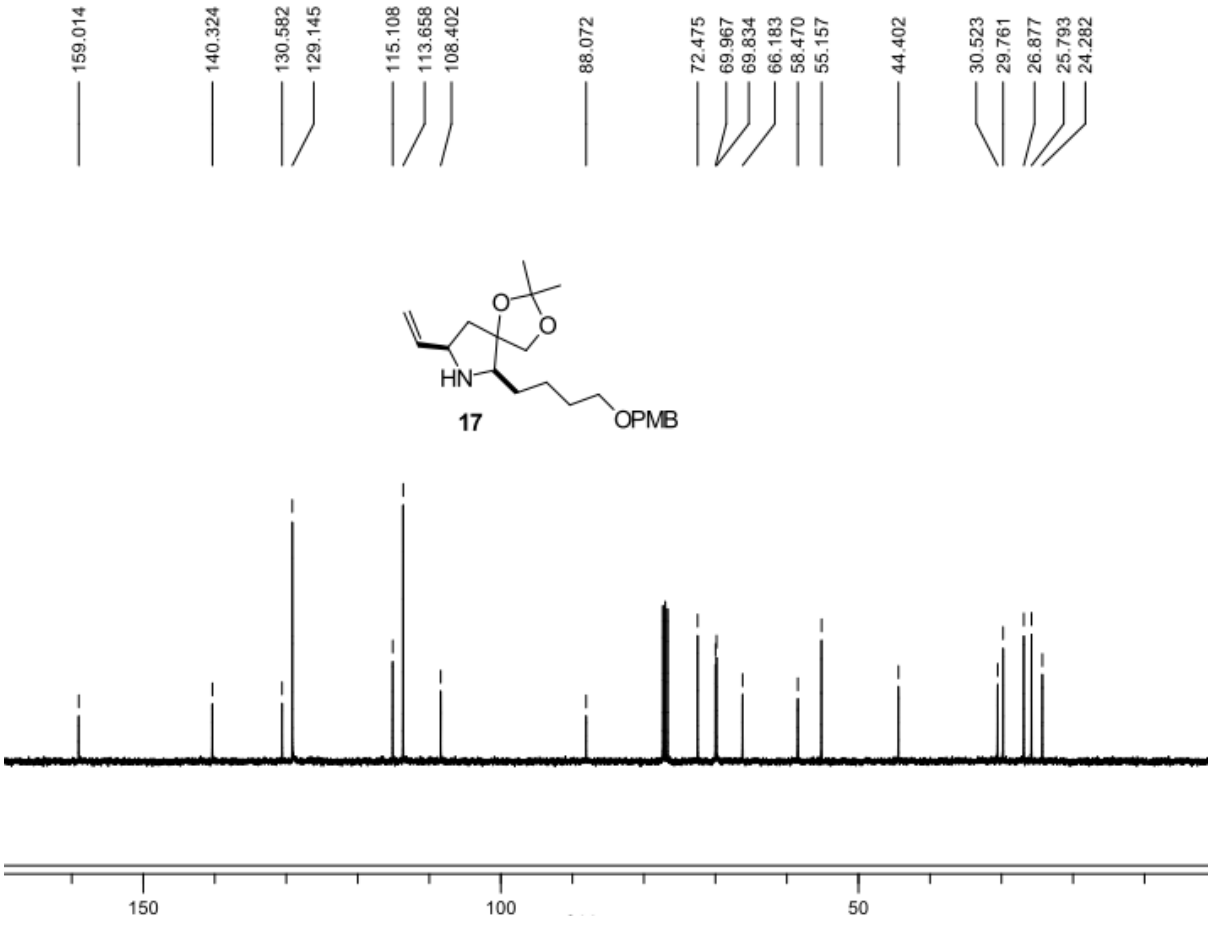
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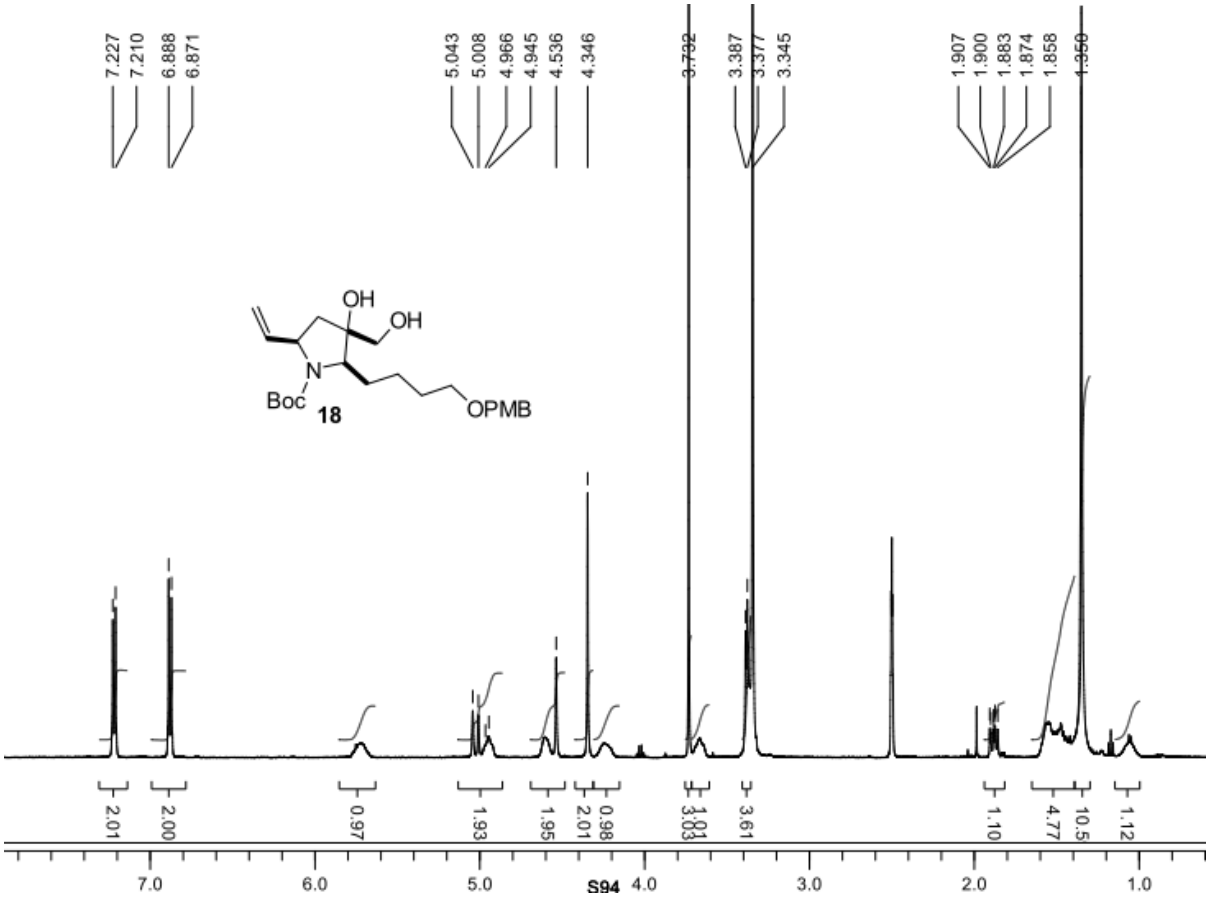
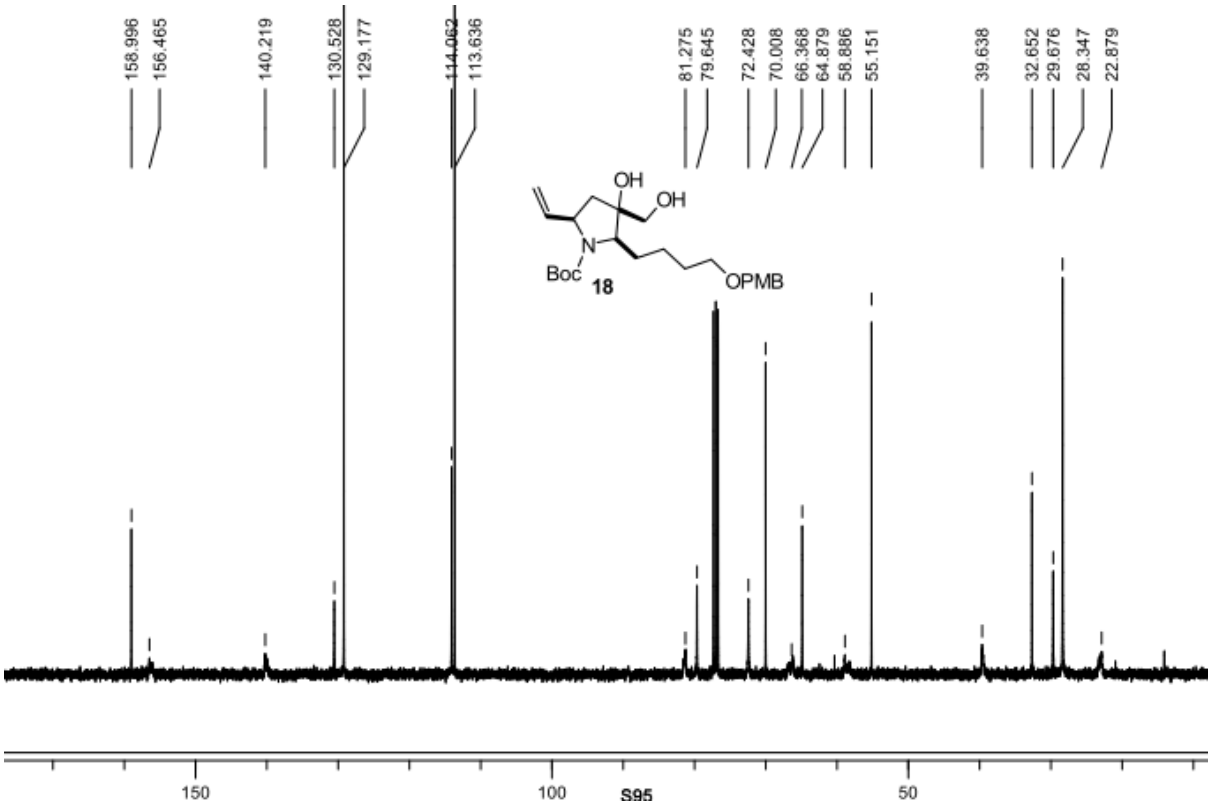


S94



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