Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cobalt(III)-Catalysed C-H Allylation with Vinylaziridines

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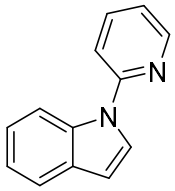
I. General considerations

All reagents were obtained from commercial sources and used as received. Solvents (THF, DCM, toluene and Et_2O) were purified and dried over Braun solvent purification system (MB-SPS-800) or dried by standard procedures prior to use.[1] Analytical Thin Layer Chromatography (TLC) was carried out on Merck silica gel60 F_{254}. Products were revealed by ultraviolet light (254 or 366 nm) and stained with dyeing reagents solutions as 5% phosphomolybdic acid solution, potassium permanganate solution or *p*-anisaldehyde solution in ethanol followed by gentle heating. Flash chromatography was performed on Combiflash® Companion or with Merck silica gel 60 (230-400 mesh). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$, DMSO-d_6 or acetone- d_6 at ambient temperature on Bruker Avance III 300 or 400 spectrometers operating at 300 and 400 MHz respectively for ^{1}H. ^{13}C nucleus was observed with ^{1}H decoupling. Solvent residual signals were used as internal standard.[2] Chemical shifts (δ) and coupling constants (*J*) are given in ppm and Hz respectively. The peaks patterns are indicated as the following format multiplicity (s: singlet; d: doublet; t: triplet; q: quartet; sept: septuplet; m: multiplet; dd: doublet of doublet; dt: doublet of triplet; dm: doublet of multiplet, etc.). The prefix br. indicates a broadened signal. HRMS were recorded on SYNAPT G2 HDMS (Waters) or on QStar Elite (Applied Biosystems SGIEX) equipped with an Atmospheric Pressure Ionization (API) source. Mass spectra were obtained using a Time Of Flight (TOF) analyser.

II. Synthesis of aromatic substrates for C-H activation

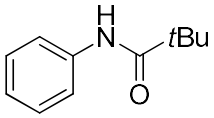
1-(Pyridin-2-yl)-1*H*-indole 1g[3]



A mixture of indole (1.17 g, 10 mmol), 2-bromopyridine (1.88 g, 12 mmol, 1.2 equiv.) and KOH (1.4 g, 25 mmol, 2.5 equiv.) in DMSO (12 mL) was stirred at 120 °C for 2 days. After cooling to room temperature, water (20 mL) was added to the mixture. The aqueous phase was extracted by ethyl acetate (3 x 50 mL). The combined organic phases were washed with water (3 x 20 mL), dried over Na_2SO_4 and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc 10:1) to give a yellow oil: 1.8 g (92 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.03 (ddd, *J*(H,H) = 4.9, 2.0 and 0.9 Hz, 1H, H^{Ar}), 8.67 (dt, *J*(H,H) = 8.3 and 0.9 Hz, 1H, H^{Ar}), 8.27 (ddd, *J*(H,H) = 8.3, 7.3 and 0.9 Hz, 1H, H^{Ar}), 8.18 (d, *J*(H,H) = 3.5 Hz, 1H, H^{Ar}), 8.12 (*J*(H,H) = 7.7 and 1.0 Hz, 1H, H^{Ar}), 7.95 (dd, *J*(H,H) = 8.2 and 0.9 Hz, 1H, H^{Ar}), 7.82-7.53 (m, 3H, H^{Ar}), 7.18 (dd, *J*(H,H) = 3.5 and 0.8 Hz, 1H, H^{Ar}). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 152.5 (*C*), 149.0 (*C*H), 138.5 (*C*H), 135.1 (*C*), 130.5 (*C*), 126.0 (*C*H), 123.2 (*C*H), 121.3 (*C*H), 121.2 (*C*H), 120.1 (*C*H), 114.6 (*C*H), 113.01 (*C*H), 105.6 (*C*H).

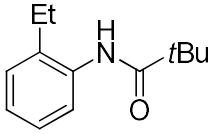
N-Phenylpivalamide 1k[4]



A solution of pivaloyl chloride (0.91 mL, 10 mmol, 1 equiv.) in dichloromethane (20 mL) was added to a solution of aniline (1.22 mL, 10 mmol) and triethylamine (2.76 mL, 20 mmol, 2 equiv.) in dichloromethane (20 mL) at 0 ˚C under argon atmosphere. The reaction was stirred at room temperature for 16 h. The mixture was washed with water (20 mL) and brine (20 mL), dried by $MgSO_4$, concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc 4:1) to give a white solid: 1.1 g (65 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.36 (m, 2H, H^{Ar}), 7.43-7.22 (m, 2H, H^{Ar}),7.17-6.97 (m, 1H, H^{Ar}), 1.32 (s, 9H, C(CH_3)$_3$). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 176.7 (*C*), 138.2 (*C*), 129.0 (*C*H), 124.3 (*C*H), 120.2 (*C*H), 39.7 (*C*), 27.7 (*C*H$_3$)

***N*-(2-Ethylphenyl)pivalamide 1l[4]**

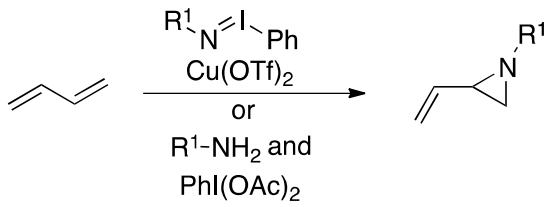


A solution of pivaloyl chloride (0.61 mL, 4.96 mmol, 1 equiv.) in dichloromethane (10 mL) was added to a solution of 2-ethyl-aniline (0.62 mL, 4.96 mmol) and triethylamine (1.40 mL, 9.91 mmol, 2 equiv.) in dichloromethane (10 mL) at 0 ˚C under argon atmosphere. The reaction was stirred at room temperature for 16 h. The mixture was washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc 4:1) to afford a white solid: 1.00 g (99 % yield)

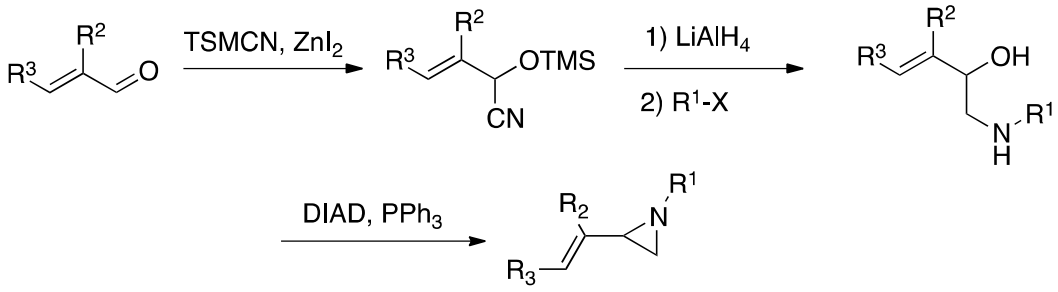
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J*(H,H) = 7.9 and 1.3 Hz, 1H H^{Ar}), 7.51-7.17 (m, 2H, H^{Ar}),7.10 (td, *J*(H,H) = 7.5 and 1.3 Hz, 1H, H^{Ar}), 2.60 (q, *J*(H,H) = 7.6 Hz, 2H, CH_2), 1.34 (s, 9H, C(CH_3)$_3$), 1.25 (t, *J*(H,H) = 7.6 Hz, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 176.6 (*C*), 135.4 (*C*), 134.67 (*C*), 128.6 (*C*H), 126.9 (*C*H), 125.3 (*C*H), 123.4 (*C*H), 39.9 (*C*), 27.8 (*C*H$_3$), 24.6 (*C*H$_2$), 14.0 (*C*H$_3$).

III. Vinylaziridine Synthesis

Route A



Route B



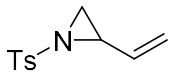
N-(*p*-Methylphenylsulfonyl)imino]phenyliodinane[5]

PhI=NTs

To a solution of *p*-toluenesulfonamide (3.42 g, 20 mmol) and potassium hydroxide (2.8 g, 50 mmol, 2.5 equiv.) in dry MeOH (80 mL), (diacetoxyiodo)benzene (6.44 g, 20 mmol, 1.0 equiv.) was added portionwise at 0 °C. The resulting reaction mixture was stirred at room temperature for 3 h. The reaction mixture was poured into water (200 mL) and aged in refrigerator overnight to precipitate a yellow solid, which was recrystallized to give a yellow solid: 2.6 g (35% yield).

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.71-7.67 (m, 2H, *H*^{Ar}), 7.48-7.40 (m, 3H, *H*^{Ar}), 7.29 (t, *J*(H,H) = 7.7 Hz, 2H, *H*^{Ar}), 7.09 (t, *J*(H,H) = 8.0 Hz, 2H, *H*^{Ar}), 2.27 (s, 3H, C*H*$_3$). **^{13}C NMR (75 MHz, DMSO-d$_6$):** δ = 142.1 (*C*), 140.2 (*C*), 137.0 (*C*), 133.1 (*C*H), 130.4 (*C*H), 130.1 (*C*H), 128.6 (*C*H), 126.1 (*C*H), 20.7 (*C*H$_3$).

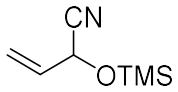
1-Tosyl-2-vinylaziridine 2a[6]



PhI=NTs (3.37 g, 10 mmol, 1 equiv.) was added to a solution of 1,3- butadiene (0.84 mL, 10 mmol) and Cu(OTf)$_2$ (0.36 g, 1 mmol, 0.1 equiv.) in dry MeCN (20 mL) at 0 ˚C under argon atmosphere. The reaction was stirred at room temperature for 3 h. The mixture was poured into 1M NaOH (200 mL) and extracted with diethyl ether (200 mL x 2). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 10:1) to afford a white solid: 900 mg (40% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.83 (d, *J*(H,H) = 8.3 Hz, 2H, *H*^{Ar}), 7.34 (d, *J*(H,H) = 8.6 Hz, 2H, *H*^{Ar}), 5.52 (ddd, *J*(H,H) = 17.0, 9.9 and 7.1 Hz, 1H, CH$_2$=C*H*), 5.42 (dd, *J*(H,H) = 17.2 and 1.6 Hz, 1H, C*H*$_2$=CH), 5.30-5.14 (m, 1H, C*H*$_2$=CH), 3.27 (td, *J*(H,H) = 7.1 and 4.5 Hz, 1H, C*H*), 2.78 (d, *J*(H,H) = 7.1 Hz, 1H, C*H*$_2$), 2.44 (s, 3H, CH$_3$), 2.22 (d, *J*(H,H) = 4.5 Hz, 1H, C*H*$_2$). **^{13}C NMR (75 MHz, CDCl$_3$):** δ = 144.7 (*C*), 135.2 (*C*), 133.1 (*C*H), 129.9 (*C*H), 128.0 (*C*H), 120.4 (*C*H$_2$), 41.1 (*C*H), 34.3 (*C*H$_2$), 21.8 (*C*H$_3$).

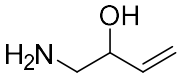
2-((Trimethylsilyl)oxy)but-3-enenitrile[7]



A mixture of freshly distilled acrolein (3.3 mL, 50 mmol), TMSCN (6.3 mL, 50 mmol, 1.0 equiv.) and a minute amount of zinc iodide (30 mg) was heated for 2 h under reflux. The reaction was monitored by ^{1}HNMR. The title product was obtained after distillation under reduced pressure (75 °C, 100 mbar) to give a colorless liquid: 5.23 g (67% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90 (ddd, *J*(H,H) = 16.9, 10.1 and 5.2 Hz, 1H, CH_2=C*H*), 5.55 (dd, *J*(H,H) = 16.9 and 1.3 Hz, 1H, CH_2=CH), 5.38 (dd, *J*(H,H) = 10.1 and 1.3 Hz, 1H, CH_2=CH), 4.95 (dt, *J*(H,H) = 5.2 and 1.4 Hz, 1H, C*H*), 0.23 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 132.9 (*C*H), 118.8 (*C*H_2), 118.2 (*C*), 62.4 (*C*H), 0.17(*C*H_3).

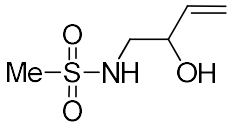
1-Aminobut-3-en-2-ol[7]



A solution of 2-((trimethylsilyl)oxy)but-3-enenitrile (5.2 g, 33mmol) in anhydrous diethyl ether (40 mL) was added dropwise to a suspension of $LiAlH_4$ (2.6 g, 70 mmol, 2.1 equiv.) in anhydrous diethyl ether (80 mL). After refluxing during 75 min., the reaction mixture was cooled to room temperature. Triethanolamine (10.8 g, 72.6 mmol, 2.2 equiv.) was then added under stirring over 20 min. followed by water (2.6 mL, 144 mmol, 4.4 equiv.) over 10 min.. A greyish mass was formed and the stirring was continued for 24 h. The mixture was then filtered and the solid was washed with diethyl ether (30 mL x 3). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was distilled under reduced pressure (85 °C, 35 mbar) to give a colorless liquid: 1.17 g (40% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (ddd, *J*(H,H) = 17.2, 10.5 and 5.5 Hz, 1H, CH_2=C*H*), 5.31 (dt, *J*(H,H) = 17.2 and 1.6 Hz, 1H, CH_2=CH), 5.17 (dt, *J*(H,H) = 10.5 and 1.6 Hz, 1H, CH_2=CH), 4.07 (dddt, *J*(H,H) = 7.1, 5.6, 4.1 and 1.4 Hz, 1H, C*H*), 2.84 (dd, , *J*(H,H) = 12.8 and 4.2 Hz, 1H, CH_2), 2.65 (dd, *J*(H,H) = 12.8 and 7.1 Hz, 1H, CH_2), 1.87 (br, 3H, NH_2 and O*H*). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 139.1 (*C*H), 115.6 (*C*H_2), 73.1 (*C*H), 47.1 (*C*H_2).

***N*-(2-Hydroxybut-3-en-1-yl)methanesulfonamide**

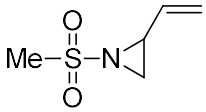


A solution of methanesulfonyl chloride (262 mg, 2.3 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added dropwise to a solution of 1-aminobut-3-en-2-ol (200 mg, 2.3 mmol) and Et_3N (0.63 mL, 4.6 mmol, 2.0 equiv.) in dichloromethane (15 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The resulting mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and

concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 1:2) to give a colorless oil: 250 mg (72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (ddd, *J*(H,H) = 17.2, 10.5 and 5.6 Hz, 1H, CH_2=C*H*), 5.38 (dt, *J*(H,H) = 17.2 and 1.4 Hz, 1H, CH_2=CH), 5.26 (dt, *J*(H,H) = 10.5 and 1.4 Hz, 1H, CH_2=CH), 4.96 (s, 1H, NH), 4.33 (ddt, *J*(H,H) = 5.4, 3.5 and 1.8 Hz, 1H, C*H*), 3.32 (ddd, *J*(H,H) = 13.3, 7.4 and 3.5 Hz, 1H, CH_2), 3.18-3.07 (m, 1H, CH_2), 3.00 (s, 3H, CH_3), 2.43 (d, 1H, O*H*). **^{13}C NMR (75 MHz, $CDCl_3$):** 137.2 (*C*H_2), 117.0 (*C*H), 71.6 (*C*H), 48.5 (*C*H_2), 40.4 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_5H_{11}NO_3SNa^+$: 188.0352 [M+Na]$^+$: found 138. 0348.

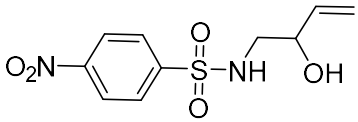
1-(Methylsulfonyl)-2-vinylaziridine 2b[8]



A solution of diisopropyl azodicarboxylate (347 mg, 1.3 mmol, 1.0 equiv.) in anhydrous THF (2 mL) was added dropwise to a solution of *N*-(2-hydroxybut-3-en-1-yl)methanesulfonamide (200 mg, 1.3 mmol) and PPh_3 (267 mg, 1.3 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at 0 ˚C under argon. The reaction mixture was stirred at 0 ˚C for 1h and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 2:1) to give a yellow oil: 147 mg (77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.64-5.54 (m, 1H, CH_2=C*H*), 5.54-5.48 (m, 1H, CH_2=CH), 5.37-5.29 (m, 1H, CH_2=CH), 3.21 (td, *J*(H,H) = 6.9 and 4.5 Hz, 1H, C*H*), 3.06 (s, 3H, CH_3), 2.77 (d, *J*(H,H) = 7.1 Hz, 1H, CH_2), 2.26 (d, *J*(H,H) = 4.5 Hz, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 133.0 (*C*H), 120.5 (*C*H_2), 40.6 (*C*H_3), 39.8 (*C*H), 33.6 (*C*H_2).

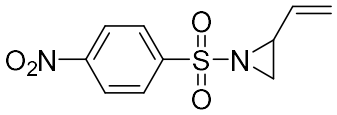
***N*-(2-Hydroxybut-3-en-1-yl)-4-nitrobenzenesulfonamide**



A solution of 4-nitrobenzenesulfonyl chloride (505 mg, 2.3 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added dropwise to a solution of 1-aminobut-3-en-2-ol (200 mg, 2.3 mmol) and Et_3N (0.63 mL, 4.6 mmol, 2.0 equiv.) in dichloromethane (15 mL) at 0 ˚C. The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The resulting mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 1:1) to give a yellow solid: 510 mg (82% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.37 (d, *J*(H,H) = 8.9 Hz, 2H, *H*^{Ar}), 8.06 (d, *J*(H,H) = 8.9 Hz, 2H, *H*^{Ar}), 5.78 (ddd, *J*(H,H) = 17.2, 10.5, and 5.7 Hz, 1H, CH_2=C*H*), 5.32 (dt, *J*(H,H) = 17.2 and 1.3 Hz, 1H, CH_2=CH), 5.27 (br, 1H, NH), 5.23 (dt, *J*(H,H) = 10.5 and 1.3Hz, 1H, CH_2=CH), 4.27 (dt, *J*(H,H) = 7.5 and 4.3 Hz, 1H, C*H*), 3.23 (dd, *J*(H,H) = 12.9 and 3.6 Hz, 1H, CH_2), 2.94 (dd, *J*(H,H) = 12.9 and 7.8 Hz, 1H, CH_2), 2.13 (br, 1H, O*H*). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 150.2 (*C*), 145.8 (*C*), 136.7 (*C*H), 128.5(*C*H), 124.6 (*C*H), 117.8 (*C*H_2), 71.5 (*C*H), 48.2 (*C*H_2). **HRMS (ESI):** *m/z*: calcd for $C_{10}H_{16}N_3O_5S^+$: 290.0805 [M+NH_4]$^+$: found 290.0805.

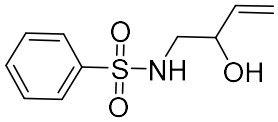
1-((4-Nitrophenyl)sulfonyl)-2-vinylaziridine 2c[9]



A solution of diisopropyl azodicarboxylate (212 mg, 0.74 mmol, 1.0 equiv.) in anhydrous THF (2 mL) was added dropwise to a solution of *N*-(2-hydroxybut-3-en-1-yl)benzenesulfonamide (200 mg, 0.74 mmol) and PPh_3 (163 mg, 0.74 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at 0 ˚C under argon. The reaction mixture was stirred at 0 ˚C for 1h and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/Et_2O 5:1) to give a yellow solid: 60 mg (32% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J*(H,H) = 8.9 Hz, 2H, H^{Ar}), 8.16 (d, *J*(H,H) = 8.9 Hz, 2H, H^{Ar}), 5.57-5.48 (m, 1H, CH_2=C*H*), 5.48-5.43 (m, 1H, CH_2=CH), 5.34-5.26 (m, 1H, CH_2=CH), 3.40 (td, *J*(H,H) = 6.8 and 4.7 Hz, 1H, C*H*), 2.91 (d, *J*(H,H) = 7.2 Hz, 1H, CH_2), 2.33 (d, *J*(H,H) = 4.7 Hz, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 150.8 (*C*), 144.2 (*C*), 132.4 (*C*H), 129.2 (*C*H), 124.5 (*C*H), 121.3 (*C*H_2), 42.0 (*C*H), 34.9 (*C*H_2).

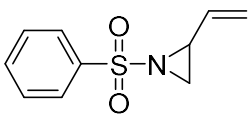
***N*-(2-Hydroxybut-3-en-1-yl)benzenesulfonamide**



A solution of benzenesulfonyl chloride (402 mg, 2.3 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added dropwise to a solution of 1-aminobut-3-en-2-ol (200 mg, 2.3 mmol) and Et_3N (0.63 mL, 4.6 mmol, 2.0 equiv.) in dichloromethane (15 mL) at 0 ˚C. The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The resulting mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 1:1) to give a colorless oil: 440 mg (77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95-7.76 (m, 2H, H^{Ar}), 7.63-7.45 (m, 3H, H^{Ar}), 5.77 (dddd, *J*(H,H) = 17.2, 10.5, 5.7 and 0.8 Hz, 1H, CH_2=C*H*), 5.30 (dt, *J*(H,H) = 17.2 and 1.3 Hz, 1H, CH_2=CH), 5.20 (dt, *J*(H,H) = 10.5 and 1.3Hz, 1H, CH_2=CH), 4.99 (br, 1H, N*H*), 4.31-4.16 (m, 1H, C*H*), 3.28-3.07 (m, 1H, CH_2), 2.98-2.72 (m, 1H, CH_2), 2.20 (br, 1H, O*H*). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 139.7 (*C*), 137.1 (*C*H), 132.9 (*C*H), 129.3(*C*H), 127.1(*C*H), 117.3 (*C*H_2), 71.4 (*C*H), 48.4 (*C*H_2). **HRMS (ESI):** *m/z*: calcd for $C_{10}H_{13}NO_3SNa^+$: 250.0508 $[M+Na]^+$: found 250.0510.

1-(Phenylsulfonyl)-2-vinylaziridine 2d[10]

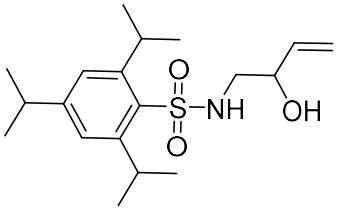


A solution of diisopropyl azodicarboxylate (196 mg, 0.88 mmol, 1.0 equiv.) in anhydrous THF (2 mL) was added dropwise to a solution of *N*-(2-hydroxybut-3-en-1-

yl)benzenesulfonamide (200 mg, 0.88 mmol) and PPh_3 (254 mg, 0.88 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at 0 ˚C under argon. The reaction mixture was stirred at 0 ˚C for 1h and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/Et_2O 10:1) to give a colorless oil: 140 mg (76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, *J*(H,H) = 8.4 and 1.4 Hz, 2H, H^{Ar}), 7.70-7.63 (m, 1H, H^{Ar}), 7.61-7.54 (m, 2H, H^{Ar}), 5.52 (ddd, *J*(H,H) = 16.9, 9.7 and 7.1 Hz, 1H, CH_2=C*H*), 5.46-5.38 (m, 1H, C*H*$_2$=CH), 5.25 (dd, *J*(H,H) = 10.1 and 1.5 Hz, 1H, C*H*$_2$=CH), 3.34 (m, 1H, C*H*), 2.82 (d, *J*(H,H) = 7.1 Hz, 1H, C*H*$_2$), 2.24 (d, *J*(H,H) = 4.5 Hz, 1H, C*H*$_2$). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 138.2(*C*), 133.7 (*C*H), 132.9 (*C*H), 129.2 (*C*H), 127.9 (*C*H), 120.6 (*C*H_2), 41.2 (*C*H), 34.4 (*C*H_2).

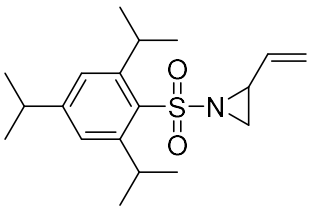
N-(2-Hydroxybut-3-en-1-yl)-2,4,6-triisopropylbenzenesulfonamide



A solution of 2,4,6-triisopropylbenzenesulfonyl chloride (694 mg, 2.3 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added dropwise to a solution of 1-aminobut-3-en-2-ol (200 mg, 2.3 mmol) and Et_3N (0.63 mL, 4.6 mmol, 2.0 equiv.) in dichloromethane (15 mL) at 0 ˚C. The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The resulting mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 3:1) to give a white solid: 350 mg (43% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (s, 2H, H^{Ar}), 5.80 (ddd, *J*(H,H) = 17.2, 10.5 and 5.7 Hz, 1H, CH_2=C*H*), 5.32 (dt, *J*(H,H) = 17.2 and 1.4 Hz, 1H, C*H*$_2$=CH), 5.21 (dt, *J*(H,H) = 10.5 and 1.4 Hz, 1H, C*H*$_2$=CH), 4.80 (dd, *J*(H,H) = 17.2, and 1.4 Hz, 1H, N*H*), 4.29 (ddt, *J*(H,H) = 5.3, 3.9 and 1.9 Hz, 1H, C*H*-OH), 4.17-4.11 (m, *J*(H,H) = 17.2 and 1.4 Hz, 2H, C*H*$(CH_3)_2$), 3.19-3.14 (m, 1H, C*H*$(CH_3)_2$), 2.94-2.87 (m, 2H, C*H*$_2$), 1.99 (d, *J*(H,H) = 4.3 Hz, 1H, O*H*), 1.28-1.25 (m, 18H, CH(C*H*$_3$)$_2$)). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 153.0 (*C*), 150.4 (*C*), 137.4 (*C*H), 132.3 (*C*), 124.0 (*C*H), 117.3 (*C*H_2), 71.4 (*C*H), 48.1 (*C*H_2), 34.3 (*C*H), 29.8 (*C*H), 25.0 (*C*H_3), 25.7 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{19}H_{32}NO_3S^+$: 354.2097 $[M+H]^+$: found 354.2099.

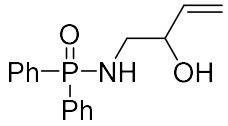
1-((2,4,6-Triisopropylphenyl)sulfonyl)-2-vinylaziridine 2e



A solution of diethyl azodicarboxylate (224 mg, 1.29 mmol, 1.3 equiv.) in anhydrous THF (2 mL) was added dropwise to a solution of *N*-(2-hydroxybut-3-en-1-yl)-2,4,6-triisopropylbenzenesulfonamide (350 mg, 0.99 mmol) and PPh_3 (311 mg, 1.18 mmol, 1.2

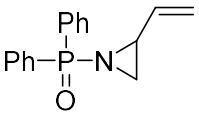
equiv.) in anhydrous THF (20 mL) at 0 ˚C under argon. The reaction mixture was stirred at 0 ˚C for 1h and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/Et_2O 50:1) to give a white solid: 190 mg (57% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (s, 2H, H^{Ar}), 5.53 (ddd, *J*(H,H) = 17.3, 10.1 and 7.3 Hz, 1H, C*H*=CH_2), 5.39 (dd, *J*(H,H) = 17.3 and 1.3 Hz, 1H, CH=CH_2), 5.22 (dd, *J*(H,H) = 10.1 and 1.3 Hz, 1H, CH=CH_2), 4.33 (hept, *J*(H,H) = 6.7 Hz, 2H, C*H*(CH_3)$_2$), 3.33 (td, *J*(H,H) = 7.1 and 4.4 Hz, 1H, C*H*), 2.90-2.82 (m, 1H, C*H*(CH_3)$_2$), 2.83 (d, *J*(H,H) = 7.1 Hz, 1H, CH_2), 2.19 (d, *J*(H,H) = 4.4 Hz, 1H, N-CH_2), 1.31-1.20 (dd, *J*(H,H) = 6.8 and 1.3 Hz, 18H, CH(CH_3)$_2$). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 153.5 (*C*), 151.2 (*C*), 133.7 (*C*H), 131.7 (*C*), 123.9 (*C*H), 119.8 (*C*H_2), 40.6 (*C*H), 34.4 (*C*H), 34.3 (*C*H_2), 29.9 (*C*H), 25.0 (*C*H_3), 23.7 (*C*H_3). **HRMS (ESI)**: *m/z*: calcd for $C_{19}H_{30}NO_2S^+$: 336.1992 [M+H]$^+$: found 336.1992.

N-(2-Hydroxybut-3-en-1-yl)-P,P-diphenylphosphinic amide



A solution of diphenylphosphinic chloride (542 mg, 2.3 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added dropwise to a solution of 1-aminobut-3-en-2-ol (200 mg, 2.3 mmol) and Et_3N (0.63 mL, 4.6 mmol, 2.0 equiv.) in dichloromethane (15 mL) at 0 ˚C. The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The resulting mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (dichloromethane/methanol10:1) to give a white solid: 550 mg (83% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99-7.80 (m, 4H, H^{Ar}), 7.57-7.38 (m, 6H, H^{Ar}), 5.80 (ddd, *J*(H,H) = 17.2, 10.5 and 5.0 Hz, 1H, CH_2=C*H*), 5.38 (dt, *J*(H,H) = 17.2 and 1.6 Hz, 1H, CH_2=CH), 5.20 (dt, *J*(H,H) = 10.5 and 1.6Hz, 1H, CH_2=CH), 4.65 (d, *J*(H,H) = 5.6 Hz, 1H, OH), 4.29-4.24 (m, 1H, C*H*), 3.36-3.33 (m, 1H, NH), 3.20-3.10 (m, 1H, CH_2), 3.05-2.94 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 138.2 (*C*H), 132.4 (d, ^{2}*J*(C,P) = 9.6 Hz, *C*H), 132.2 (d, ^{2}*J*(C,P) = 9.3 Hz, *C*H), 132.0 (d, ^{1}*J*(C,P) = 130.3 Hz, *C*), 131.7 (d, ^{1}*J*(C,P) = 130.7 Hz, *C*), 131.1 (d, ^{3}*J*(C,P) = 3.3 Hz, *C*H), 128.8 (d, ^{4}*J*(C,P) = 1.4 Hz, *C*H), 128.7 (d, ^{4}*J*(C,P) = 1.4 Hz, *C*H), 116.3 (*C*H_2), 72.5 (d, ^{3}*J*(C,P) = 3.8 Hz, *C*H), 47.7 (d, ^{2}*J*(C,P) = 2.0 Hz, *C*H_2). **^{31}P NMR (121 MHz, $CDCl_3$)** : 26.7 (s). **HRMS (ESI):** *m/z*: calcd for $C_{16}H_{19}NO_2P^+$: 288.1148 [M+H]$^+$: found 288.1149.

Diphenyl(2-vinylaziridin-1-yl)phosphine oxide 2f

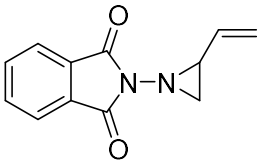


A solution of diisopropyl azodicarboxylate (200 mg, 1.00 mmol, 1.0 equiv.) in anhydrous THF (2 mL) was added dropwise to a solution of t N-(2-Hydroxybut-3-en-1-yl)-P,P-diphenylphosphinic amide (280 mg, 1.00 mmol) and PPh_3 (260 mg, 1.00 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at 0 ˚C under argon. The reaction mixture was stirred at 0 ˚C

for 1h and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc 1:4) to give a white solid: 180 mg (67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00-7.77 (m, 4H, H^{Ar}), 7.59-7.34 (m, 6H, H^{Ar}), 5.66 (ddd, *J*(H,H) = 17.2, 10.3 and 7.8 Hz, 1H, CH_2=C*H*), 5.38 (dd, *J*(H,H) = 17.2 and 1.3 Hz, 1H, CH_2=CH), 5.20 (dd, *J*(H,H) = 10.3 and 1.3Hz, 1H, CH_2=CH), 3.33-3.03 (m, 1H, C*H*), 2.72 (ddd, *J*(H,H) = 17.3, 6.0 and 1.4 Hz, 1H, CH_2), 2.10 (ddd, *J*(H,H) = 13.2, 3.4 and 1.4 Hz, 1H, CH_2). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 136.0 (d, ^3J(C,P) = 5.0 Hz, *C*H), 133.0 (d, ^1J(C,P) = 127.1 Hz, *C*), 132.8 (d, ^1J(C,P) = 128.3 Hz, *C*), 131.9 (d, ^4J(C,P) = 2.6 Hz, *C*H), 131.8 (d, ^4J(C,P) = 2.6 Hz, *C*H), 131.7 (d, ^2J(C,P) = 9.4 Hz, *C*H), 131.1 (d, ^4J(C,P) = 9.4 Hz, *C*H), 128.6 (d, ^3J(C,P) = 3.8 Hz, *C*H), 128.5 (d, ^3J(C,P) = 3.8 Hz, *C*H), 118.8 (*C*H_2), 37.0 (d, ^2J(C,P) = 5.4 Hz, *C*H), 30.4 (d, ^2J(C,P) = 6.9 Hz, *C*H_2). **^{31}P NMR (162 MHz, $CDCl_3$):** 32.3 (s). **HRMS (ESI):** *m/z*: calcd for $C_{16}H_{17}NOP^+$: 270.1042 $[M+H]^+$: found 270.1043.

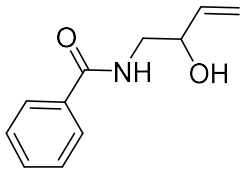
2-(2-Vinylaziridin-1-yl)isoindoline-1,3-dione 2g[11]



Butadiene (1.62 mL, 18.5 mmol, 3.0 equiv.) was added to a solution of 2-aminoisoindoline-1,3-dione (1 g, 6.17 mmol) and (diacetoxyiodo)benzene (1.41 g, 4.63 mmol, 0.75 equiv.) in anhydrous dichloromethane (30 mL) at -10 ˚C. The reaction temperature was slowly increased to room temperature and the reaction mixture was stirred at room temperature for 12 h. The transparent solution was then diluted wih dichloromethane (30 mL) and the mixture was washed with water (3 x 30 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/dichloromethane 1:1) to give a yellow solid: 450 mg (45% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81-7.74 (m, 2H, H^{Ar}), 7.72-7.65 (m, 2H, H^{Ar}), 5.78 (ddd, *J*(H,H) = 17.3, 10.3 and 7.0 Hz, 1H, CH_2=C*H*), 5.54 (dd, *J*(H,H) = 10.3 and 1.4 Hz, 1H, CH_2=CH), 5.36 (dd, *J*(H,H) = 10.3 and 1.4 Hz, 1H, CH_2=CH), 3.16-3.04 (m, 1H, C*H*), 2.73 (dd, *J*(H,H) = 7.8 and 2.3 Hz, 1H, CH_2), 2.51 (dd, *J*(H,H) = 5.8 and 2.3 Hz, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 165.1 (*C*), 134.3 (*C*H), 134.1 (*C*H), 130.5 (*C*), 123.2 (*C*H), 119.7 (*C*H_2), 44.1 (*C*H_2), 38.8 (*C*H).

***N*-(2-Hydroxybut-3-en-1-yl)benzamide**[12]

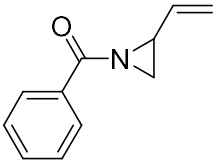


A solution of benzoyl chloride (322 mg, 2.3 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added dropwise to a solution of 1-aminobut-3-en-2-ol (200 mg, 2.3 mmol) and Et_3N (0.63 mL, 4.6 mmol, 2.0 equiv.) in dichloromethane (15 mL) at 0 ˚C. The reaction mixture

was stirred at room temperature for 12 h before adding water (100 mL). The resulting mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 1:2) to give a yellow oil: 300 mg (68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.69 (m, 2H, H^{Ar}), 7.56-7.47 (m, 1H, H^{Ar}), 7.46-7.37 (m, 2H, H^{Ar}), 6.6 (s, 1H, NH), 5.92 (ddd, *J*(H,H) = 17.1, 10.5 and 5.5 Hz, 1H, CH_2=C*H*), 5.39 (dt, *J*(H,H) = 17.2 and 1.5 Hz, 1H, CH_2=CH), 5.20 (dt, *J*(H,H) = 10.5 and 1.5Hz, 1H, CH_2=CH), 4.46-4.30 (m, 1H, C*H*), 3.77 (ddd, *J*(H,H) = 13.9, 6.5 and 3.4 Hz, 1H, CH_2), 3.40 (ddd, *J*(H,H) = 13.9, 7.3 and 5.1 Hz, 1H, CH_2), 2.78 (d, *J*(H,H) = 4.0 Hz, 1H, O*H*). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 168.7 (*C*), 138.0 (*C*H), 134.1(*C*), 131.7 (*C*H), 128.6 (*C*H), 127.1(*C*H), 116.3 (*C*H_2), 72.0 (*C*H), 45.8 (*C*H_2).

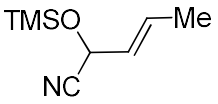
Phenyl(2-vinylaziridin-1-yl)methanone 2h[13]



A solution of diisopropyl azodicarboxylate (259 mg, 1.42 mmol, 1.0 equiv.) in anhydrous THF (2 mL) was added dropwise to a solution of N-(2-hydroxybut-3-en-1-yl)benzamide (220 mg, 1.42 mmol) and PPh_3 (329 mg, 1.42 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at 0 ˚C under argon. The reaction mixture was stirred at 0 ˚C for 1h and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc 50:1) to give a colorless oil: 55 mg (27% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-7.94 (m, 2H, H^{Ar}),7.63-7.50 (m, 1H, H^{Ar}), 7.50-7.38 (m, 2H, H^{Ar}), 5.64 (ddd, *J*(H,H) = 17.1, 10.2 and 7.8 Hz, 1H, CH_2=C*H*), 5.49 (dd, *J*(H,H) = 17.1 and 1.3 Hz, 1H, CH_2=CH), 5.32 (dd, *J*(H,H) = 10.1 and 1.3 Hz, 1H, CH_2=CH), 3.02 (ddd, *J*(H,H) = 7.8, 5.9 and 3.5 Hz, 1H, C*H*), 2.76 (d, *J*(H,H) = 5.9 Hz, 1H, CH_2), 2.24 (d, *J*(H,H) = 3.5 Hz, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 178.8 (*C*), 135.5 (*C*), 133.0 (*C*), 132.9 (*C*H), 129.4 (*C*H), 128.5 (*C*H), 119.6 (*C*H_2), 40.7 (*C*H), 32.5 (*C*H_2).

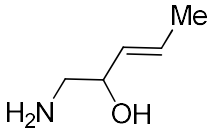
(*E*)-2-((Trimethylsilyl)oxy)pent-3-enenitrile[14]



A mixture of freshly distilled (*E*)-but-2-enal (4.1 mL, 50 mmol), TMSCN (6.3 mL, 50 mmol, 1.0 equiv.) and a minute amount of zinc iodide (30 mg) was heated for 2 h under reflux. The reaction was monitored by ^{1}HNMR. The title product was obtained after distillation under reduced pressure (78 °C, 100 mbar) to give a colorless liquid: 5.95 g (70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.07-5.85 (m, 1H, CH_3-CH=C*H*), 5.55 (ddq, *J*(H,H) = 15.2, 6.3 Hz and 1.7 Hz, 1H, CH_3-C*H*=CH), 4.88 (dt, *J*(H,H) = 6.1 and 1.1 Hz, 1H, C*H*), 1.76 (ddd, *J*(H,H) = 6.6, 1.8 Hz and 1.0 Hz, 3H, CH_3) 0.21 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 131.4 (*C*H), 126.3 (*C*H), 118.9 (*C*), 62.2 (*C*H), 17.5 (*C*H_3), 0.2 (*C*H_3).

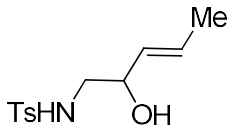
(*E*)-1-Aminopent-3-en-2-ol[15]



A solution of (*E*)-2-((trimethylsilyl)oxy)pent-3-enenitrile (4.23 g, 25 mmol) in anhydrous diethyl ether (40 mL) was added dropwise to a suspension of $LiAlH_4$ (1.99 g, 52 mmol, 2.1 equiv.) in anhydrous diethyl ether (80 mL). After refluxing during 75 min., the reaction mixture was cooled to room temperature. Triethanolamine (8.11 g, 52.4 mmol, 2.2 equiv.) was then added under stirring over 20 min. followed by water (1.87 mL, 110 mmol, 4.4 equiv.) over 10 min.. A greyish mass was formed and stirring was continued for 24 h. The mixture was then filtered and the solid was washed with diethyl ether (30 mL x 3). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was distilled under reduced pressure (90 °C, 35 mbar) to give a colorless liquid: 1.50 g (59% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88-5.59 (m, 1H, CH_3-CH=C*H*), 5.43 (ddq, *J*(H,H) = 15.3 Hz, 6.6 Hz and 1.6 Hz, 1H, CH_3-CH=C*H*), 3.99 (m, 1H, C*H*), 2.77 (dd, , *J*(H,H) = 12.7 and 4.3 Hz, 1H, CH_2), 2.65 (dd, *J*(H,H) = 12.7 and 7.4 Hz, 1H, CH_2), 2.00 (br, 3H, NH_2 and O*H*), 1.69 (ddd, *J*(H,H) = 6.5 Hz, 1.7 Hz and 0.9 Hz, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 131.8 (*C*H), 127.9 (*C*H), 73.2 (*C*H), 47.6 (*C*H_2), 17.9 (*C*H_3).

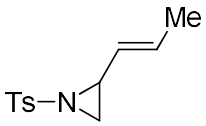
(*E*)-*N*-(2-Hydroxypent-3-en-1-yl)-4-methylbenzenesulfonamide[16]



A solution of 4-methylbenzenesulfonyl chloride (1.05 mg, 5.5 mmol, 1.1 equiv.) in dichloromethane (15 mL) was added dropwise to a solution of (*E*)-1-aminopent-3-en-2-ol (506 mg, 5 mmol) and Et_3N (1.35 mL, 10 mmol, 2.0 equiv.) in dichloromethane (15 mL) at 0 ˚C. The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The resulting mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/AcOEt 1:2) to give a yellow oil: 578 mg (45% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J*(H,H) = 8.3 Hz, 2H, H^{Ar}), 7.30 (d, *J*(H,H) = 8.0 Hz, 2H, H^{Ar}), 5.80-5.63 (m, 1H, CH_3-CH=C*H*), 5.37 (ddd, *J*(H,H) = 15.4, 6.8 and 1.7 Hz, 1H, CH_3-C*H*=CH), 5.04 (dd, *J*(H,H) = 7.5 and 5.1 Hz, 1H, O*H*), 4.14 (m, 1H, C*H*), 3.06 (ddd, *J*(H,H) = 12.8, 7.5 and 3.8 Hz, 1H, CH_2), 2.92-2.76 (m, 1H, CH_2), 2.42 (s, 3H, Ar-CH_3), 1.97 (br, 1H, N*H*), 1.66 (dd, *J*(H,H) = 6.8 and 1.8 Hz, 3H, CH-CH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** 143.6 (*C*), 136.9 (*C*), 130.2 (*C*H), 129.9 (*C*H), 129.5 (*C*H), 127.2 (*C*H), 71.3 (*C*H), 48.6 (*C*H_2), 21.7 (*C*H_3), 17.8 (*C*H_3).

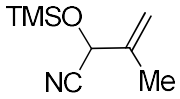
(*E*)-2-(Prop-1-en-1-yl)-1-tosylaziridine 2i[17]



A solution of diisopropyl azodicarboxylate (485 mg, 2.4 mmol, 1.2 equiv.) in anhydrous THF (2 mL) was added dropwise to a solution of (*E*)-*N*-(2-hydroxypent-3-en-1-yl)-4-methylbenzenesulfonamide (510 mg, 2 mmol) and PPh_3 (629 mg, 2.4 mmol, 1.2 equiv.) in anhydrous THF (20 mL) at 0 ˚C under argon. The reaction mixture was stirred at 0 ˚C for 1 h and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc 9:1) to give a colorless oil: 347 mg (73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J*(H,H) = 8.3 Hz, 2H, H^{Ar}), 7.3 (d, *J*(H,H) = 8.1 Hz, 2H, H^{Ar}), 5.88 (dq, *J*(H,H) = 15.5 and 6.6 Hz, 1H, CH_3-CH=C*H*), 5.15 (ddd, *J*(H,H) = 15.4, 7.8 and 1.7 Hz, 1H, CH_3-CH=C*H*), 3.27 (td, *J*(H,H) = 7.2 and 4.6 Hz, 1H, C*H*), 2.73 (d, *J*(H,H) = 7.1 Hz, 1H, CH_2), 2.44 (s, 3H, Ar-CH_3), 2.18 (d, *J*(H,H) = 4.6 Hz, 1H, CH_2), 1.68 (dd, *J*(H,H) = 6.6 and 1.7 Hz, 3H, CH-CH_3). **^{13}C NMR (100 MHz, $CDCl_3$):** 144.6 (*C*), 135.4 (*C*), 132.4 (*C*H), 129.8 (*C*H), 127.9 (*C*H), 126.1 (*C*H), 41.1(*C*H), 34.4 (*C*H_2), 21.7 (*C*H_3), 17.9 (*C*H_3).

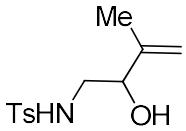
3-Methyl-2-((trimethylsilyl)oxy)but-3-enenitrile[18]



A mixture of freshly distilled methacrylaldehyde (500 mg, 7.1 mmol), TMSCN (700 mg, 7.1 mmol, 1.0 equiv.) and zinc iodide (15 mg) was heated for 1 h under reflux. The title product was obtained after distillation under reduced pressure (65°C, 35 mbar) to give a colorless liquid: 1.05 g (83% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.24 (q, *J*(H,H) = 1.0 Hz, 1H, CH_2=C), 5.06 (dt, *J*(H,H) = 1.6 and 0.8 Hz,1H, CH_2=C), 4.81 (t, *J*(H,H) = 1.0 Hz, 1H, C*H*), 1.86 (t, *J*(H,H) = 1.2 Hz, 3H, CH_3), 0.22 (s, 9H, Si(CH_3)$_3$). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 140.1 (*C*), 118.5 (*C*), 114.9 (*C*H_2), 65.6 (*C*H), 17.6 (*C*H_3), 0.3 (*C*H_3).

***N*-(2-Hydroxy-3-methylbut-3-en-1-yl)-4-methylbenzenesulfonamide**

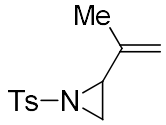


A solution of 3-methyl-2-((trimethylsilyl)oxy)but-3-enenitrile (1 g, 5.9 mmol) in anhydrous diethyl ether (10 mL) was added dropwise by dropping funnel to a suspension of $LiAlH_4$ (0.47 g, 14.9 mmol, 2.1 equiv.) in anhydrous diethyl ether (20 mL). After refluxing during 75 min., the reaction mixture was cooled to room temperature. Triethanolamine (1.93 g, 13 mmol, 2.2 equiv.) was then added under stirring over 20 min. followed by water (0.5 mL, 26 mmol, 4.4 equiv.) over 10 min.. A greyish mass was formed and stirring was continued for 24 h. The mixture was then filtered and the solid was washed with diethyl ether (3 x 30 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue and Et_3N (0.36 mL, 2.80 mmol, 2 equiv.) was dissolved in dichloromethane (10 mL), followed by a

solution of 4-methylbenzenesulfonyl chloride (260 mg, 1.34 mmol, 1 equiv.) in dichloromethane (5 mL). The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The resulting mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with brine (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc 1:1) to give a colorless oil: 300 mg (30% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J*(H,H) = 8.3 Hz, 2H, H^{Ar}), 7.36-7.29 (m, 2H, H^{Ar}), 5.00 (q, *J*(H,H) = 1.1 Hz, 1H, CH_2=C), 4.92 (dt, *J*(H,H) = 2.2 and 1.1 Hz, 1H, CH_2=C), 4.80-4.70 (m, 1H, C*H*), 4.12 (d, *J*(H,H) = 7.2 Hz, 1H, O*H*), 3.25-3.06 (m, 1H, CH_2), 2.89 (ddd, *J*(H,H) = 12.6, 7.9 and 4.5 Hz, 1H, CH_2), 2.43 (s, 3H, Ar-CH_3), 1.97 (br, 1H, N*H*), 1.66 (d, *J*(H,H) = 1.1 Hz, 3H, CH-CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 144.3 (*C*), 143.7 (*C*), 137.0 (*C*), 129.9 (*C*H), 127.3 (*C*H), 112.7 (*C*H_2), 73.8 (*C*H), 47.2 (*C*H_2), 21.7 (*C*H_3), 18.5 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{12}H_{18}NO_3S^+$: 256.1002 $[M+H]^+$: found 256.1003.

2-(Prop-1-en-2-yl)-1-tosylaziridine 2j



A solution of diisopropyl azodicarboxylate (178 mg, 0.76 mmol, 1.3 equiv.) in anhydrous THF (2 mL) was added dropwise to a solution of *N*-(2-hydroxy-3-methylbut-3-en-1-yl)-4-methylbenzenesulfonamide (150 mg, 0.59 mmol) and PPh_3 (200 mg, 0.76 mmol, 1.3 equiv.) in anhydrous THF (20 mL) at 0 ˚C under argon. The reaction mixture was stirred at 0 ˚C for 1h and concentrated. The residue was purified by silica gel flash chromatography (petroleum ether/EtOAc 10:1) to give a colorless oil: 90 mg (65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J*(H,H) = 8.3 Hz, 2H, H^{Ar}), 7.39-7.28 (m, 2H, H^{Ar}), 5.06 (dt, *J*(H,H) = 1.6 and 0.9 Hz, 1H, CH_2=C), 4.95 (t, *J*(H,H) = 1.5 Hz, 1H, CH_2=C), 3.26 (ddd, *J*(H,H) = 7.2, 4.6 and 0.9 Hz, 1H, C*H*), 2.72 (d, *J*(H,H) = 7.2 Hz, 1H, CH_2), 2.45 (s, 3H, Ar-CH_3), 2.30 (d, *J*(H,H) = 4.6 Hz, 1H, CH_2), 1.58 (t, *J*(H,H) = 1.2 Hz, 3H, CH-CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 144.6 (*C*), 139.0 (*C*), 135.3 (*C*), 129.8 (*C*H), 128.0 (*C*H), 115.6 (*C*H_2), 43.5 (*C*H), 32.6 (*C*H_2), 21.8 (*C*H_3), 17.9 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{12}H_{15}NO_2SNa^+$: 260.0716 $[M+Na]^+$: found 260.0716.

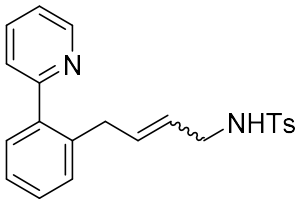
IV. Cobalt-mediated catalysis

General Procedure : Cobalt(III)-Catalysed C−H Allylation of Arene

In a dry Schlenk tube under argon atmosphere were introduced in turn Cp*Co(CO)I_2 (6.0 mg, 0.0125 mmol, 0.05 equiv.), $AgSbF_6$ (8.6 mg, 0.025 mmol, 0.1 equiv.), pivalic acid (2.4 mg, 0.025 mmol, 0.1 equiv.) and anhydrous 1,4-dioxane (0.5 mL). The mixture was stirred for 5 min. at room temperature before to add arene partner **1** (0.25 mmol) and vinylaziridine **2** (0.25 mmol, 1.0 equiv). The reaction was stirred at 40 ˚C for 2 h. Volatiles were removed under vacuum and the residue was purified by silica gel flash

chromatography to give the expected product as an inseparable mixture of *E*- and *Z*-isomers.

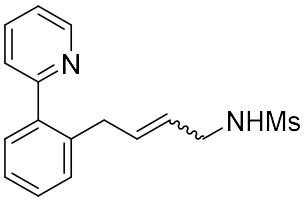
4-Methyl-*N*-(4-(2-(pyridin-2-yl)phenyl)but-2-en-1-yl)benzenesulfonamide 3aa



According to the general procedure, the product was isolated after silica gel flash chromatography (petroleum ether/EtOAc 1:1) as a colorless oil (*E*/*Z* = 1:1.3): 71 mg (75% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.71-8.60 (m, 1H, H^{Ar}), 7.81-7.63 (m, 3H, H^{Ar}), 7.44-7.00 (m, 8H, H^{Ar}), 5.67-5.48 (m, 1H, Ar-CH_2-C*H*=CH), 5.35-5.07 (m, 1H, Ar-CH_2-CH=C*H*), 4.62 (t, *J*(H,H) = 6.0 Hz, 0.56H, N*H, Z*-isomer), 4.12 (t, *J*(H,H) = 6.0 Hz, 0.47H, N*H, E*-isomer), 3.65-2.92 (m, 4H, Ar-CH_2-CH=CH-CH_2), 2.42 (s, 1.71H, CH_3), 2.41 (s, 1.29H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 159.9 (*C*), 159.8 (*C*), 149.2 (*C*H), 149.1 (*C*H), 143.33 (*C*), 143.30 (*C*), 140.4 (*C*), 140.2 (*C*), 137.9 (*C*), 137.4 (*C*), 137.3 (*C*), 137.2 (*C*), 136.6 (*C*H), 136.4 (*C*H), 133.4 (*C*H), 132.8 (*C*H), 130.1 (*C*H), 130.0 (*C*H), 128.8 (*C*H), 129.7 (*C*H), 128.7 (*C*H), 128.6 (*C*H), 127.2 (*C*H), 126.52 (*C*H), 126.48 (*C*H), 127.76 (*C*H), 124.75 (*C*H), 124.3 (*C*H), 124.2 (*C*H), 122.0 (*C*H), 121.9 (*C*H), 45.1 (*C*H_2), 39.9 (*C*H_2), 36.0 (*C*H_2), 31.2 (*C*H_2), 21.6 (*C*H_3). **HRMS (ESI)**: *m/z*: calcd for $C_{22}H_{23}N_2O_2S^+$: 379.1475 $[M+H]^+$: found 379.1475.

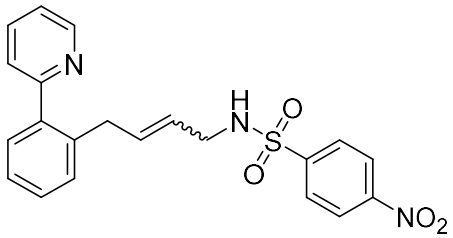
***N*-(4-(2-(Pyridin-2-yl)phenyl)but-2-en-1-yl)methanesulfonamide 3ab**



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 1:1) as a colorless oil (*E*/*Z* = 1: 1.2): 55 mg (72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 8.62-8.54 (m, 1H, H^{Ar}*)*, 7.73 (m, 1H, H^{Ar}), 7.41-7.15 (m, 6H, H^{Ar}), 5.72-5.59 (m, 1H, Ar-CH_2-C*H*=CH), 5.45-5.34 (m, 0.55H, Ar-CH_2-CH=C*H, Z*-isomer), 5.24-5.14 (m, 0.45H, Ar-CH_2-CH=C*H, E*-isomer), 4.93 (br, 0.51H, N*H, Z*-isomer), 4.29 (br, 0.44H, N*H, E*-isomer), 3.60-3.37 (m, 4H, Ar-CH_2-CH=CH-CH_2), 2.80 (s, 1.33H, CH_3), 2.77 (s, 1.67H, CH_3) **^{13}C NMR (75 MHz, $CDCl_3$):** 159.8 (*C*), 159.6 (*C*), 148.93 (*C*H), 148.87 (*C*H), 140.0 (*C*), 138.0 (*C*), 137.5 (*C*), 137.1 (*C*H), 136.9 (*C*H), 133.5 (*C*H), 133.1 (*C*H), 130.2 (*C*H), 130.1 (*C*H), 129.9 (*C*H), 129.0 (*C*H), 128.9 (*C*H), 126.7 (*C*H), 126.6 (*C*H), 126.3 (*C*H), 125.4 (*C*H), 124.5 (*C*H), 124.4 (*C*H), 122.2 (*C*H), 45.1 (*C*H_2, *E*), 40.8 (*C*H_3), 40.0 (*C*H_2, *E*), 36.0 (*C*H_2, *Z*), 31.2 (*C*H_2, *Z*). **HRMS (ESI):** *m/z*: calcd for $C_{16}H_{19}N_2O_2S^+$: 303.1162 $[M+H]^+$: found 303.1161.

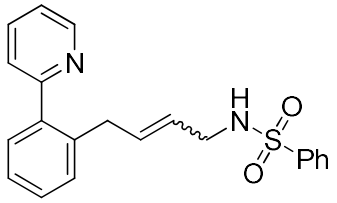
4-Nitro-*N*-(4-(2-(pyridin-2-yl)phenyl)but-2-en-1-yl)benzenesulfonamide 3ac



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 2:1) as a colorless oil (*E*/*Z* = 1: 1.2): 40 mg (61% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.73-8.60 (m, 1H, H^{Ar}), 8.43-8.08 (m, 2H, H^{Ar}), 8.03-7.88 (m, 1H, H^{Ar}), 7.89 -7.67 (m, 2H, H^{Ar}), 7.42-7.09 (m, 6H, H^{Ar}), 6.52 (s, 0.50H, N*H, Z*-isomer), 5.76-5.51 (m, 1H, Ar-CH_2-C*H*=CH), 5.44-5.23 (m, 0.56H, Ar-CH_2-CH=C*H, Z*-isomer), 5.17-5.02 (m, 0.46H, Ar-CH_2-CH=C*H, E*-isomer), 4.47 (s, 0.41H, N*H, E*-isomer), 3.68-3.13 (m, 4H, Ar-CH_2-CH=CH-CH_2). **^{13}C NMR (100 MHz, $CDCl_3$):** 159.8 (*C*), 159.7 (*C*), 150.0 (*C*), 149.8 (*C*), 149.2 (*C*H), 148.8 (*C*H), 146.9 (*C*), 146.4 (*C*), 140.4 (*C*), 139.8 (*C*), 137.6 (*C*), 137.2 (*C*H), 136.6 (*C*H), 134.0 (*C*H), 133.4 (*C*H), 130.3 (*C*H), 130.04 (*C*H), 130.03 (*C*H), 129.8 (*C*H), 128.9 (*C*H), 128.7 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 126.7 (*C*H), 126.6 (*C*H), 125.2 (*C*H), 124.7 (*C*H), 124.6 (*C*H), 124.3 (*C*H), 124.2 (*C*H), 122.3 (*C*H), 122.2 (*C*H), 45.2 (CH_2), 39.6 (CH_2), 36.0 (CH_2), 31.0 (CH_2). **HRMS (ESI):** m/z: calcd for $C_{21}H_{20}N_3O_4S^+$: 410.1169 $[M+H]^+$: found 410.1169.

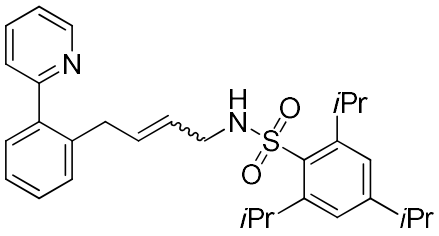
***N*-(4-(2-(Pyridin-2-yl)phenyl)but-2-en-1-yl)benzenesulfonamide 3ad**



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 2:1) as a colorless oil (*E*/*Z* = 1: 1.2): 80 mg (88% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.63 (m, *J*(H,H) = 8.8, 4.8 and 1.4 Hz, 1H, H^{Ar}), 7.85-7.65 (m, 3H, H^{Ar}), 7.57-7.36 (m, 3H, H^{Ar}), 7.34-7.11 (m, 6H, H^{Ar}), 5.62-5.44 (m, 1H, Ar-CH_2-C*H*=CH), 5.28-4.95 (m, 1.52H, Ar-CH_2-CH=C*H* and N*H, Z*-isomer), 4.64 (t, *J*(H,H) = 6.0 Hz, 0.45H, N*H, E*-isomer), 3.53-3.23 (m, 4H, Ar-CH_2-CH=CH-CH_2). **^{13}C NMR (75 MHz, $CDCl_3$):** 159.9 (*C*), 159.8 (*C*), 149.2 (*C*H), 149.1 (*C*H), 140.44 (*C*), 140.41 (*C*), 140.3 (*C*), 140.2 (*C*), 137.8 (*C*), 137.4 (*C*), 136.7 (*C*H), 136.4 (*C*H), 133.6(*C*H), 132.9 (*C*H), 132.60 (*C*H), 132.56 (*C*H), 130.13 (*C*H), 130.10 (*C*H), 129.98 (*C*H), 129.8 (*C*H), 129.1 (*C*H), 128.8 (*C*H), 128.6 (*C*H), 127.1 (*C*H), 126.6 (*C*H), 126.5 (*C*H), 125.6 (*C*H), 124.7 (*C*H), 124.3 (*C*H), 124.2 (*C*H), 122.03 (*C*H), 121.97 (*C*H), 45.2 (CH_2), 40.0 (CH_2), 36.0 (CH_2), 31.2 (CH_2). **HRMS (ESI):** m/z: calcd for $C_{21}H_{21}N_2O_2S^+$: 365.1318 $[M+H]^+$: found 365.1315; calcd for $C_{21}H_{20}N_2O_2SNa^+$: 387.1138 $[M+Na]^+$: found 387.1137.

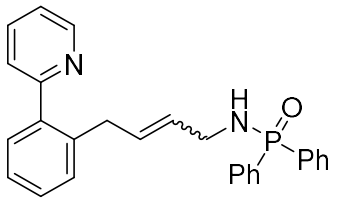
2,4,6-Triisopropyl-N-(4-(2-(pyridin-2-yl)phenyl)but-2-en-1-yl)benzenesulfonamide 3ae



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 4:1) as a colorless oil (*E*/*Z* = 1: 1.5): 70 mg (55% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.68-8.62 (m, 1H, H^{Ar}), 8.65 (tt, *J*(H,H) = 7.7 and 2.2 Hz, 1H, H^{Ar}), 7.49-7.06 (m, 8H, H^{Ar}), 5.71-5.38 (m, 1H, Ar-CH_2-C*H*=CH), 5.35-5.14 (m, 1H, Ar-CH_2-CH=C*H*), 4.41 (t, *J*(H,H) = 6.1 Hz, 0.66 H, N*H, Z*-isomer), 4.24-3.99 (m, 2H, C*H*(CH_3)$_2$), 3.55-3.37 (m, 4H, Ar-C*H*$_2$-CH=CH-C*H*$_2$), 2.98-2.79 (m, 1H, C*H*(CH_3)$_2$), 1.32-1.10 (m, 18H, CH(C*H*$_3$)$_3$). **NMR (75 MHz, $CDCl_3$):** 160.0 (*C*), 152.8 (*C*), 150.5 (*C*), 150.4 (*C*), 149.2 (*C*H), 140.5 (*C*), 140.3 (*C*), 137.9 (*C*), 137.4 (*C*), 136.6 (*C*), 136.4 (*C*H), 133.8 (*C*H), 133.1 (*C*H), 132.6 (*C*H), 130.2 (*C*H), 130.1 (*C*H), 130.0 (*C*H), 129.82 (*C*H), 128.76 (*C*H), 128.62 (*C*H), 126.61 (*C*H), 126.56 (*C*H), 125.9 (*C*H), 124.8 (*C*H), 124.3 (*C*H), 124.2 (*C*H), 123.9 (*C*H), 122.00 (*C*H), 121.95 (*C*H), 45.0 (*C*H_2), 39.7 (*C*H_2), 36.1 (*C*H_2), 34.3 (*C*H), 31.3 (*C*H_2), 29.72 (*C*H), 29.68 (*C*H), 24.99 (*C*H_3), 24.97 (*C*H_3), 23.7 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{30}H_{39}N_2O_2S^+$: 491.2727 $[M+H]^+$: found 491.2730.

***P,P*-Diphenyl-*N*-(4-(2-(pyridin-2-yl)phenyl)but-2-en-1-yl)phosphinic amide 3af**

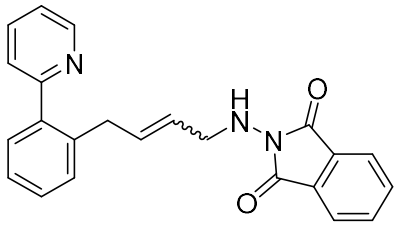


According to the general procedure, the expected product was isolated as after silica gel flash chromatography (dichloromethane/methanol 20:1) as a colorless oil (*E*/*Z* = 1: 1.9): 44 mg (41% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.56 (dd, *J*(H,H) = 4.9 and 1.7 Hz, 0.28H, H^{Ar}), 8.51 (dd, *J*(H,H) = 5.0 and 1.7 Hz, 0.62H, H^{Ar}), 7.89-7.67 (m, 4H, H^{Ar}), 7.65-7.52 (m, 1H, H^{Ar}), 7.89-7.67 (m, 12H, H^{Ar}), 5.64-5.50 (m, 0.34H, Ar-CH_2-C*H*=C*H, E*-isomer), 5.48-5.35 (m, 1.32H, Ar-CH_2-C*H*=C*H, Z*-isomer), 5.38-5.17 (m, 0.34H, Ar-CH_2-C*H*=C*H, E*-isomer), 3.45-3.30 (m, 4H, Ar-C*H*$_2$-CH=CH-C*H*$_2$) 2.80-2.60 (m, 1H, N*H*). **^{13}C NMR (75 MHz, $CDCl_3$):** 160.0 (*C*), 149.2 (*C*), 140.5 (*C*), 140.4 (*C*), 138.3 (*C*), 137.9 (*C*), 136.4 (*C*H), 136.3 (*C*H), 132.5 (d, ^1J(C,P) = 130.3 Hz, *C*), 133.3 (d, ^2J(C,P) = 9.4 Hz, *C*H), 133.2 (d, ^2J(C,P) = 9.4 Hz, *C*H), 131.97 (*C*H), 131.94 (*C*H), 131.7 (*C*H), 131.5 (*C*H), 131.3 (*C*H), 130.2 (*C*H), 130.1 (*C*H), 130.0 (*C*H), 129.8 (*C*H), 129.1 (*C*H), 129.0 (*C*H), 128.7 (d, ^4J(C,P) = 1.8 Hz, *C*H), 128.6 (d, ^3J(C,P) = 3.1 Hz, *C*H), 128.5 (d, ^4J(C,P) = 1.8 Hz, *C*H), 128.1 (*C*H), 128.0 (*C*H), 126.5 (*C*H), 126.4 (*C*H), 124.3 (*C*H), 124.2 (*C*H), 121.89 (*C*H), 121.86 (*C*H), 42.6 (*C*H_2), 37.6 (*C*H_2), 36.2 (*C*H_2), 31.2 (*C*H_2). **^{31}P NMR**

(121 MHz, $CDCl_3$): 23.74 (s). **HRMS (ESI):** *m/z*: calcd for $C_{27}H_{26}N_2OP^+$: 425.1777 $[M+H]^+$: found 425.1779.

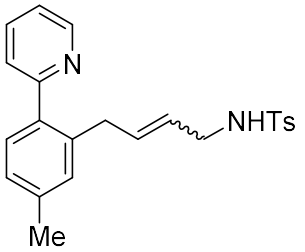
2-((4-(2-(Pyridin-2-yl)phenyl)but-2-en-1-yl)amino)isoindoline-1,3-dione 3ag



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 2:1) as a colorless oil (*E*/*Z* = 1: 1.9): 60 mg (65% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.67-8.62 (m, 1H, H^{Ar}), 7.86-7.17 (m, 5H, H^{Ar}), 7.39-7.05 (m, 6H, H^{Ar}), 5.87-5.23 (m, 2H, Ar-CH_2-C*H*=C*H*), 3.81-3.15 (m, 4H, Ar-C*H*$_2$-CH=CH-C*H*$_2$). **^{13}C NMR (100 MHz, $CDCl_3$):** 160.6 (*C*), 159.84 (*C*), 159.75 (*C*), 149.2 (*C*H), 149.1 (*C*H), 140.2 (*C*), 138.0 (*C*), 137.5 (*C*H), 136.3 (*C*H), 136.2 (*C*H), 135.3 (*C*H), 134.2 (*C*H), 134.2 (*C*H), 133.8 (*C*H), 130.3 (*C*), 130.2 (*C*), 129.9 (*C*H), 129.84 (*C*H), 129.80 (*C*H), 129.51 (*C*H), 128.46 (*C*H), 128.4 (*C*H), 126.3 (*C*H), 126.2 (*C*H), 125.8 (*C*H), 124.6 (*C*H), 124.2 (*C*H) 124.1 (*C*H), 123.40 (*C*H), 123.37 (*C*H), 121.7 (*C*H), 53.2 (*C*H$_2$), 47.9 (*C*H$_2$), 36.0 (*C*H$_2$), 31.3 (*C*H$_2$). **HRMS (ESI):** *m/z*: calcd for $C_{23}H_{20}N_3O_2^+$: 370.1550 $[M+H]^+$: found 370.1549.

4-Methyl-*N*-(4-(5-methyl-2-(pyridin-2-yl)phenyl)but-2-en-1-yl)benzenesulfonamide 3ba

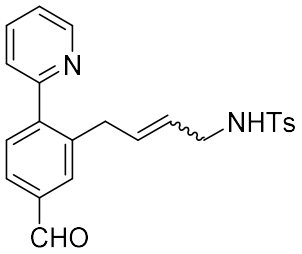


According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 2:1) as a colorless oil (*E*/*Z* = 1:1.0): 72 mg (73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (dd, *J*(H,H) = 13.6 and 4.9 Hz, 1H, H^{Ar}), 7.78-7.55 (m, 3H, H^{Ar}), 7.39-7.15 (m, 5H, H^{Ar}), 7.09 (dd, *J*(H,H) = 10.4 and 8.2 Hz, 1H, H^{Ar}), 7.01 (d, *J*(H,H) = 5.5 Hz, 1H, H^{Ar}), 5.62-5.46 (m, 1H, Ar-CH_2-C*H*=CH), 5.32-5.20 (m, 0.50H, Ar-CH_2-CH=C*H, Z*-isomer), 5.14 (dt, *J*(H,H) = 15.7 and 6.5 Hz, 0.50H, *E*-isomer), 4.77 (t, *J*(H,H) = 6.1 Hz, 0.50H, N*H, Z*-isomer), 4.21 (t, *J*(H,H) = 6.1 Hz, 0.50H, N*H, E*-isomer), 3.50-3.35 (m, 4H, Ar-C*H*$_2$-CH=CH-C*H*$_2$), 2.42 (s, 1.5H, Ar-C*H*$_3$), 2.42 (s, 1.5H, Ar-C*H*$_3$), 2.36 (s, 3H, Ar-C*H*$_3$). **^{13}C NMR (100 MHz, $CDCl_3$):** 159.9 (*C*), 159.7 (*C*), 149.1 (*C*H), 149.0 (*C*H), 143.23 (*C*), 143.19 (*C*), 138.4 (*C*), 138.3 (*C*), 137.6 (*C*H), 137.5 (*C*H), 137.31 (*C*), 137.27 (*C*), 137.17 (*C*), 137.11 (*C*), 136.6 (*C*H), 136.3 (*C*), 133.4 (*C*H), 132.8 (*C*H), 130.7 (CH), 130.5 (*C*H), 130.0 (*C*H), 129.9 (*C*H), 129.6 (*C*H), 127.20 (*C*H), 127.15 (*C*H), 127.11 (*C*H), 125.6 (*C*H), 124.6 (*C*H), 124.3 (*C*H), 124.2 (*C*H), 121.8 (*C*H), 121.7 (*C*H), 45.1 (*C*H$_2$), 39.9 (*C*H$_2$), 35.9 (*C*H$_2$), 31.1

(*C*H$_2$), 21.54 (*C*H$_3$), 21.52 (*C*H$_3$), 21.2 (*C*H$_3$). **HRMS (ESI):** *m/z*: calcd for $C_{23}H_{25}N_2O_2S^+$: 393.1631 $[M+H]^+$: found 393.1631.

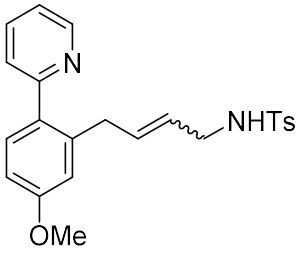
N-(4-(5-Formyl-2-(pyridin-2-yl)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide 3ca



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 1:1) as a colorless oil (*E*/*Z* = 1:1.0): 70 mg (69% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.04 (s, 0.5H, C*H*=O), 10.03 (s, 0.5H, C*H*=O), 8.69 (dd, *J*(H,H) = 12.3 and 4.9 Hz, 1H, *H*^{Ar}), 7.88-7.64 (m, 5H, *H*^{Ar}), 7.51 (dd, *J*(H,H) = 17.0 and 7.8 Hz, 1H, *H*^{Ar}), 7.41-7.21 (m, 5H, *H*^{Ar}), 5.68-5.45 (m, 1H, Ar-CH$_2$-C*H*=CH), 5.35-5.25 (m, 0.50H, Ar-CH$_2$-CH=C*H, Z*-isomer), 5.19 (dt, *J*(H,H) = 14.2 and 6.3 Hz, 0.50H, *E*-isomer), 4.62 (t, *J*(H,H) = 6.1 Hz, 0.50H, N*H, Z*-isomer), 4.25 (t, *J*(H,H) = 6.1 Hz, 0.50H, N*H, E*-isomer), 3.55-3.40 (m, 4H, Ar-C*H*$_2$-CH=CH-C*H*$_2$), 2.42 (s, 1.5H, C*H*$_3$), 2.41 (s, 1.5H, C*H*$_3$). **^{13}C NMR (100 MHz, CDCl$_3$):** 192.2 (*C*), 192.1 (*C*), 158.4 (*C*), 158.2 (*C*), 149.3 (*C*H), 145.9 (*C*), 145.8 (*C*), 143.42 (*C*), 143.40 (*C*), 139.1 (*C*), 138.7 (*C*), 137.1 (*C*), 137.0 (*C*H), 136.8 (*C*H), 136.3 (*C*), 136.2 (*C*), 132.1 (*C*H), 131.5 (*C*H), 131.4 (*C*H), 131.0 (CH), 130.83 (*C*H), 130.75 (*C*H), 129.72 (*C*H), 129.69 (*C*H), 127.79 (*C*H), 127.76 (*C*H), 127.1 (*C*H), 126.7 (*C*H), 125.7 (*C*H), 124.23 (*C*H), 124.17 (*C*H), 122.8 (*C*H), 45.0 (*C*H$_2$), 40.0 (*C*H$_2$), 35.8 (*C*H$_2$), 31.0 (*C*H$_2$), 21.55 (*C*H$_3$), 21.53 (*C*H$_3$). **HRMS (ESI):** *m/z*: calcd for $C_{23}H_{23}N_2O_3S^+$: 407.1424 $[M+H]^+$: found 407.1425.

N-(4-(5-Methoxy-2-(pyridin-2-yl)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide 3da

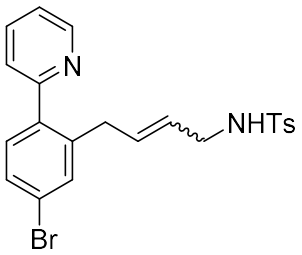


According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 1:1) as a colorless oil (*E*/*Z* = 1:1.0): 60 mg (59% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.69-8.55 (m, 1H, *H*^{Ar}), 7.78-7.65 (m, 3H, *H*^{Ar}), 7.36-7.18 (m, 5H, *H*^{Ar}), 6.89-6.67 (m, 2H, *H*^{Ar}), 5.70-5.47 (m, 1H, Ar-CH$_2$-C*H*=CH), 5.36-5.07 (m, 1H, Ar-CH$_2$-CH=C*H*), 4.69 (t, *J*(H,H) = 6.0 Hz, 0.50H, N*H, Z*-isomer), 4.11 (t, *J*(H,H) = 6.0 Hz, 0.50H, N*H, E*-isomer), 3.83 (s, 3H, CH$_3$), 3.56-3.32 (m, 4H, Ar-C*H*$_2$-CH=CH-C*H*$_2$), 2.42 (s,

1.5H, CH_3), 2.41 (s, 1.5H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 159.9 (*C*), 159.8 (*C*), 159.7 (*C*), 159.6 (*C*), 149.2 (*C*H), 149.1 (*C*H), 143.4 (*C*), 143.3 (*C*), 139.5 (*C*), 139.1 (*C*), 137.4 (*C*H), 137.2 (*C*H), 136.6 (*C*H), 136.3 (*C*H), 133.4 (*C*H), 133.2 (*C*), 133.0 (*C*), 132.7 (*C*H), 131.5 (*C*H), 131.3 (*C*H), 129.7 (CH), 127.2 (*C*H), 125.9 (*C*H), 125.0 (*C*H), 124.3 (*C*H), 124.2 (*C*H), 121.63 (*C*H), 121.59 (*C*H), 115.8 (*C*H), 115.5 (*C*H), 111.7 (*C*H), 55.4 (*C*H_3), 45.2 (*C*H_2), 40.0 (*C*H_2), 36.2 (*C*H_2), 31.4 (*C*H_2), 21.59 (*C*H_3), 21.57 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{23}H_{25}N_2O_3S^+$: 409.1580 $[M+H]^+$: found 409.1588.

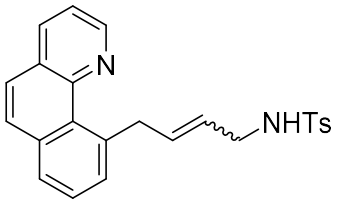
N-(4-(5-Bromo-2-(pyridin-2-yl)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide 3ea



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 2:1) as a colorless oil (*E*/*Z* = 1:1.1): 103 mg (90% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67-8.63 (m, 1H, H^{Ar}), 7.89-7.53 (m, 3H, H^{Ar}), 7.51-6.95 (m, 7H, H^{Ar}), 5.66-5.43 (m, 1H, Ar-CH_2-C*H*=CH), 5.36-5.10 (m, 1H, Ar-CH_2-CH=C*H*), 4.71 (t, *J*(H,H) = 6.0 Hz, 0.50H, N*H, Z*-isomer), 4.24 (t, *J*(H,H) = 6.3 Hz, 0.47H, N*H, E*-isomer), 3.51-3.35 (m, 4H, Ar-CH_2-CH=CH-CH_2), 2.43 (s, 1.52H, CH_3), 2.41 (s, 1.38H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 158.6 (*C*), 158.5 (*C*), 149.3 (*C*H), 149.2 (*C*H), 143.3 (*C*), 140.2 (*C*), 139.8 (*C*), 139.3(*C*), 137.24 (*C*H), 137.18 (*C*H), 136.8 (*C*H), 136.6 (*C*H), 132.8 (*C*H), 132.5 (*C*H), 132.2(*C*H), 131.6 (*C*H), 131.51 (*C*H), 131.50 (*C*H), 129.7 (CH), 129.6 (*C*H), 129.53 (*C*H), 129.49 (*C*H), 127.1 (*C*H), 126.6 (*C*H), 125.6 (*C*H), 124.2 (*C*H), 124.1 (*C*H), 122.7 (*C*), 122.5 (*C*), 122.3 (*C*H), 122.2 (*C*H), 45.0 (*C*H_2), 39.9 (*C*H_2), 35.7 (*C*H_2), 30.9 (*C*H_2), 25.55 (*C*H_3), 25.53 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{22}H_{22}BrN_2O_2S^+$: 457.0580 $[M+H]^+$: found 457.0583.

N-(4-(Benzo[*h*]quinolin-10-yl)but-2-en-1-yl)-4-methylbenzenesulfonamide 3fa

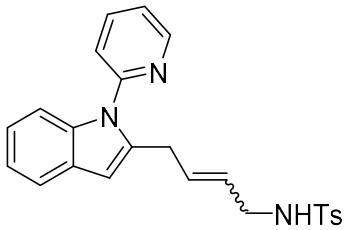


According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 4:1) as a colorless oil (*E*/*Z* = 1:1.0): 51 mg (52% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.96 (dd, *J*(H,H) = 4.3 and 1.9 Hz, 0.50H, H^{Ar}), 8.93 (dd, *J*(H,H) = 4.3 and 1.9 Hz, 0.50H, H^{Ar}) 8.20-8.13 (m, 1H, H^{Ar}), 7.84 -7.74 (m, 3H, H^{Ar}), 7.69-7.42 (m, 5H, H^{Ar}), 7.31-7.18 (m, 2H, H^{Ar}), 6.11 (dddd, *J*(H,H) = 15.2, 6.6, 5.8 and 1.4, 0.5H,

Ar-CH_2-C*H*=CH, *E*-isomer), 6.01-5.86 (m, 0.5H, Ar-CH_2-C*H*=CH, *Z*-isomer), 5.52-5.28 (m, 1H, Ar-CH_2-CH=C*H*), 4.69-4.57 (m, 2H, C*H*$_2$-NH), 4.37 (t, *J*(H,H) = 6.0 Hz, 0.5H, N*H, Z*-isomer), 4.14 (t, *J*(H,H) = 6.0 Hz, 0.5H, N*H, E*-isomer), 3.91 (d, *J*(H,H) = 6.2 Hz, 1H, Ar-C*H*$_2$-CH), 3.50 (d, *J*(H,H) = 6.2 Hz, 1H, Ar-C*H*$_2$-CH), 2.39 (s, 1.5H, C*H*$_3$), 2.38 (s, 1.5H, C*H*$_3$). **^{13}C NMR (75 MHz, $CDCl_3$):** 148.23 (*C*), 148.19 (*C*), 147.3 (*C*H), 143.4 (*C*), 143.28 (*C*), 140.1 (*C*), 140.0 (*C*), 137.2 (*C*), 136.0 (*C*H), 135.7 (*C*H), 135.6 (*C*H), 135.5 (*C*), 135.4 (*C*H), 130.9 (*C*H), 130.5 (*C*H), 129.8 (*C*H), 129.7 (*C*H), 129.2 (*C*H), 129.0 (*C*H), 128.9 (*C*H), 127.67 (*C*H), 127.65 (*C*H), 127.62 (*C*H), 127.6 (*C*H), 127.3 (*C*H), 127.2 (*C*H), 125.74 (*C*H), 125.68 (*C*H), 124.3 (*C*H), 123.5 (*C*H), 121.0 (*C*H), 120.9(CH), 45.7 (*C*H_2), 40.9 (*C*H_2), 40.8 (*C*H_2), 36.1 (*C*H_2), 21.56 (*C*H_3), 21.54 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{24}H_{23}N_2O_2S^+$: 403.1475 $[M+H]^+$: found 403.1479.

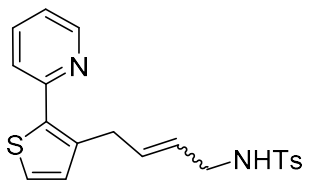
4-Methyl-*N*-(4-(1-(pyridin-2-yl)-1*H*-indol-2-yl)but-2-en-1-yl)benzenesulfonamide 3ga



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 2:1) as a colorless oil (*E*/*Z* = 2.7:1): 60 mg (58% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 8.78-8.50 (m, 1H, *H*^{Ar}), 7.97-7.73 (m, 1H, *H*^{Ar}) , 7.68 (dd, *J*(H,H) = 8.2 and 6.0 Hz, 2H, *H*^{Ar}), 7.61-7.47 (m, 1H, *H*^{Ar}), 7.47-6.97 (m, 7H, *H*^{Ar}), 6.43-6.24 (m, 1H, *H*^{Ar}), 5.68-5.53 (m, 1H, Ar-CH_2-C*H*=CH), 5.44-5.12 (m, 1H, Ar-CH_2-CH=C*H*), 4.49 (t, *J*(H,H) = 6.1 Hz, 0.26H, NH, *Z*-isomer), 4.23 (t, *J*(H,H) = 6.2 Hz, 0.70H, NH, *E*-isomer), 3.62-3.36 (m, 4H, Ar-C*H*$_2$-CH=CH-C*H*$_2$), 2.39 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 151.4 (*C*), 151.3 (*C*), 149.8 (*C*H), 149.7 (*C*H), 143.5 (*C*), 143.4 (*C*), 138.7 (*C*), 138.6 (*C*), 138.5 (*C*), 137.5 (*C*), 137.1 (*C*), 137.1 (*C*), 130.8 (*C*H), 130.0 (*C*H), 129.8(*C*H), 129.7 (*C*H), 128.5 (*C*H), 127.2 (*C*H), 126.9 (*C*H), 126.2 (*C*H), 122.33 (*C*H), 122.30 (*C*H), 122.2 (*C*H), 122.1 (*C*H), 121.2 (*C*H), 121.1 (*C*H), 121.0 (*C*H), 120.9 (*C*H), 120.24 (*C*H), 120.21(*C*H), 110.24 (*C*H), 110.18 (*C*H), 103.4 (*C*H), 103.1 (*C*H), 45 (*C*H_2), 40.0 (*C*H_2), 30.6 (*C*H_2), 26.1 (*C*H_2), 21.6 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{24}H_{24}N_3O_2S^+$: 418.1584 $[M+H]^+$: found 418.1581.

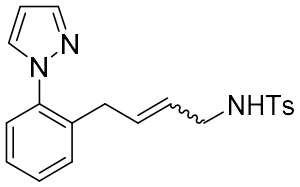
4-Methyl-*N*-(4-(2-(pyridin-2-yl)thiophen-3-yl)but-2-en-1-yl)benzenesulfonamide 3ha



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 1:1) as a colorless oil (*E*/*Z* = 1:1.5): 50 mg (52% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.65-8.60 (m, 1H, H^{Ar}), 7.76-7.63 (m, 3H, H^{Ar}), 7.51-7.40 (m, 1H, H^{Ar}), 7.34-7.14 (m, 4H, H^{Ar}), 6.87 (dd, *J*(H,H) = 11.9 and 5.1 Hz, 1H, H^{Ar}), 5.92-5.62 (m,1H, Ar-CH_2-C*H*=CH), 5.51-5.29 (m, 1H, Ar-CH_2-CH=C*H*), 4.96 (t, *J*(H,H) = 6.0 Hz, 0.57H, N*H, Z*-isomer), 4.14 (t, *J*(H,H) = 6.0 Hz, 0.38H, N*H, E*-isomer), 3.79-3.37 (m, 4H, Ar-CH_2-CH=CH-CH_2), 2.40 (s, 3H CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 153.3 (*C*), 153.1 (*C*), 149.7 (*C*H), 149.6 (*C*H), 143.5 (*C*), 143.4 (*C*), 137.9 (*C*), 137.6 (*C*), 137.4 (*C*), 137.2 (*C*), 137.1 (*C*), 136.8 (*C*H), 136.6 (*C*H), 132.58 (*C*H), 132.55 (*C*H), 130.9 (*C*H), 130.5 (*C*H), 129.8(*C*H), 129.7 (*C*H), 127.2 (*C*H), 126.2 (*C*H), 125.9 (*C*H), 125.8 (*C*H), 125.1 (*C*H), 122.5 (*C*H), 121.9 (*C*H), 121.8 (*C*H), 121.7 (*C*H), 45.2 (*C*H_2), 40.1 (*C*H_2), 32.3 (*C*H_2), 27.7 (*C*H_2), 21.6 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{20}H_{21}N_2O_2S_2^+$: 385.1039 [M+H]$^+$: found 385.1043.

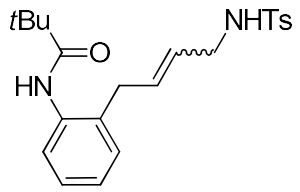
N-(4-(2-(1*H*-Pyrazol-1-yl)phenyl)but-2-en-1-yl)-4-methylbenzenesulfonamide 3ia



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 1:1) as a colorless oil (*E*/*Z* = 1.6:1): 67 mg (73% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.75-7.60 (m, 3H, H^{Ar}), 7.55 (dd, *J*(H,H) = 4.2 and 2.4 Hz, 1H, H^{Ar}), 7.39-7.14 (m, 6H, H^{Ar}), 6.40 (t, *J*(H,H) = 2.1 Hz, 1H, H^{Ar}), 5.59-5.36 (m,1H, Ar-CH_2-C*H*=CH), 5.36-5.07 (Ar-CH_2-CH=C*H*), 4.57 (t, *J*(H,H) = 6.1 Hz, 0.36H, N*H, Z*-isomer), 4.35 (t, *J*(H,H) = 6.1 Hz, 0.56H, N*H, E*-isomer), 3.52-3.38 (m, 2H, CH_2-NH), 3.31-3.19 (m, 2H, Ar-CH_2-CH), 2.41 (s, 1.15H, CH_3), 2.39 (s, 1.85H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** 143.4 (*C*), 140.6 (*C*H), 140.4 (*C*H), 139.7 (*C*), 139.5 (*C*), 137.3 (*C*), 137.2 (*C*), 136.0 (*C*), 135.6 (*C*), 132.1 (*C*H), 131.5 (*C*H), 130.93 (*C*H), 130.85 (*C*H), 130.7 (*C*H), 130.4 (*C*H), 129.74 (*C*H), 129.70 (*C*H), 129.0 (*C*H), 128.8 (*C*H), 127.3 (*C*H), 127.22 (*C*H), 127.20 (*C*H), 127.17 (*C*H), 126.66 (*C*H), 126.63 (*C*H), 126.3 (*C*H), 125.5 (*C*H), 106.5 (*C*H), 106.4 (*C*H), 45.1 (*C*H_2), 40.0 (*C*H_2), 34.3 (*C*H_2), 29.5 (*C*H_2), 21.6 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{20}H_{22}N_3O_2S^+$: 368.1427 [M+H]$^+$: found 368.1428.

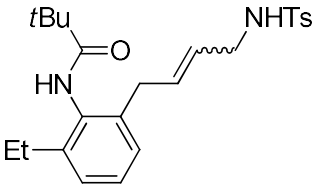
N-(2-(4-((4-Methylphenyl)sulfonamido)but-2-en-1-yl)phenyl)pivalamide 3ka



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 1:1) as a colorless oil (*E*/*Z* = 0.8:1): 38 mg (38% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.72 (m, *J*(H,H) = 8.5 Hz, 2H, H^{Ar}), 7.42 (d, *J*(H,H) = 8.4 Hz, 1H, H^{Ar}), 7.33-7.18 (m, 4H, H^{Ar} and NH), 7.15-6.92 (m, 2H, H^{Ar}), 5.85-5.56 (m, 1H, Ar-CH_2-C*H*=CH), 5.51-5.19 (m, 1H, Ar-CH_2-CH=C*H*), 4.49 (t, *J*(H,H) = 6.1 Hz, 0.45H, N*H, Z*-isomer), 4.37 (t, *J*(H,H) = 6.1 Hz, 0.54H, N*H, E*-isomer), 3.64-3.42 (m, 2H, CH_2-NH), 3.34-3.11 (m, 2H, Ar-CH_2-CH), 2.42 (s, 3H, CH_3), 1.31 (s, 4.91H, C(CH_3)$_3$), 1.29 (s, 4.07H, C(CH_3)$_3$).**^{13}C NMR (75 MHz, $CDCl_3$):** 175.9 (*C*), 175.6 (*C*), 142.64 (*C*), 142.57 (*C*), 136.2 (*C*), 136.1 (*C*), 135.5 (*C*), 134.9 (*C*), 134.5 (*C*H), 132.6 (*C*H), 130.7 (*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.8 (*C*H), 128.1 (*C*H), 126.7 (*C*H), 126.30 (*C*H), 126.25 (*C*H), 126.1 (*C*H), 125.0 (*C*H), 124.6 (*C*H), 123.6 (*C*H), 119.4 (*C*H), 44.3 (*C*H_2), 44.0 (*C*H_2), 38.7 (*C*), 37.0 (*C*H_2), 33.9 (*C*H_2), 26.9 (*C*H_3), 26.8 (*C*H_3), 20.7 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{22}H_{29}N_2O_3S^+$: 401.1893 $[M+H]^+$: found 401.1893.

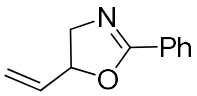
N-(2-Ethyl-6-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phenyl)pivalamide 3la



According to the general procedure, the expected product was isolated as after silica gel flash chromatography (petroleum ether/EtOAc 1:1) as a colorless oil (*E*/*Z* = 0.5:1): 38 mg (38% yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.71 (m, 3H, H^{Ar}), 7.36-7.05 (m, 3H, H^{Ar}), 7.03-6.81 (m, 2H, H^{Ar} and NH), 5.81-5.48 (m, 1H, Ar-CH_2-C*H*=CH), 5.46-5.16 (m, 1H, Ar-CH_2-CH=C*H*), 4.68 (t, *J*(H,H) = 5.8 Hz, 0.3H, N*H, Z*-isomer), 4.41 (t, *J*(H,H) = 6.7 Hz, 0.6H, N*H, E*-isomer), 3.64-3.42 (m, 2H, CH_2-NH), 3.34-3.10 (m, 2H, Ar-CH_2-CH),2.55 (m, *J*(H,H) = 7.6 and 3.8 Hz, 2H, CH_2-CH_3), 2.42 (s, 2H, CH_3), 2.41 (s, 1H, CH_3), 1.34 (s, 6H, C(CH_3)$_3$), 1.33 (s, 3H, C(CH_3)$_3$), 1.25-1.07 (m, 3H, CH_2-CH_3) . **^{13}C NMR (75 MHz, $CDCl_3$):** 177.2 (*C*), 176.5 (*C*), 143.4 (*C*), 143.3 (*C*), 142.1 (*C*), 137.4 (*C*), 137.1 (*C*), 136.9 (*C*), 136.4 (*C*), 135.1 (*C*), 133.5 (*CH*), 133.4 (*C*), 132.7 (*C*H), 129.7 (*C*H), 129.6 (*C*H), 128.7 (*C*H), 127.7 (*C*H), 127.6 (*C*H), 127.15 (*C*H), 127.12 (*C*H), 127.07 (*C*H), 126.7 (*C*H), 126.1 (*C*H), 125.8 (*C*H), 123.8 (*C*H), 45.2 (*C*H_2), 45.1 (*C*H_2), 39.6 (*C*H_2), 38.1 (*C*), 34.9 (*C*H_2), 27.73 (*C*H_3), 27.68 (*C*H_3), 27.66 (*C*H_3), 24.8 (*C*H_2), 24.5 (*C*H_2), 24.5 (*C*H_3), 14.4 (*C*H_3), 14.0 (*C*H_3). **HRMS (ESI):** *m/z*: calcd for $C_{24}H_{33}N_2O_3S^+$: 429.2206 $[M+H]^+$: found 429.2205.

2-Phenyl-5-vinyloxazoline[13]



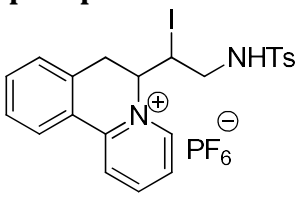
According to the general procedure using vinylaziridine **2h**, the expected allylated product was not observed, but only the 2-phenyl-5-vinyloxazoline was isolated (in addition to unreactive starting materials) as a colorless oil: 30 mg (55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98-7.94 (m, 2H, H^{Ar}), 7.50-7.38 (m, 3H, H^{Ar}), 5.95 (ddd, *J*(H,H) = 17.2, 10.4 and 6.9 Hz, 1H, CH_2=C*H*), 5.38 (dt, *J*(H,H) = 17.1 and 1.2 Hz, CH_2=CH),

5.26 (dt, *J*(H,H) = 10.4 and 1.1 Hz, 1H, CH_2=CH), 5.12 (dddt, *J*(H,H) = 10.0, 8.0, 7.0 and 1.0 Hz, 1H, C*H*), 4.21 (dd, *J*(H,H) = 14.6 and 9.9 Hz, 1H, CH_2), 3.78 (dd, *J*(H,H) = 14.6 and 7.9 Hz, 1H, CH_2).

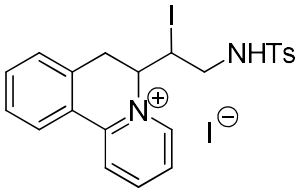
V. Iodocyclization

6-(1-iodo-2-(4-methylphenylsulfonamido)ethyl)-6,7-dihydropyrido[2,1-a]isoquinolin-5-ium hexafluorophosphate 4



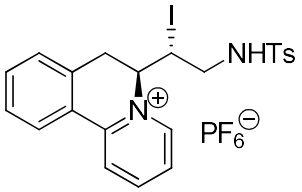
Iodine (80 mg, 0.32 mmol, 2 equiv.) was added to a solution of 4-methyl-*N*-(4-(2-(pyridin-2-yl)phenyl)but-2-en-1-yl)benzenesulfonamide **3aa** (60 mg, 0.16 mmol) in toluene (2 mL) at room temperature under argon atmosphere. The reaction was stirred at room temperature for 30 minutes. The solvent was removed under vacuum and the residue was dissolved in dichloromethane (15 mL). An aqueous solution of KPF_6 (58.4 mg, 0.32 mmol, 2 equiv.) in water (10 mL) was added in the mixture. After the reaction was stirred at room temperature for 1 hour, the mixture was extracted by dichloromethane (2 x 10 mL). The combined organic phase was dried by Na_2SO_4 and the solvent was removed under vacuum to give a white solid: 92 mg (*syn*/*anti* = 0.8:1, 89% yield).

6-(1-iodo-2-(4-methylphenylsulfonamido)ethyl)-6,7-dihydropyrido[2,1-a]isoquinolin-5-ium iodine 4



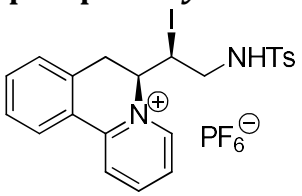
Iodine (80 mg, 0.32 mmol, 2 equiv.) was added to a solution of 4-methyl-*N*-(4-(2-(pyridin-2-yl)phenyl)but-2-en-1-yl)benzenesulfonamide **3aa** (60 mg, 0.16 mmol) in toluene (2 mL) at room temperature under argon atmosphere. The reaction was stirred at room temperature for 30 minutes. The solvent was removed under vacuum. The two diastereomers were partially separated by silica gel flash chromatography (dichloromethane/methanol = 20:1) to afford yellow solids: diastereomer ***anti*-4**: 19 mg (11% yield), diastereomer ***syn*-4** 36 mg (36% yield). For accurate analyses, ***anti*-4** and ***syn*-4** were converted into PF_6 salts.

(*R**,*S**)-6-(1-iodo-2-(4-methylphenylsulfonamido)ethyl)-6,7-dihydropyrido[2,1-a]isoquinolin-5-ium hexafluorophosphate *anti*-4



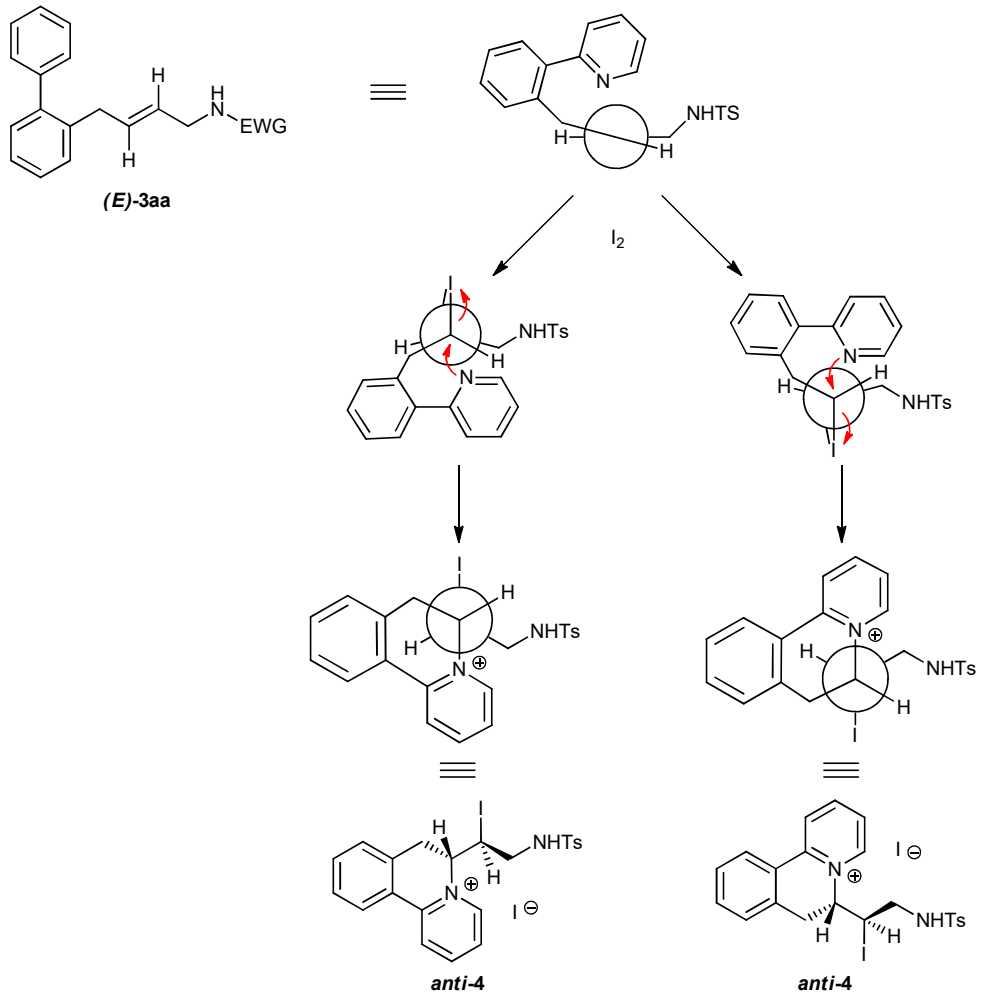
^{1}H NMR (400 MHz, $CDCl_3$): 8.97 (d, *J*(H,H) = 6.0 Hz, 1H, H^{Ar}), 8.56-8.54 (m, 1H, H^{Ar}), 8.36 (dd, *J*(H,H) = 8.3 Hz and 1.3 Hz, 1H, H^{Ar}), 8.08 (dd, *J*(H,H) = 7.9 Hz and 1.2 Hz, 1H, H^{Ar}), 7.96 (ddd, *J*(H,H) = 7.8 Hz, 6.2 Hz and 1.4 Hz, 1H, H^{Ar}), 7.75-7.55 (m, 4H, H^{Ar}), 7.45 (m, 1H, H^{Ar}), 7.27 (d, *J*(H,H) = 8.0 Hz, 2H, H^{Ar}), 5.26 (dt, *J*(H,H) = 9.9 and 3.6 Hz, 1H, C*H*-N$^+$), 5.02 (t, *J*(H,H) = 6.1 Hz, 1H, N*H*), 4.38 (ddd, *J*(H,H) = 9.8 Hz, 7.5 Hz and 4.2 Hz, 1H, C*H*-I), 3.78 (d, *J*(H,H) = 3.5 Hz, 2H, CH_2), 3.40-3.20 (m, 2H, CH_2-NH), 2.38 (s, 3H, CH_3). **^{13}C NMR (75 MHz, CD_3COCD_3):** 149.2 (*C*), 147.8 (*C*H), 146.7 (*C*H), 144.4 (*C*), 137.1 (*C*), 134.9 (*C*H), 133.0 (*C*), 130.5 (*C*H), 130.4 (*C*H), 129.8 (*C*H), 128.0 (*C*H), 127.5 (*C*H), 126.9 (*C*H), 126.6 (*C*), 126.2 (*C*H), 68.4 (*C*H), 49.4 (*C*H_2), 33.4 (*C*H_2), 26.7 (*C*H), 21.1 (*C*H_3). **^{31}P NMR (121 MHz, $CDCl_3$):** 148.38 (sept, *J*(P,F) = 710.3 Hz). **^{19}F NMR (282 MHz, $CDCl_3$):** -76.08 (d, *J*(P,F) = 713.7 Hz). **HRMS (ESI):** *m/z*: calcd for $C_{23}H_{20}N_3O_2^+$: 370.1550 [M+H]$^+$: found 370.1549.

(*R,*R**)-6-(1-iodo-2-(4-methylphenylsulfonamido)ethyl)-6,7-dihydropyrido[2,1-a]isoquinolin-5-ium hexafluorophosphate *syn*-4**



^{1}H NMR (400 MHz, $CDCl_3$): 8.78 (d, *J*(H,H) = 6.1 Hz, 1H, H^{Ar}), 8.54-8.48 (m, 1H, H^{Ar}), 8.32 (dd, *J*(H,H) = 8.2 Hz, 1H, H^{Ar}), 8.00-7.90 (m, 2H, H^{Ar}), 7.72-7.66 (m, 3H, H^{Ar}), 7.59-7.49 (m, 2H, H^{Ar}), 7.31 (d, *J*(H,H) = 8.1 Hz, 2H, H^{Ar}), 5.43 (t, *J*(H,H) = 6.4 Hz, 1H, N*H*), 5.33 (dd, *J*(H,H) = 9.7 Hz and 5.3 Hz, 1H, C*H*-I), 4.33 (dt, *J*(H,H) = 8.7 Hz and 5.9 Hz, 1H, C*H*-N$^+$), 3.78 (dd, *J*(H,H) = 17.3 Hz and 5.1 Hz, 1H, CH_2), 3.64 (d, *J*(H,H) = 17.3 Hz, 1H, CH_2 CH_2-NH), 3.36 (t, *J*(H,H) = 6.2 Hz, 2H, CH_2-NH), 2.42 (s, 3H, CH_3). **^{13}C NMR (75 MHz, CD_3COCD_3):** 148.9 (*C*), 148.1 (*C*H), 147.6 (*C*H), 144.3 (*C*), 138.1 (*C*), 135.2 (*C*H), 133.2 (*C*), 130.5 (*C*H), 130.4 (*C*H), 129.9 (*C*H), 127.8 (*C*H), 127.5(*C*H), 126.5 (*C*), 126.1 (*C*H), 125.9 (*C*H), 68.9 (*C*H), 48.8 (*C*H_2), 31.3 (*C*H_2), 29.7 (*C*H), 21.1 (*C*H_3). **^{31}P NMR (121 MHz, $CDCl_3$):** 148.38 (sept, *J*(P,F) = 710.3 Hz). **^{19}F NMR (282 MHz, $CDCl_3$):** -76.08 (d, *J*(P,F) = 713.7 Hz). **HRMS (ESI):** *m/z*: calcd for $C_{23}H_{20}N_3O_2^+$: 370.1550 [M+H]$^+$: found 370.1549.

Mechanistic and diastereoselective considerations of the iodocycloisomerisation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I2
I
NHTs
H
H
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NHTs
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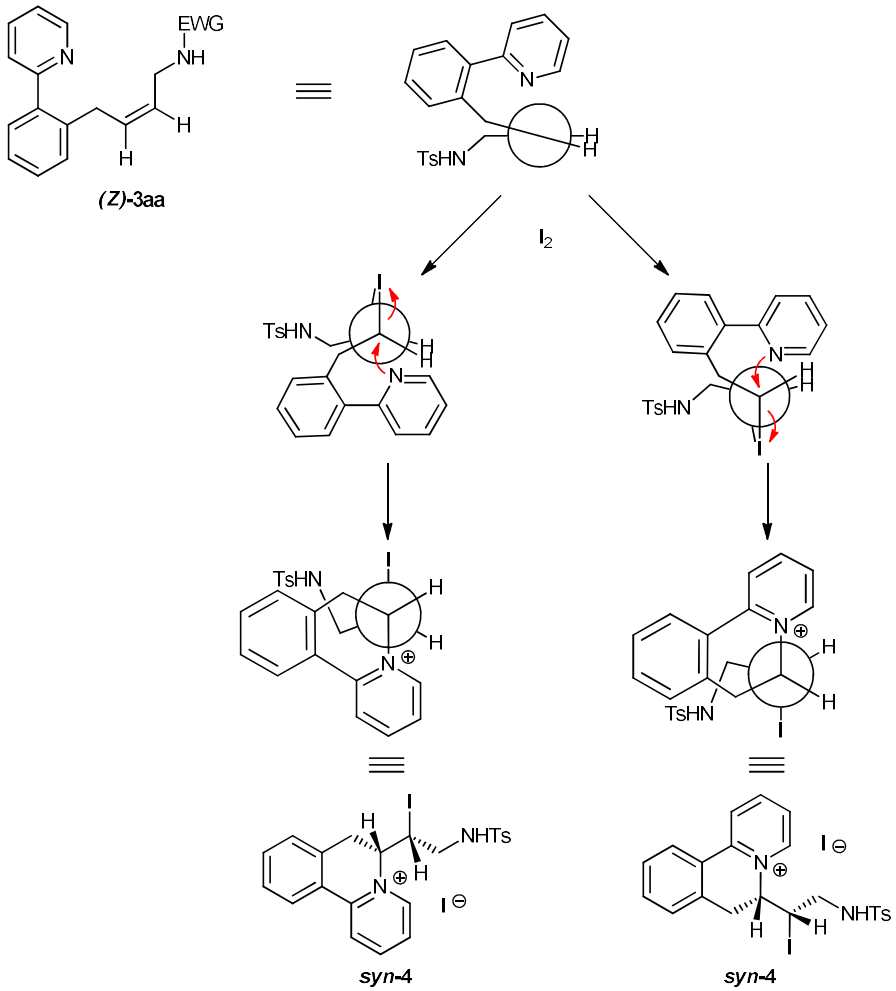

VI. References

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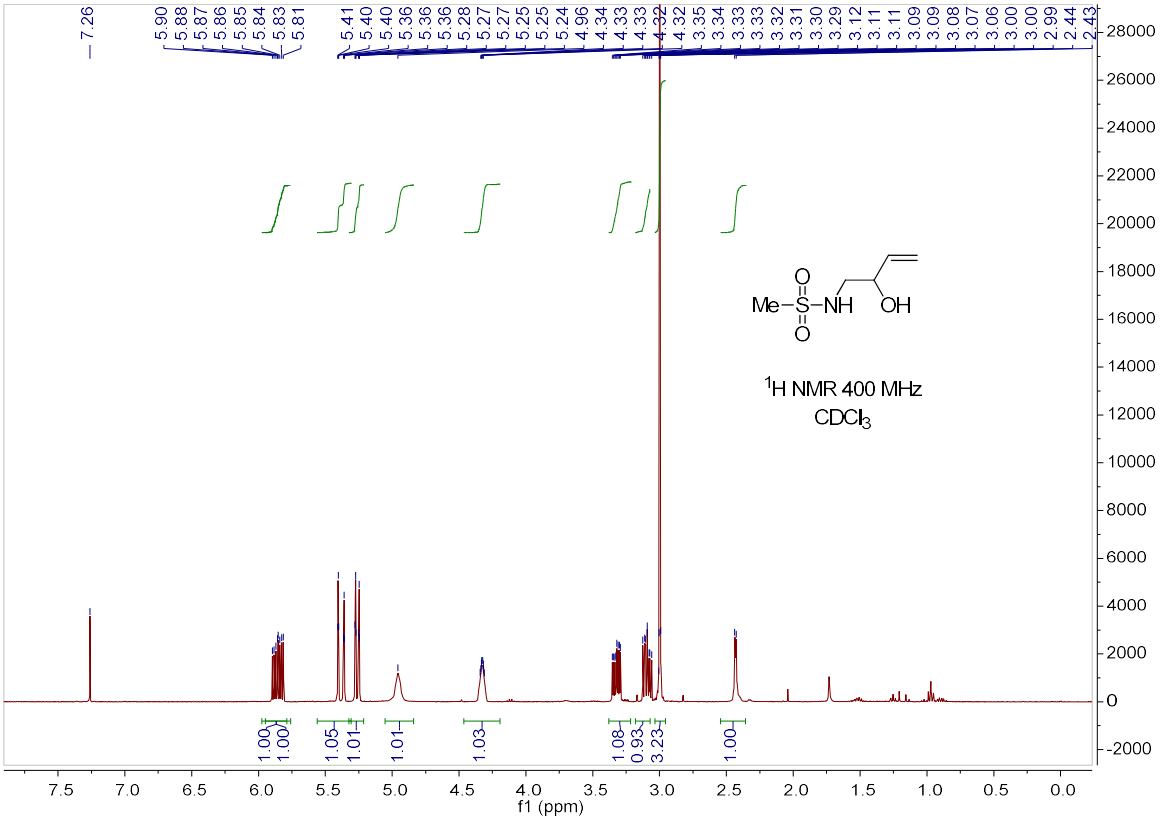
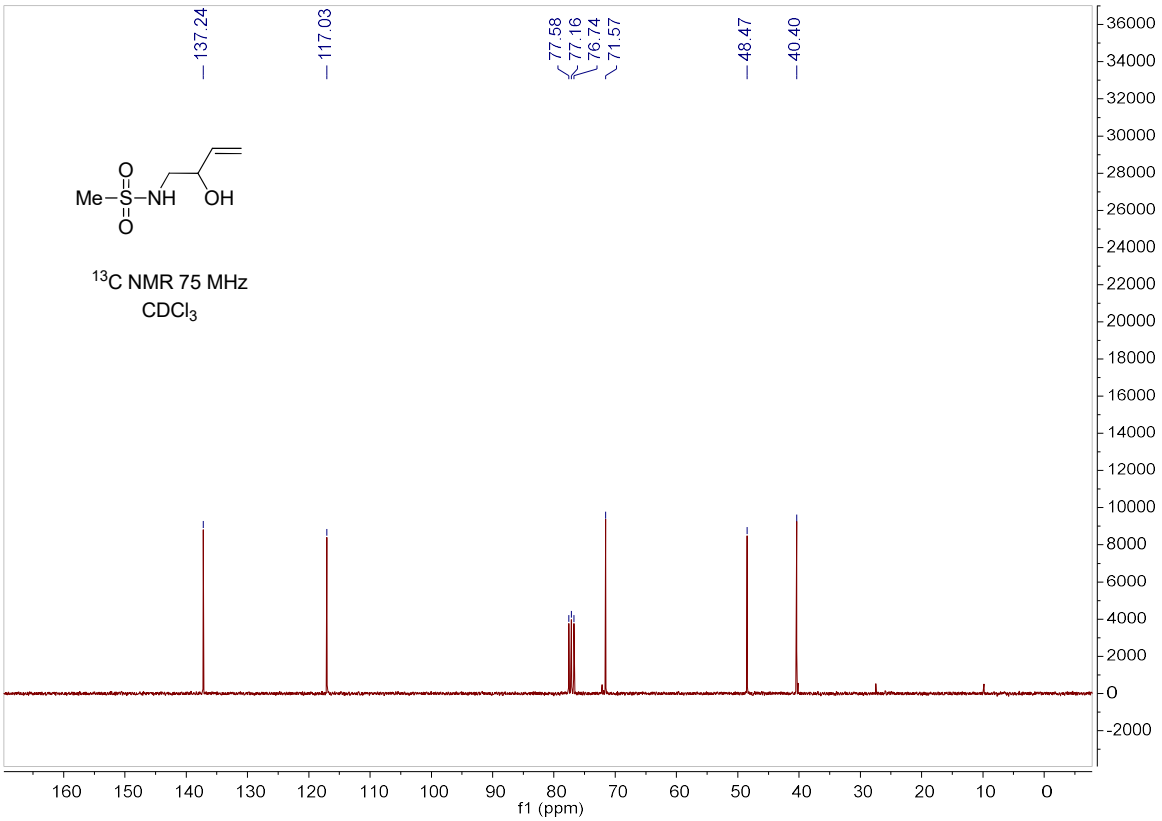
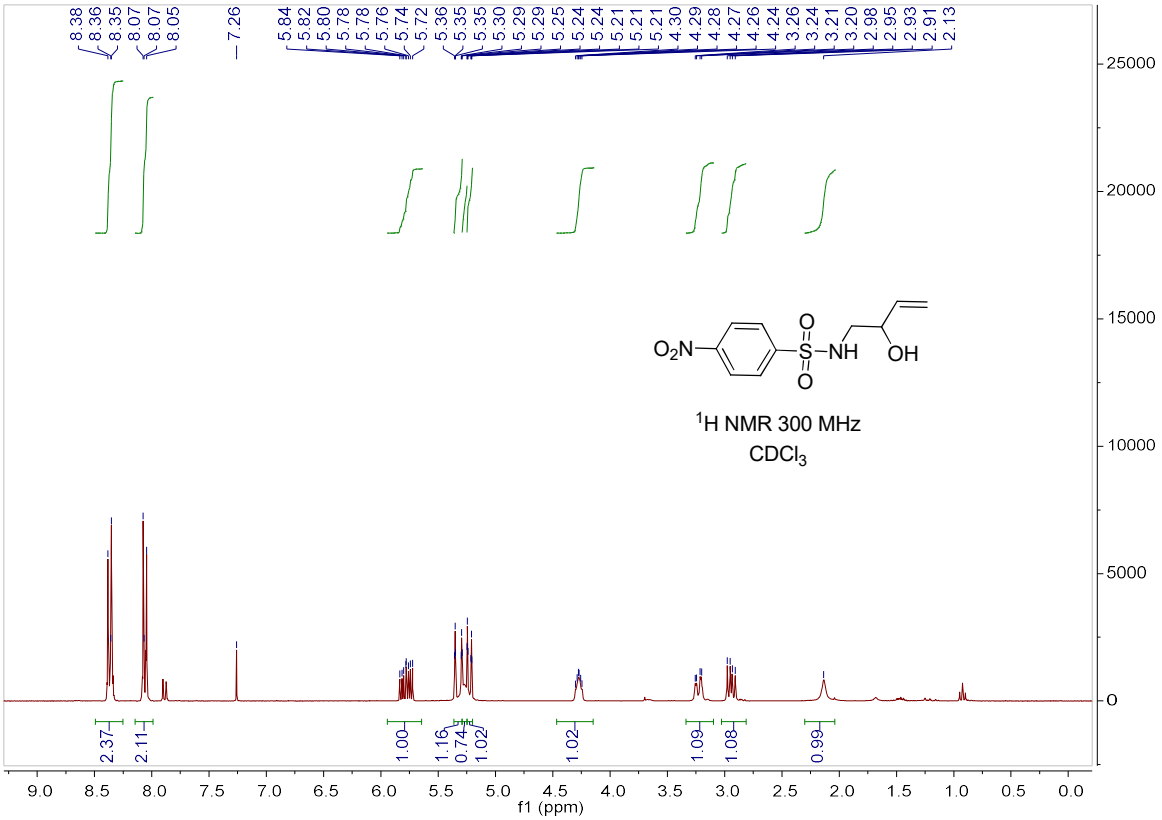
VIII. NMR Spectra of the new compounds



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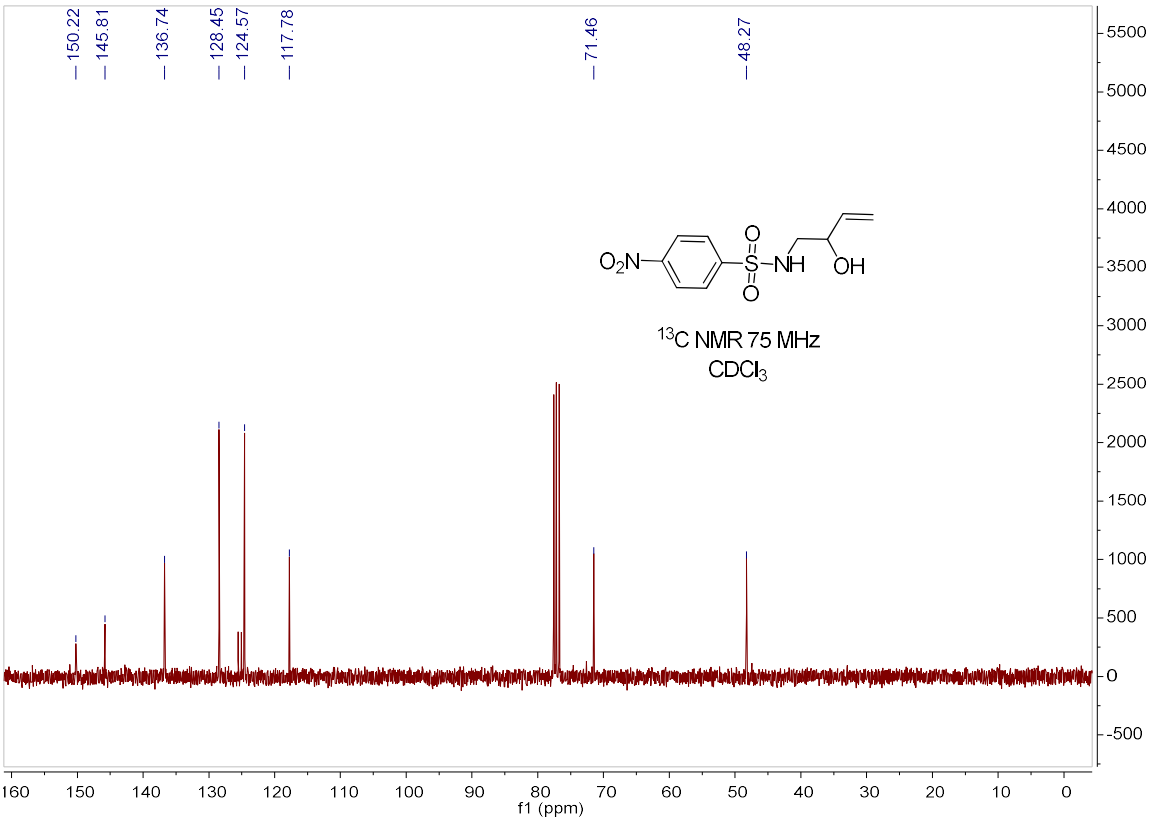
8.36
8.35
8.07
8.05
7.26
5.84
5.82
5.80
5.78
5.78
5.76
5.74
5.72
5.36
5.35
5.35
5.30
5.29
5.29
5.25
5.24
5.24
5.21
5.21
5.21
4.30
4.29
4.28
4.27
4.26
4.24
3.26
3.24
3.21
3.20
2.98
2.95
2.93
2.91
2.13
O2N
S
NH
OH
1H NMR 300 MHz
CDCl3
2.37
2.11
1.00
1.16
0.74
1.02
1.02
1.09
1.08
0.99
f1 (ppm)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145.81
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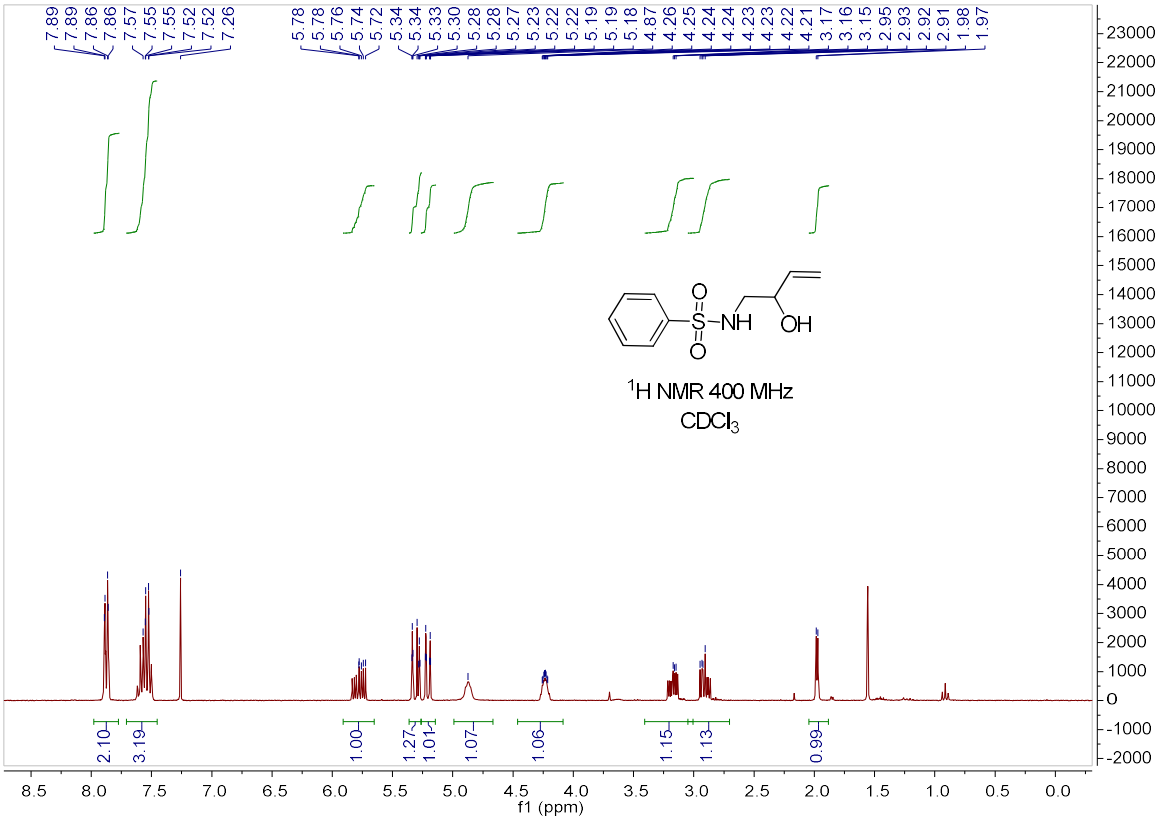
71.46
48.27
O2N
S
NH
OH
13C NMR 75 MHz
CDCl3
f1 (ppm)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7.89
7.86
7.86
7.57
7.55
7.55
7.52
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7.26
5.78
5.78
5.76
5.74
5.72
5.34
5.34
5.33
5.30
5.28
5.28
5.27
5.23
5.22
5.22
5.19
5.19
5.18
4.87
4.26
4.25
4.24
4.24
4.23
4.23
4.22
4.21
3.17
3.16
3.15
2.95
2.93
2.92
2.91
1.98
1.97
O
S
NH
OH
O
1H NMR 400 MHz
CDCl3
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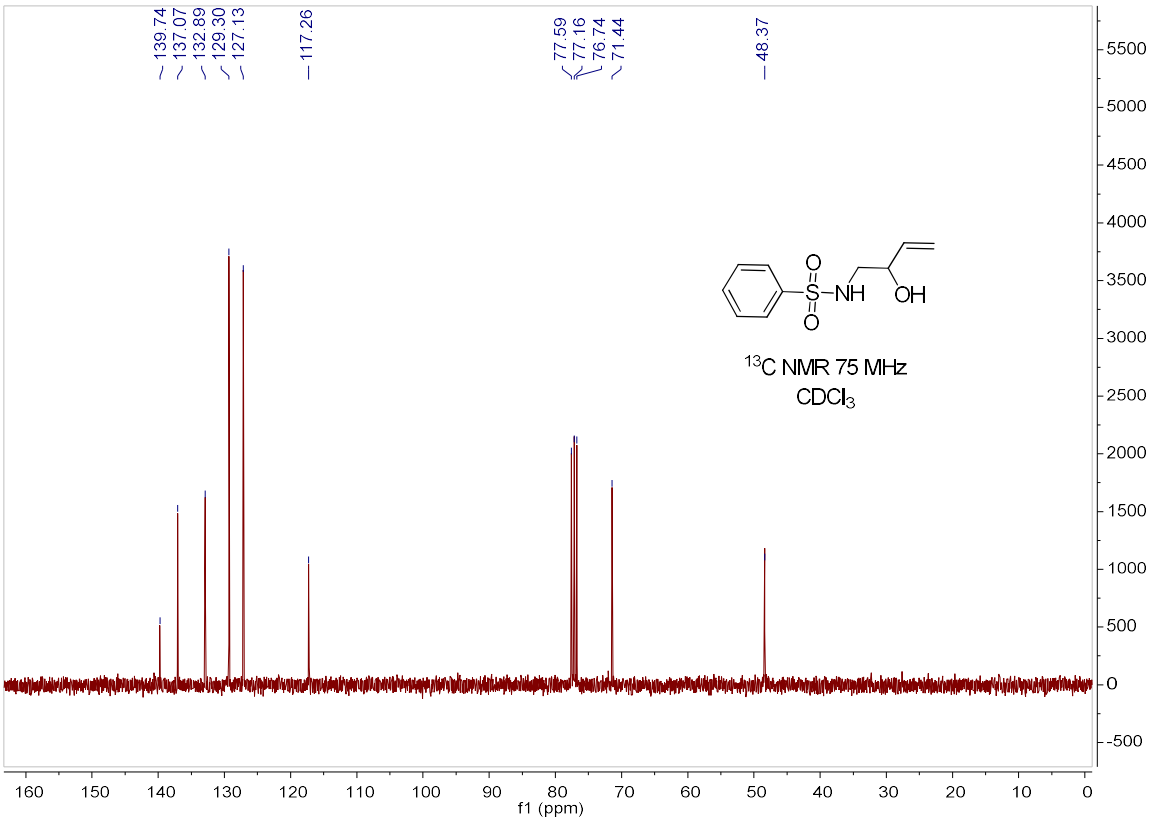
1.00
1.27
1.01
1.07
1.06
1.15
1.13
0.99
f1 (ppm)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117.26
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77.16
76.74
71.44
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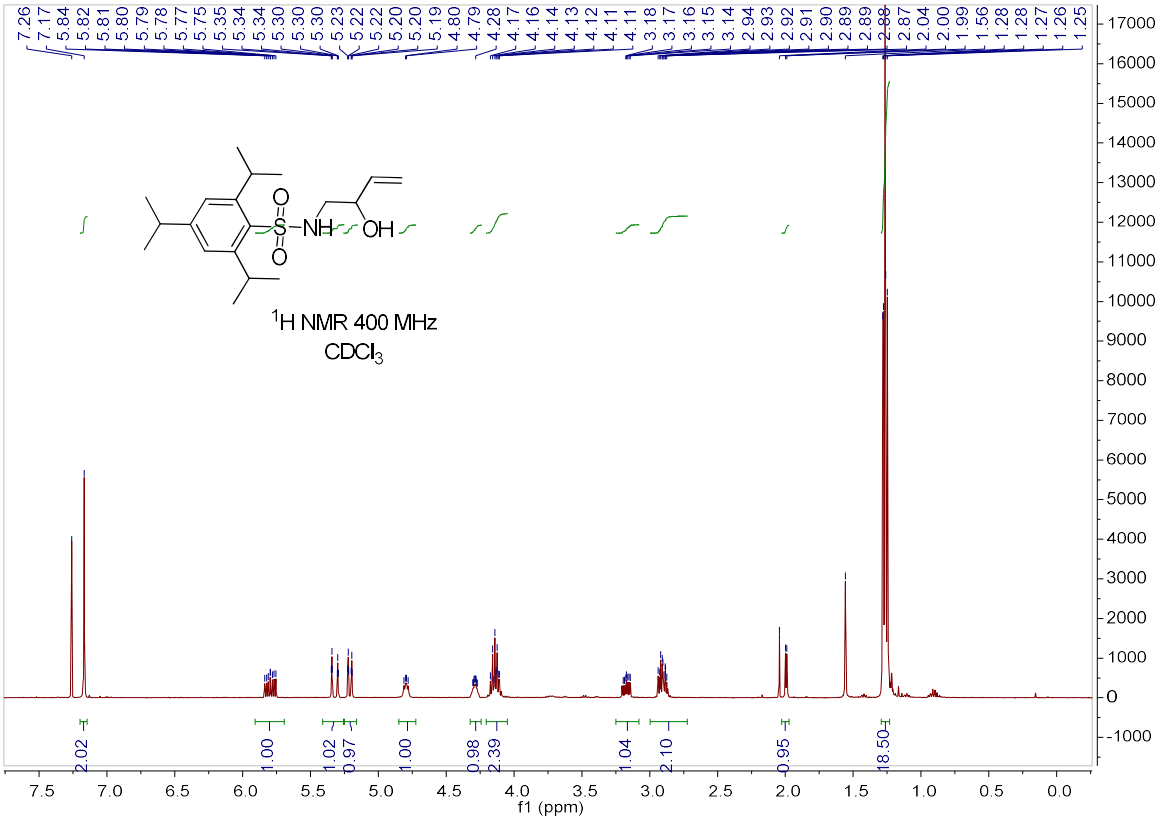
S
NH
OH
O
13C NMR 75 MHz
CDCl3
f1 (ppm)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O
S
NH
OH
O
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CDCl3
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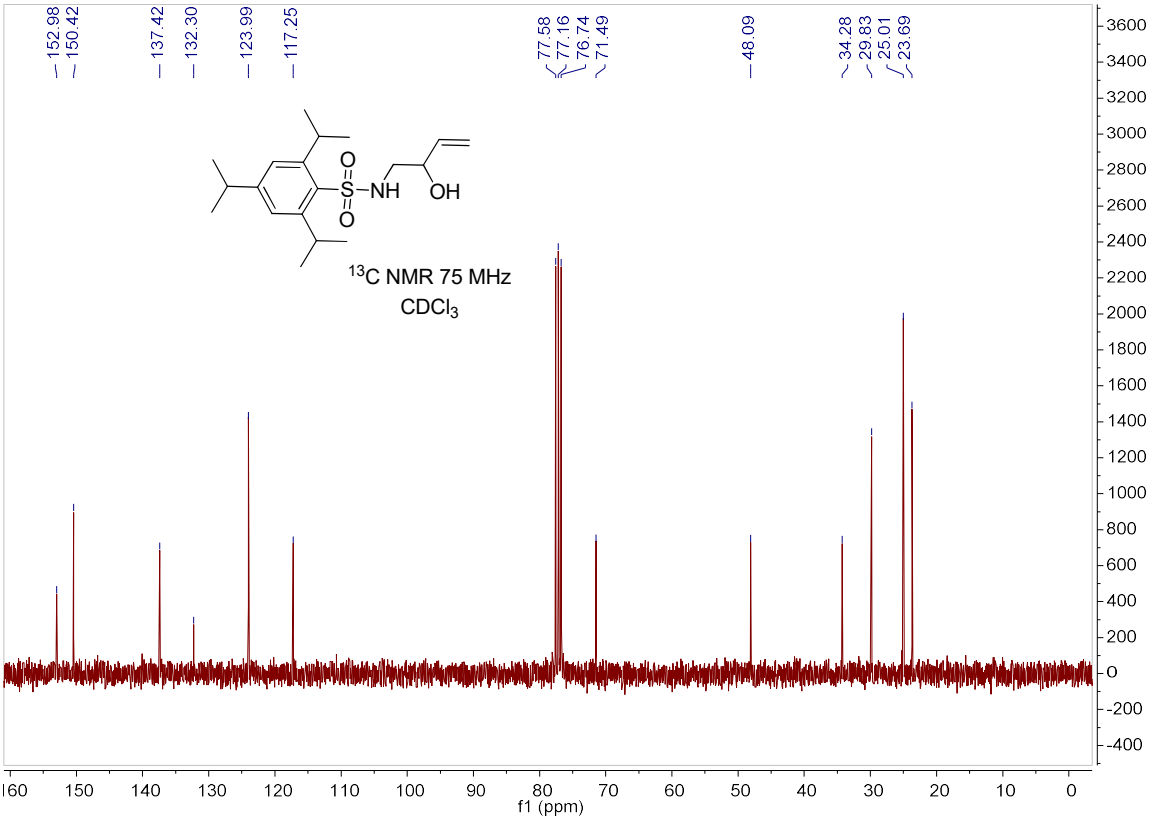
f1 (ppm)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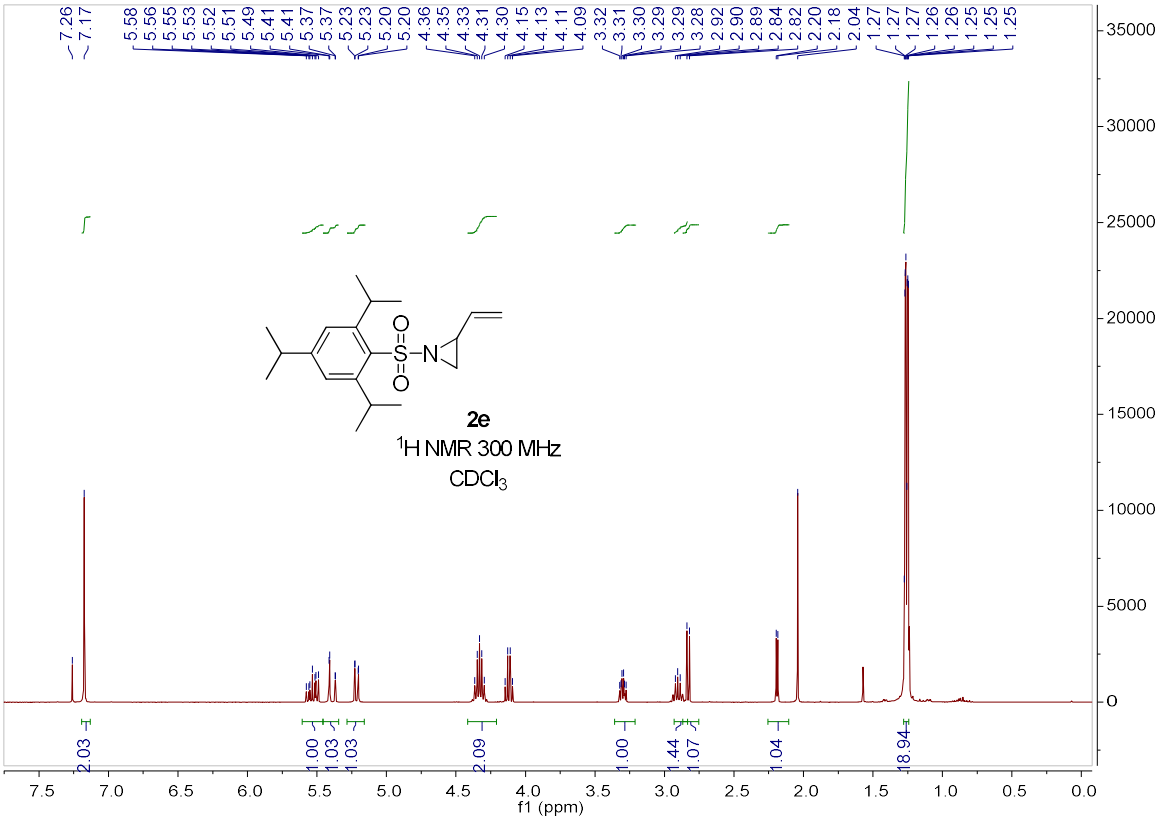
O
S
NH
OH
O
13C NMR 75 MHz
CDCl3
f1 (ppm)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7.17
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5.55
5.53
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5.51
5.49
5.41
5.41
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5.37
5.23
5.23
5.20
5.20
4.36
4.35
4.33
4.31
4.30
4.15
4.13
4.11
4.09
3.32
3.31
3.30
3.29
3.29
3.28
2.92
2.90
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2.84
2.82
2.20
2.18
2.04
1.27
1.27
1.27
1.26
1.26
1.25
1.25
1.25
2e
1H NMR 300 MHz
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1.03
2.09
1.00
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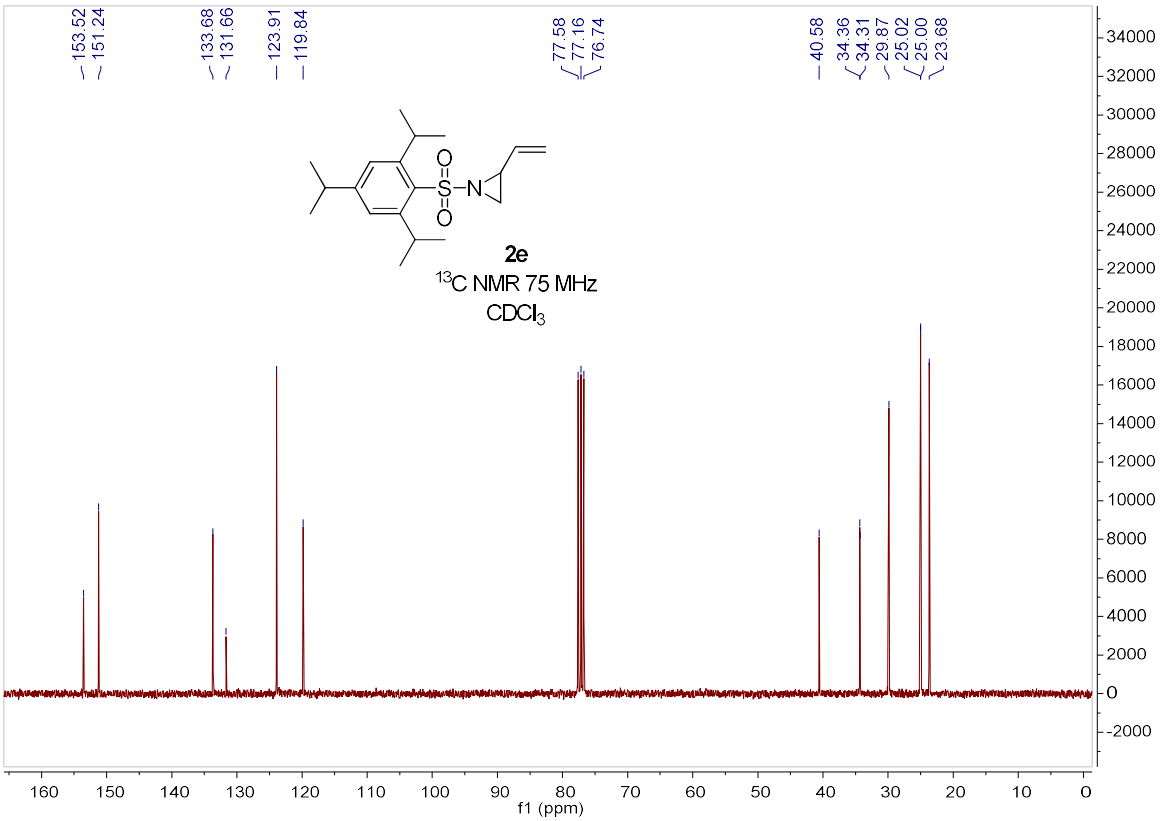
1.07
1.04
18.94
f1 (ppm)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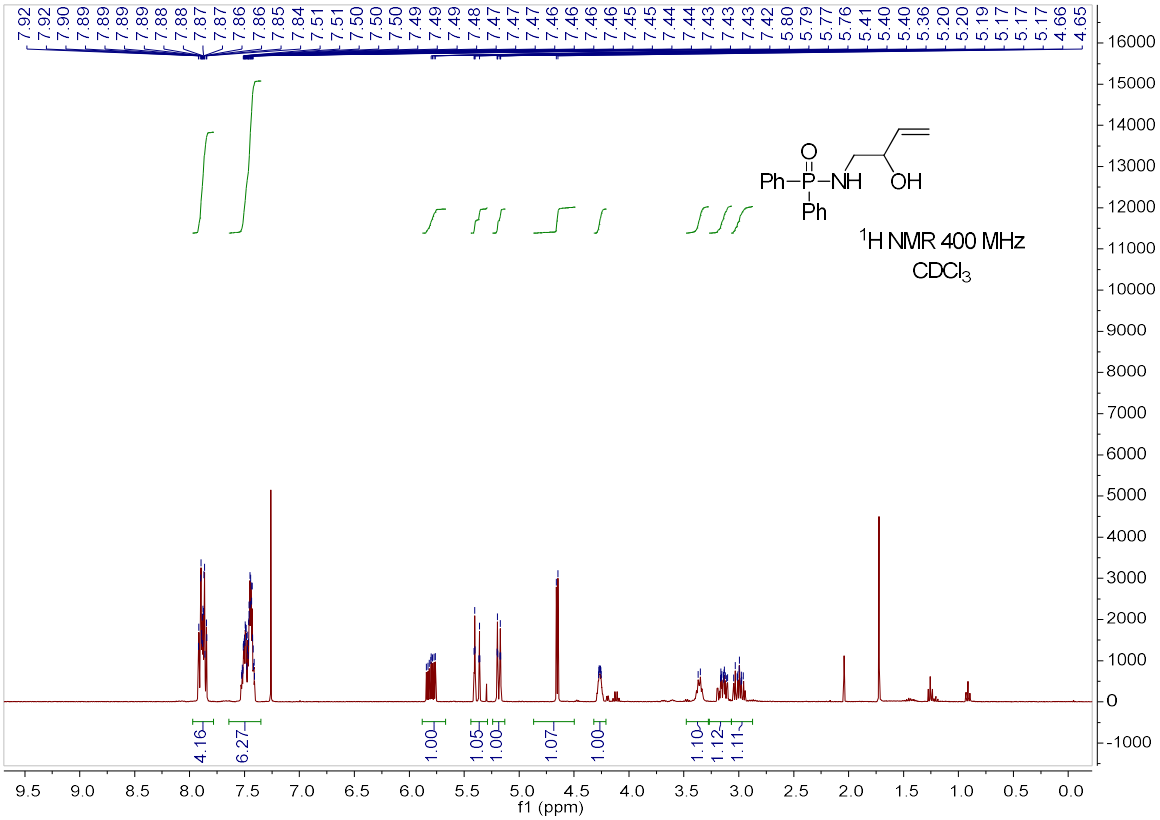
2e
13C NMR 75 MHz
CDCl3
f1 (ppm)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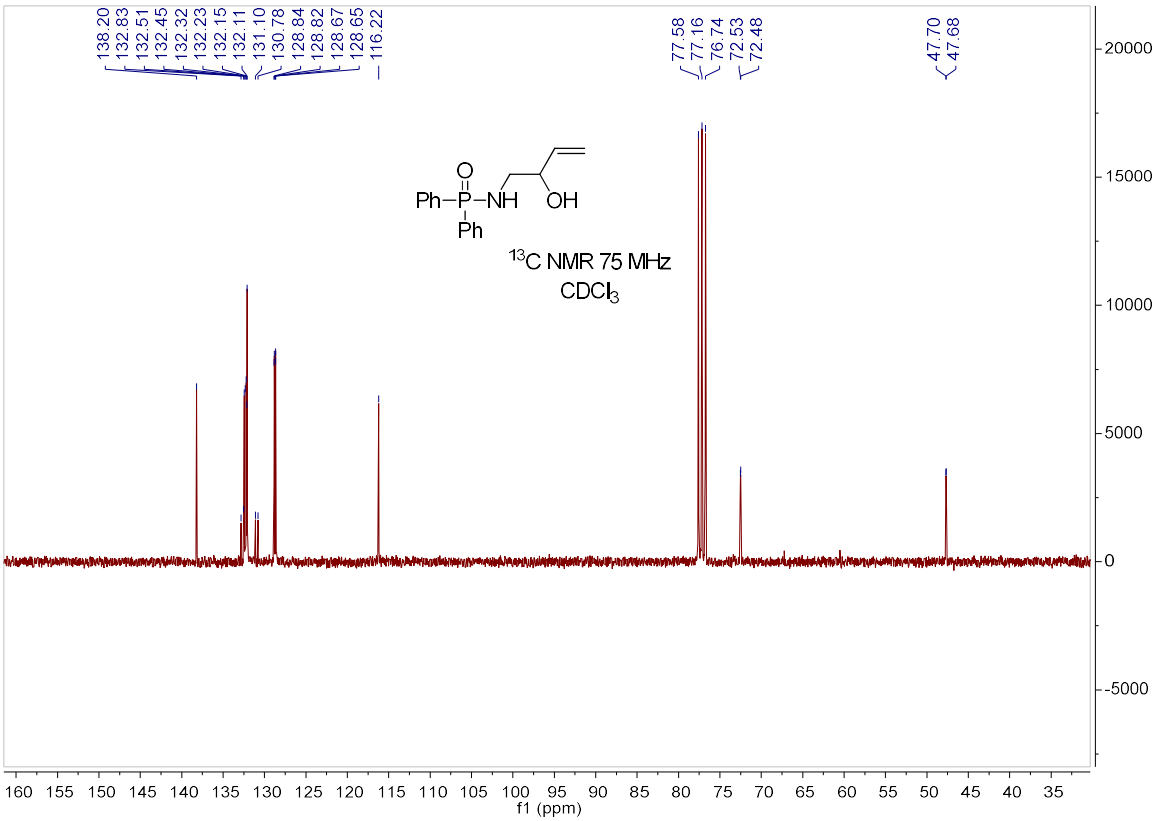
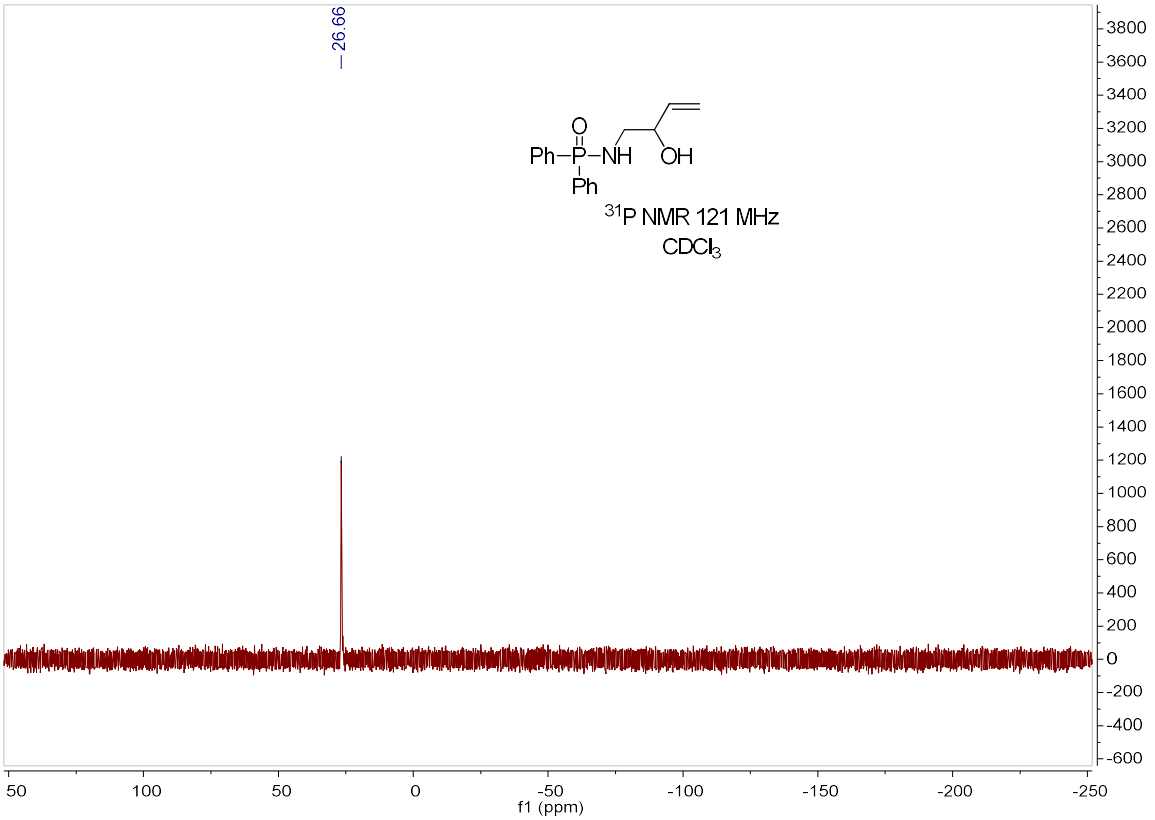
f1 (ppm)


Ph–P(=O)(Ph)–NH–OH
^{13}C NMR 75 MHz
$CDCl_3$
f1 (ppm)


26.66
Ph–P(=O)(Ph)–NH–CH(OH)–CH=CH2
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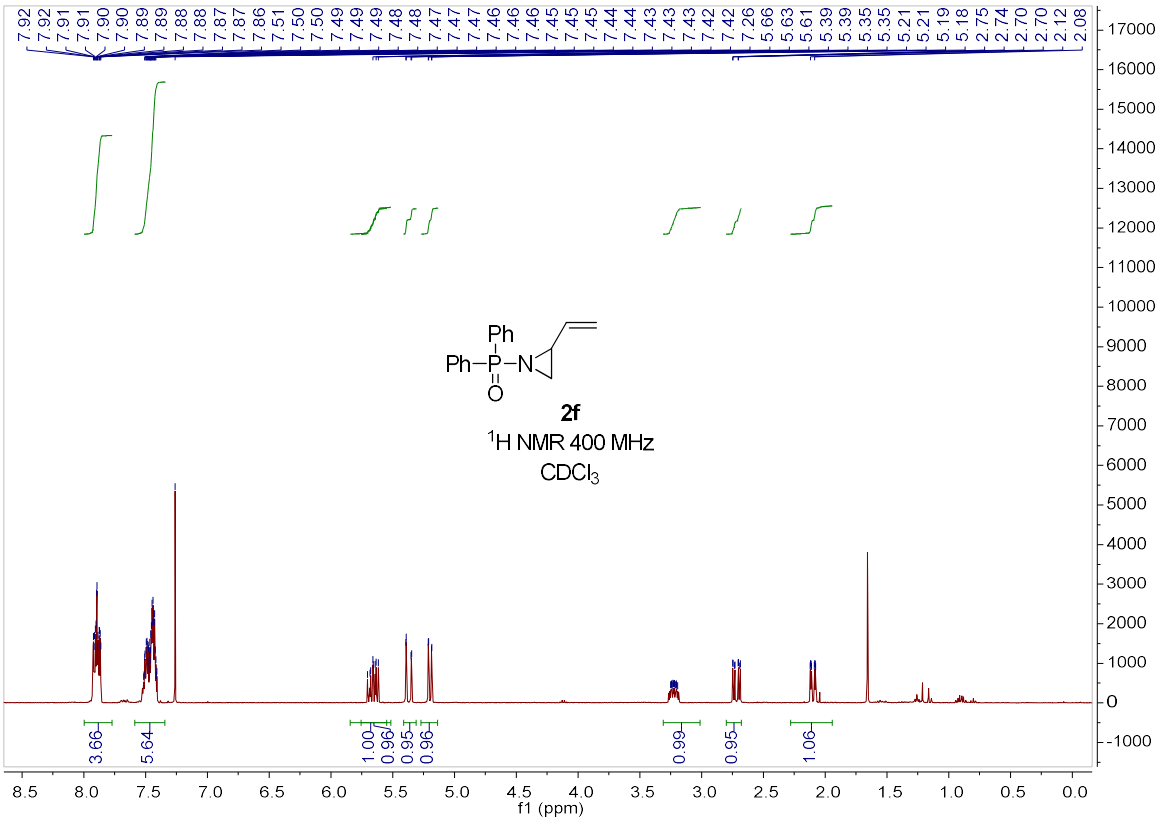
CDCl3
f1 (ppm)


Ph
Ph–P(=O)–N
2f
1H NMR 400 MHz
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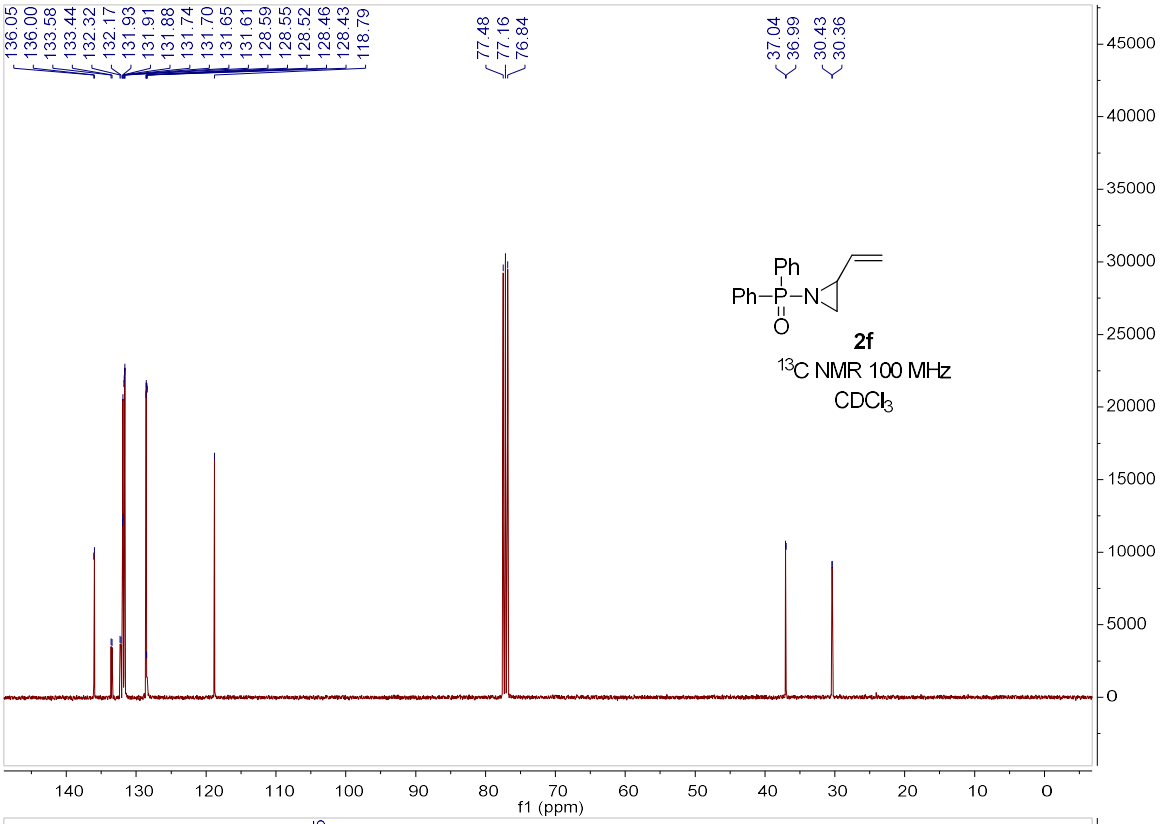
0.95
0.96
0.99
0.95
1.06
f1 (ppm)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128.59
128.55
128.52
128.46
128.43
118.79
77.48
77.16
76.84
37.04
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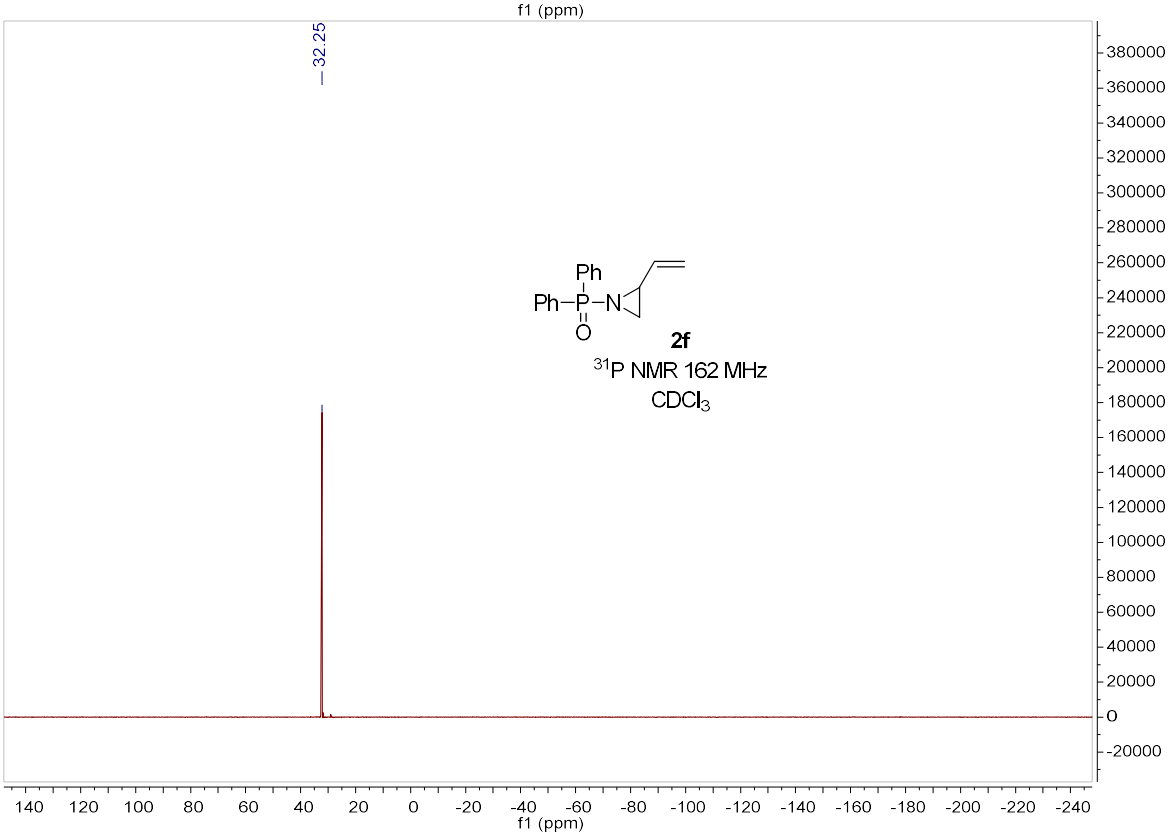
30.43
30.36
Ph
Ph–P–N
O
2f
13C NMR 100 MHz
CDCl3
f1 (ppm)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2f
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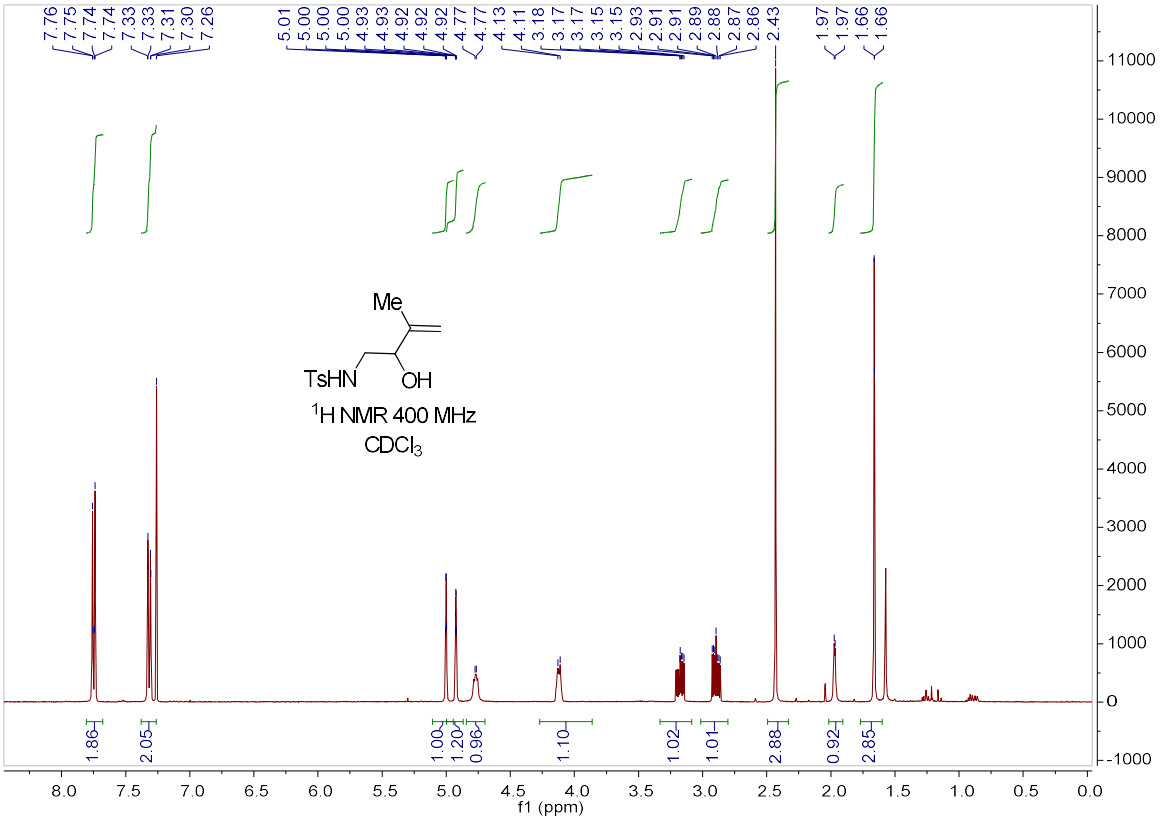
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1.97
1.97
1.66
1.66
Me
TsHN
OH
1H NMR 400 MHz
CDCl3
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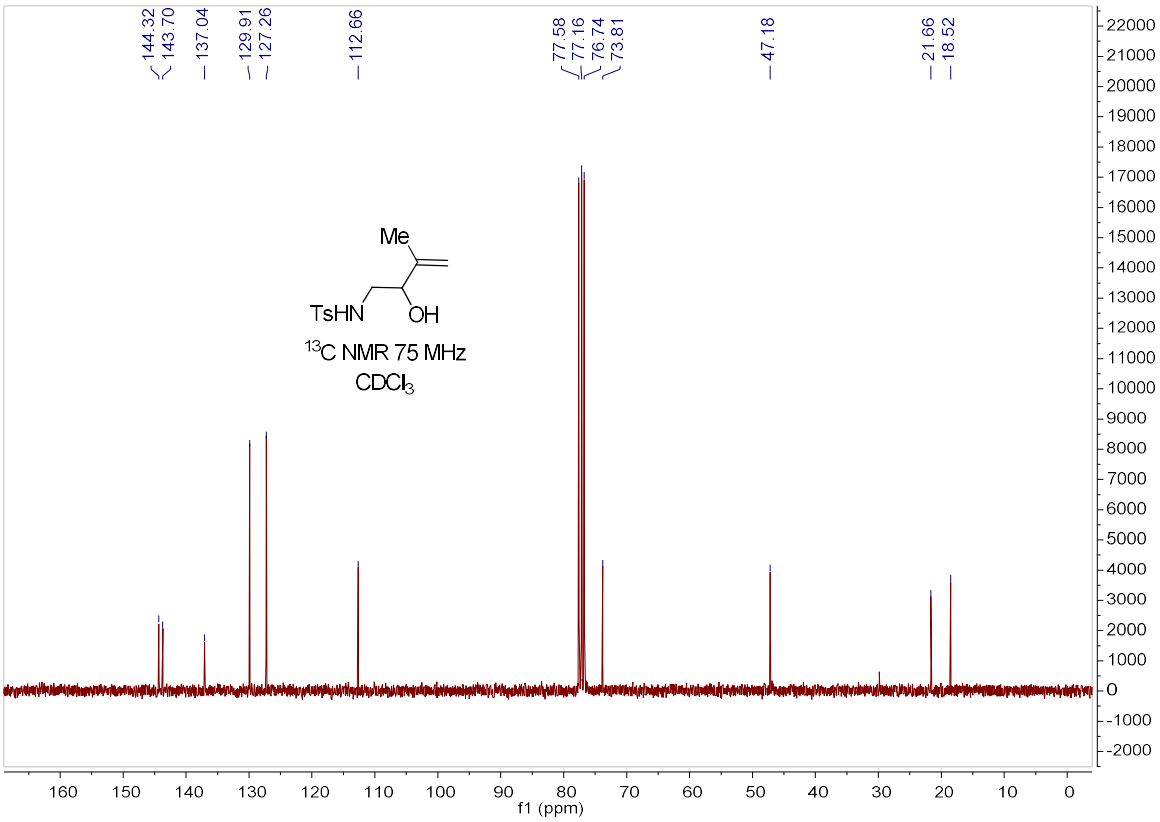
0.92
2.85
f1 (ppm)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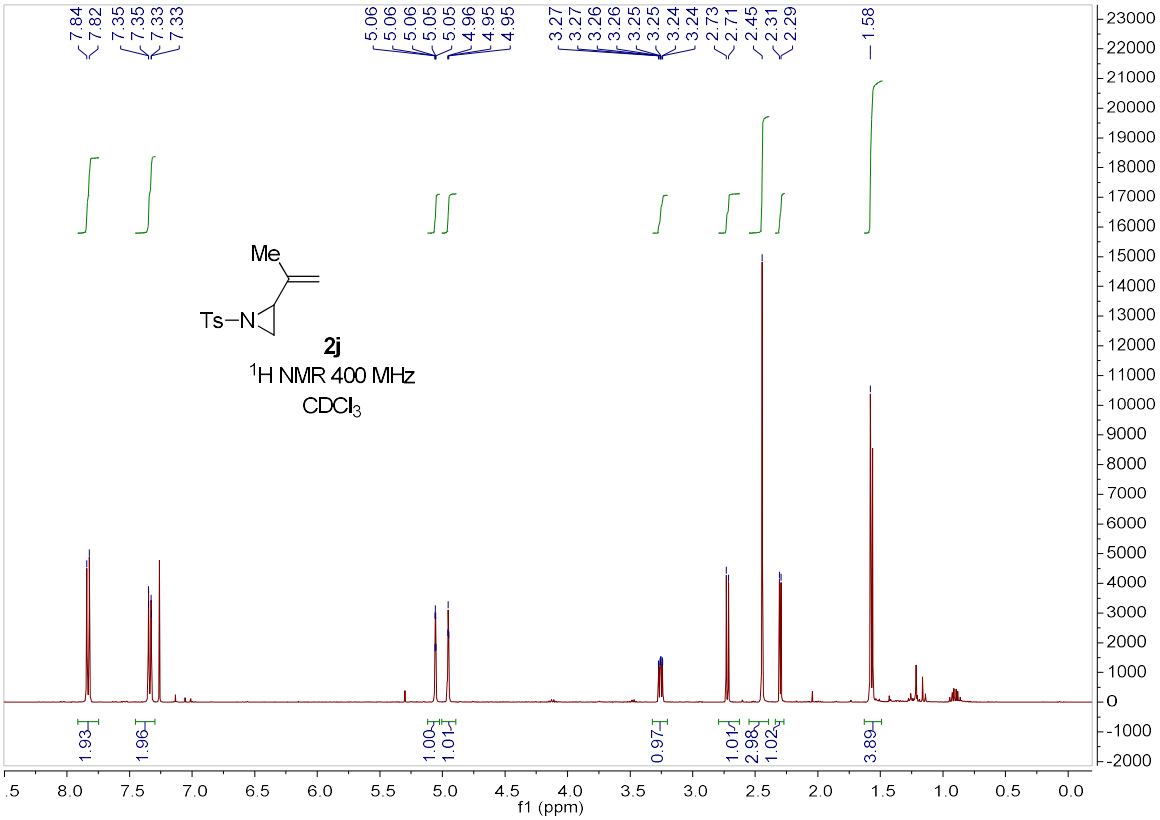
CDCl3
f1 (ppm)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5.06
5.06
5.05
5.05
4.96
4.95
4.95
3.27
3.27
3.26
3.26
3.25
3.25
3.24
3.24
2.73
2.71
2.45
2.31
2.29
1.58
Me
Ts–N
2j
1H NMR 400 MHz
CDCl3
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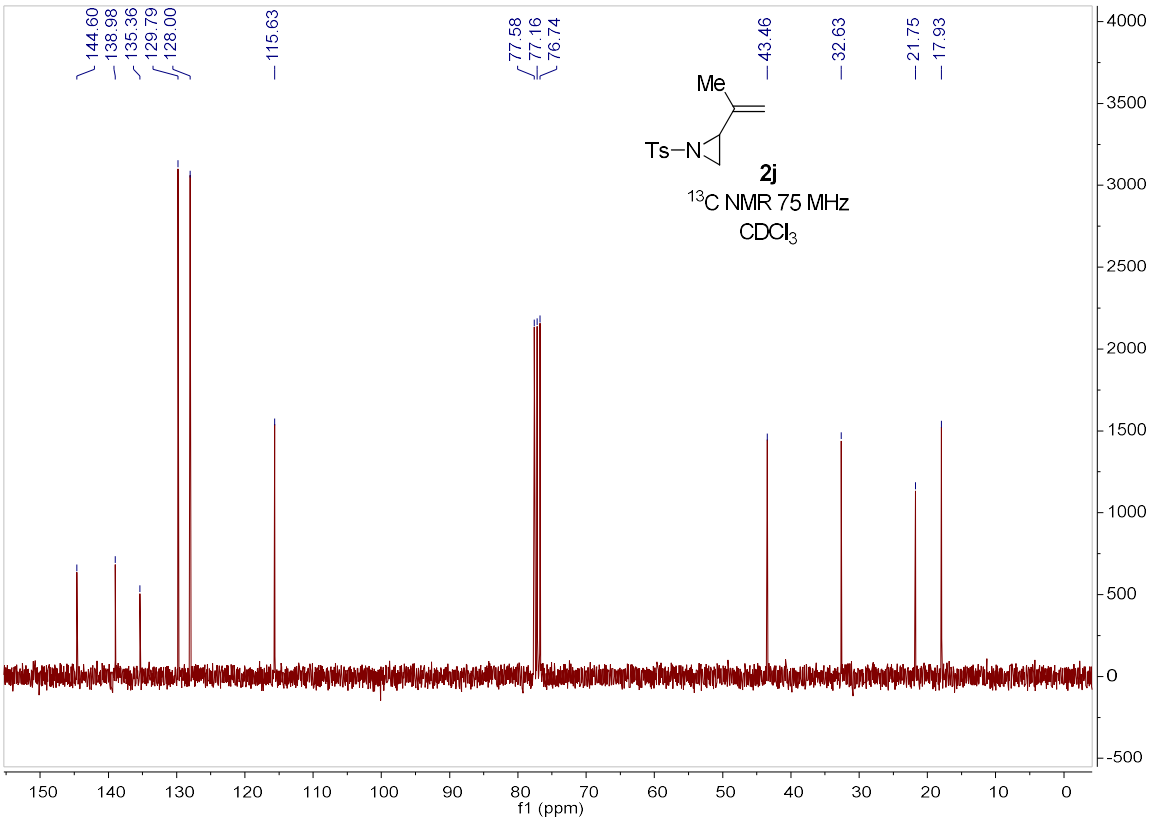
1.96
1.00
1.01
0.97
1.01
2.98
1.02
3.89
f1 (ppm)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Ts–N
2j
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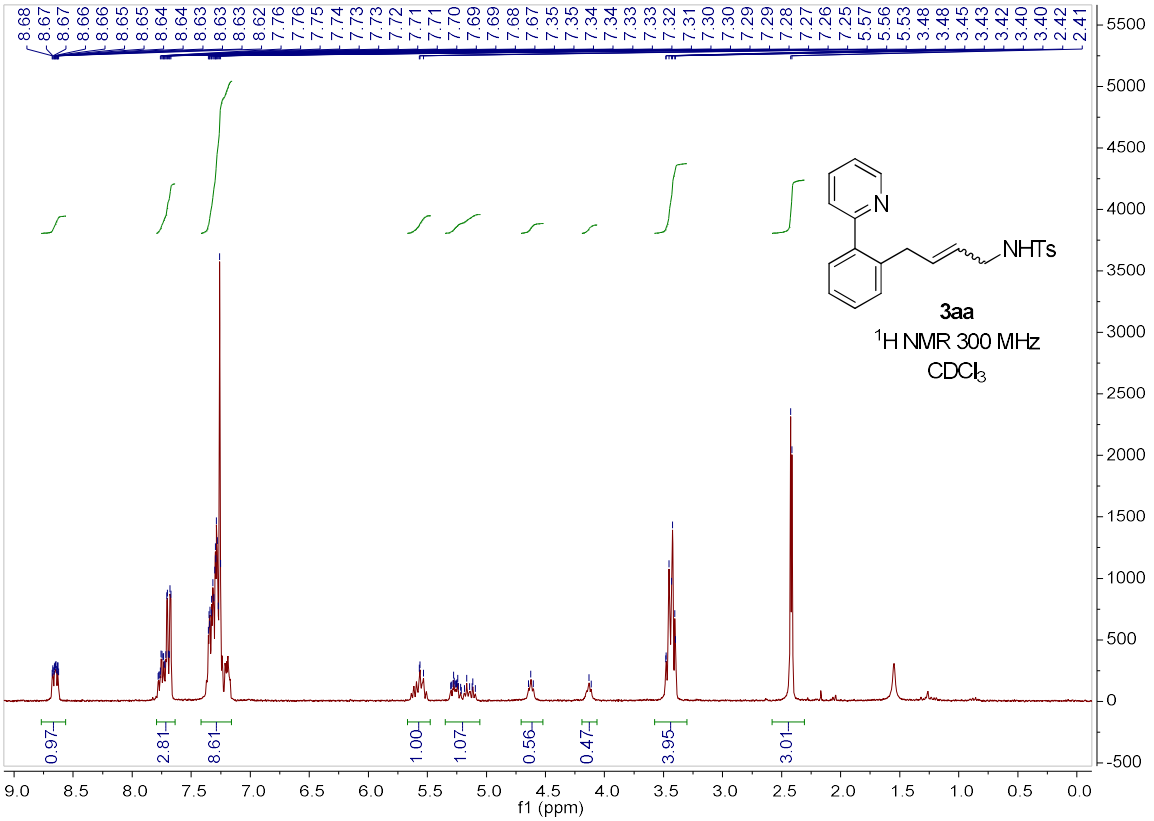
f1 (ppm)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N
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$CDCl_3$
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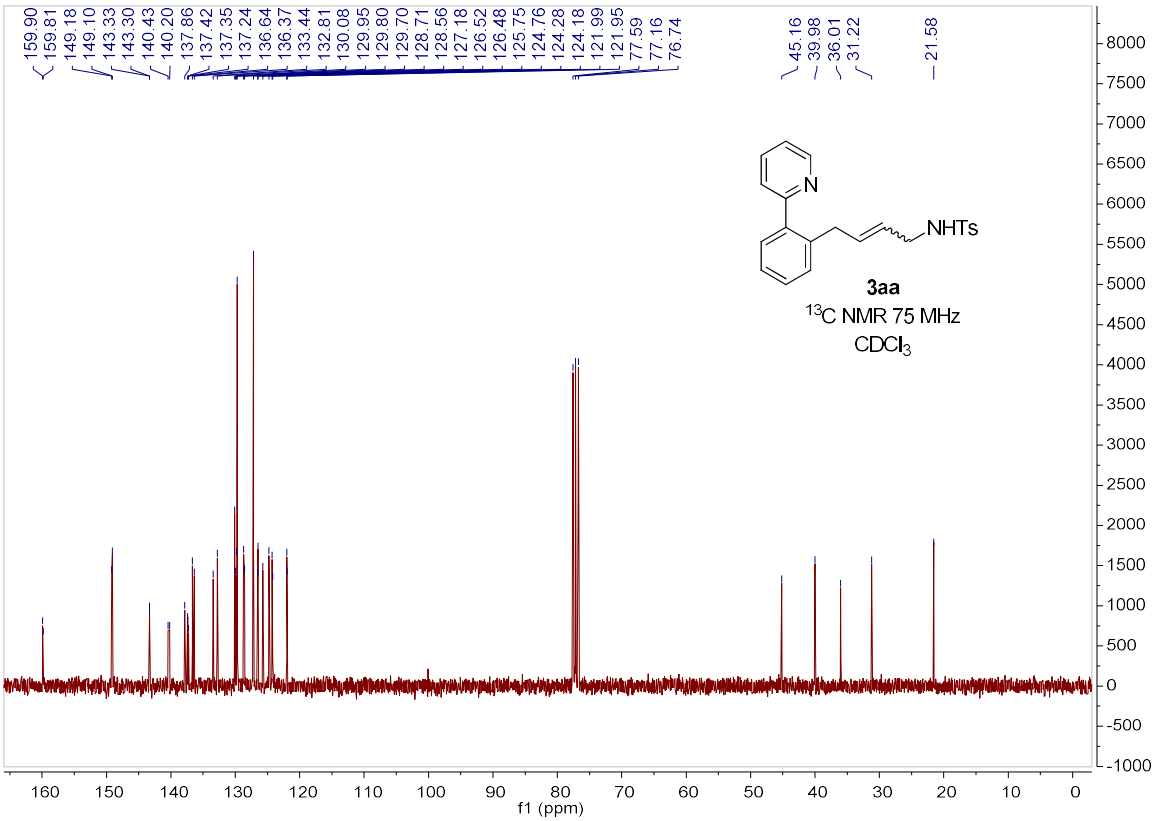
f1 (ppm)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^{13}C NMR 75 MHz
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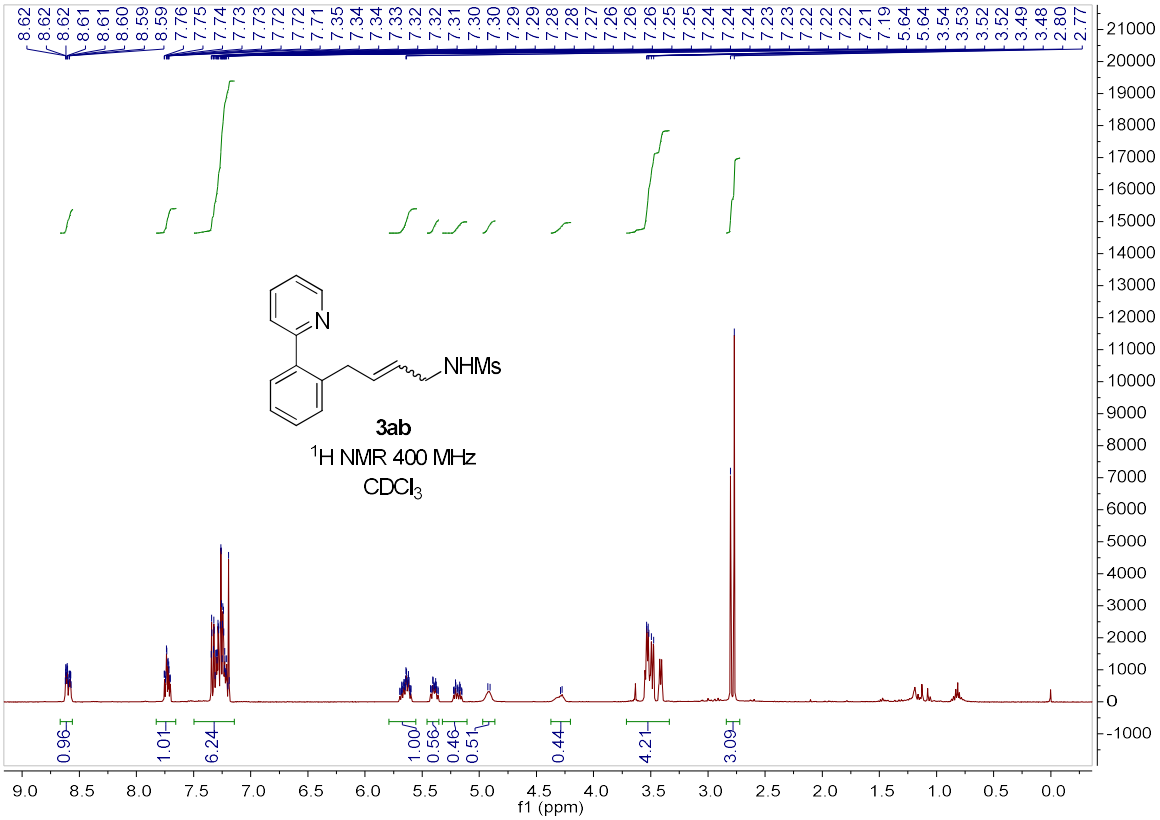
f1 (ppm)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1H NMR 400 MHz
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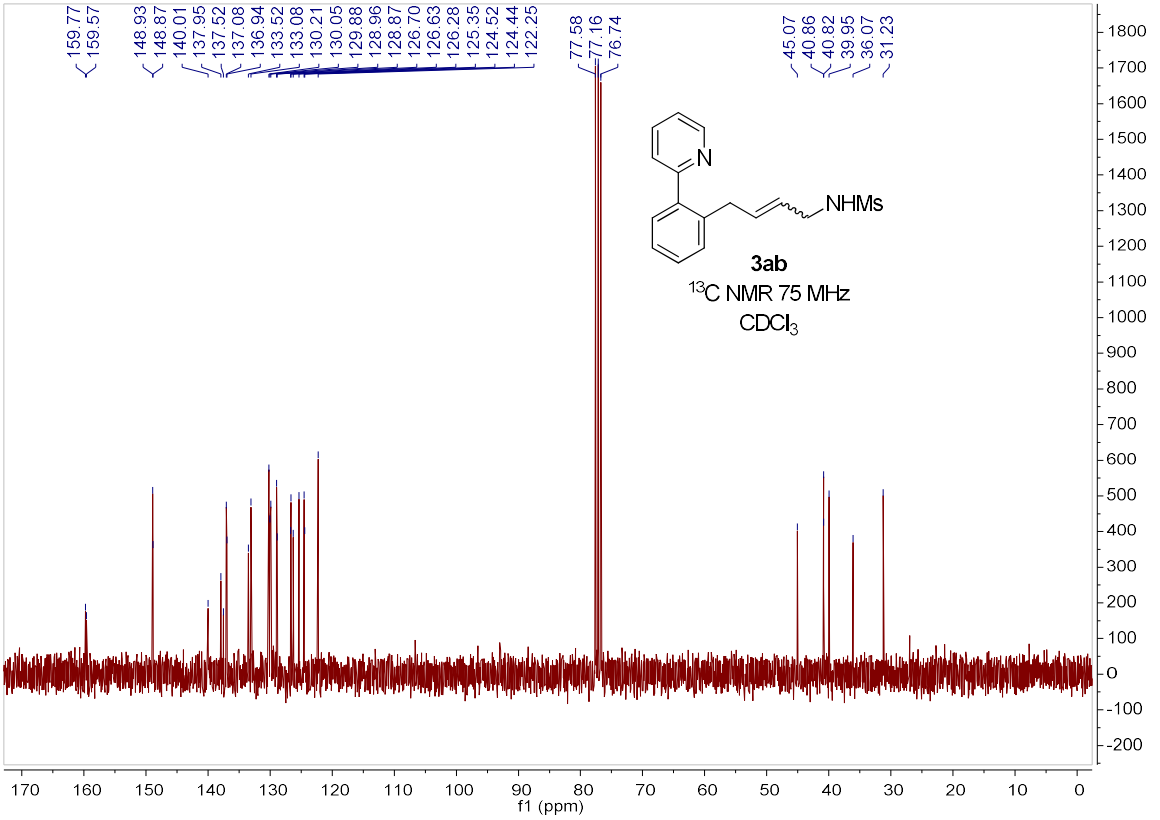
f1 (ppm)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3ab
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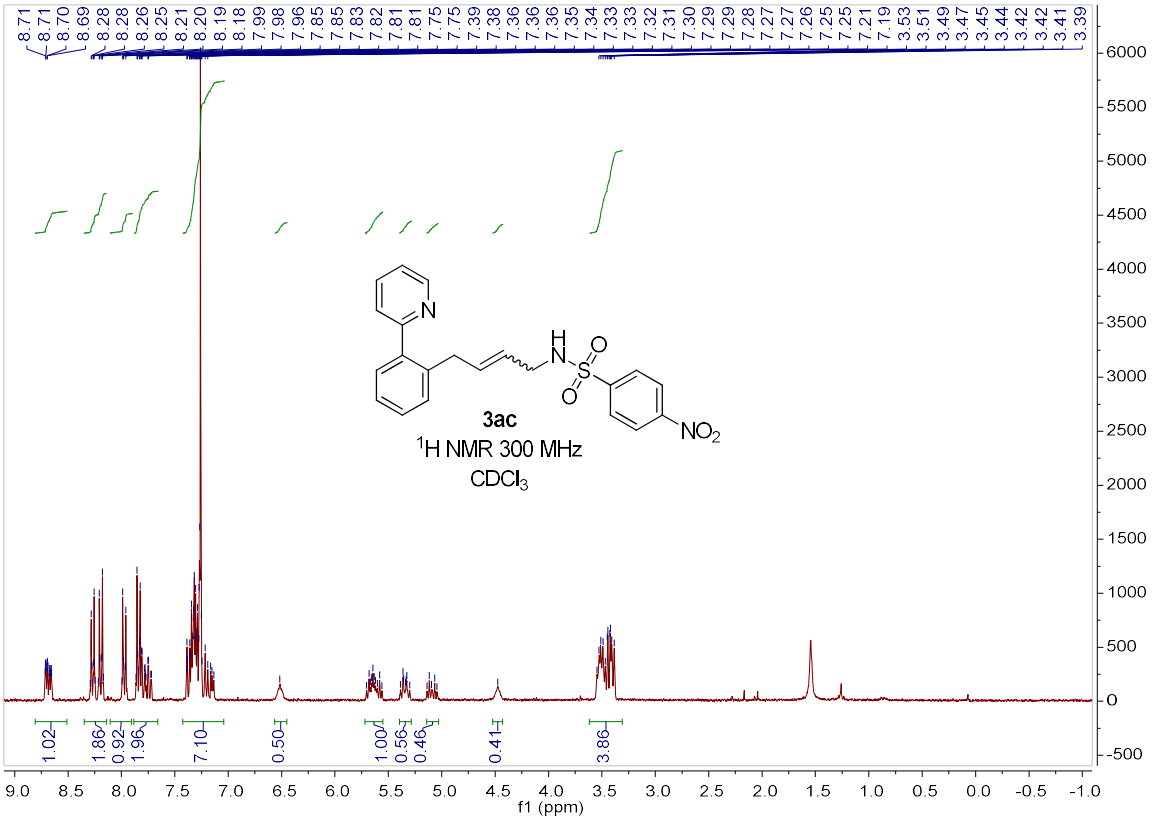
CDCl3
f1 (ppm)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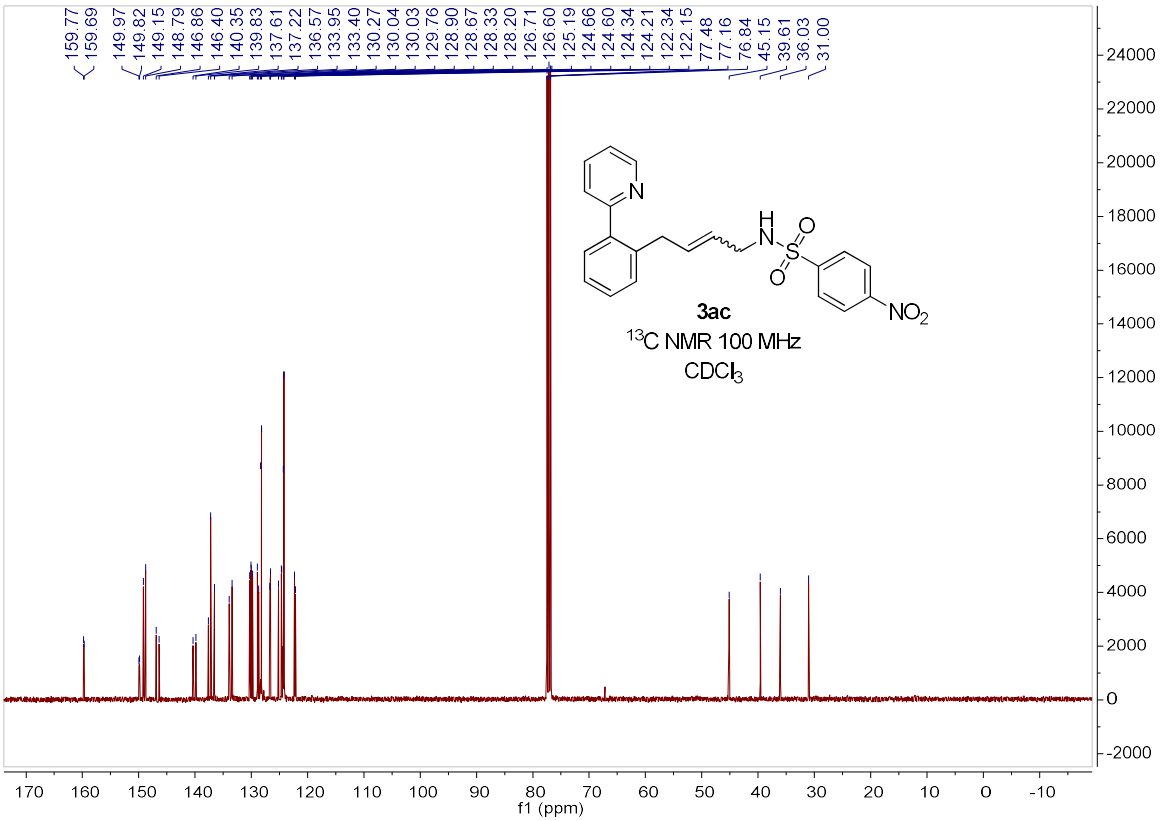
CDCl3
NO2
f1 (ppm)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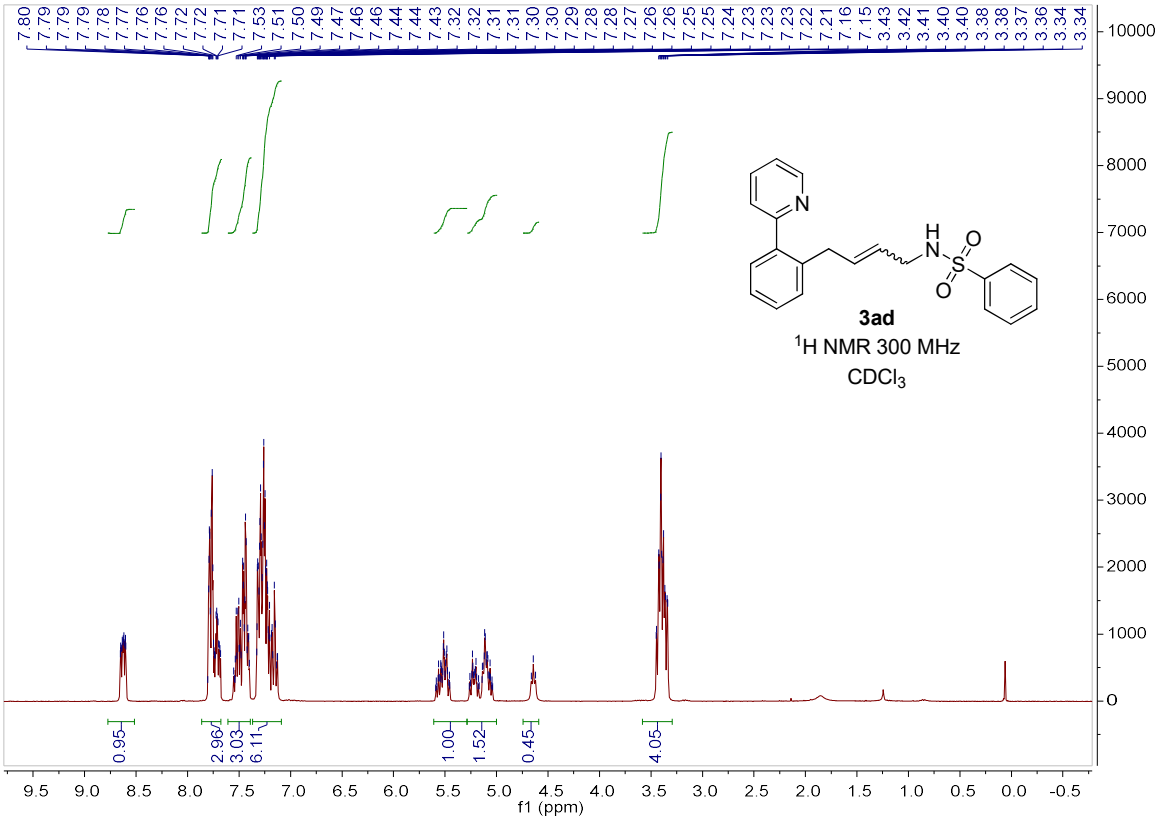
CDCl3
NO2
f1 (ppm)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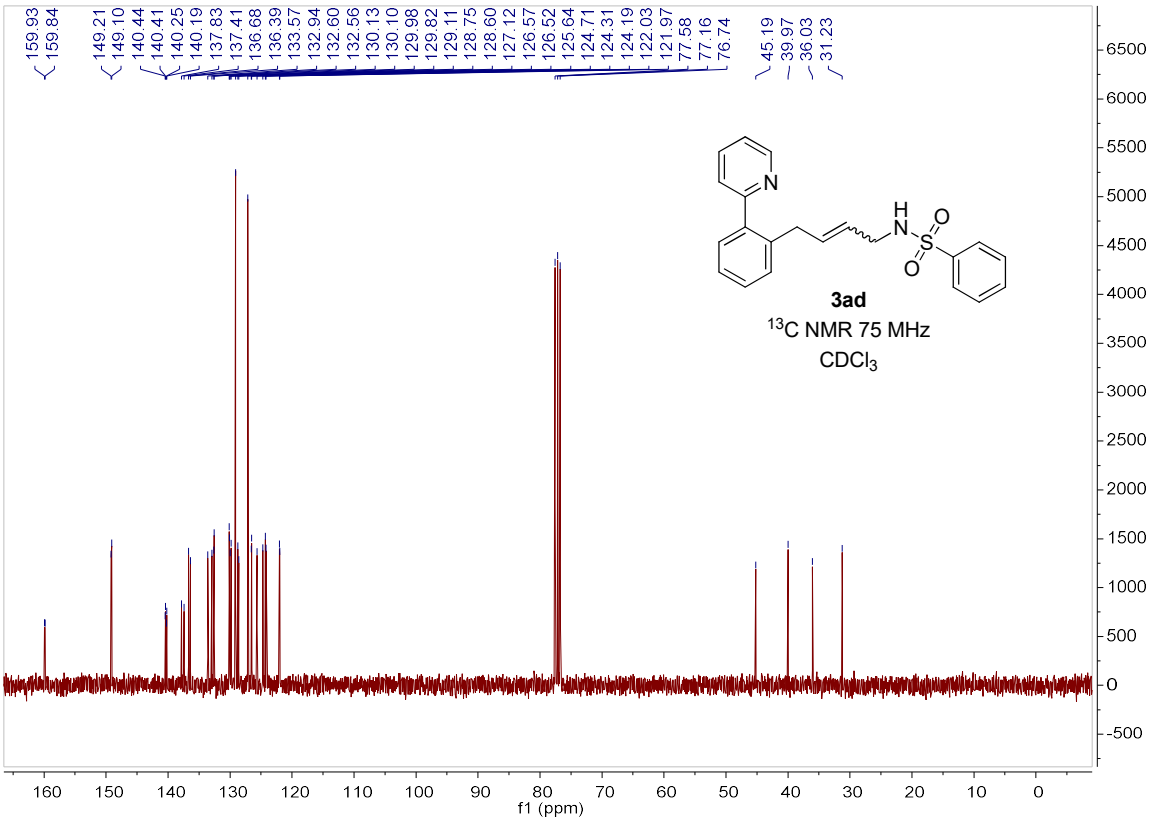
f1 (ppm)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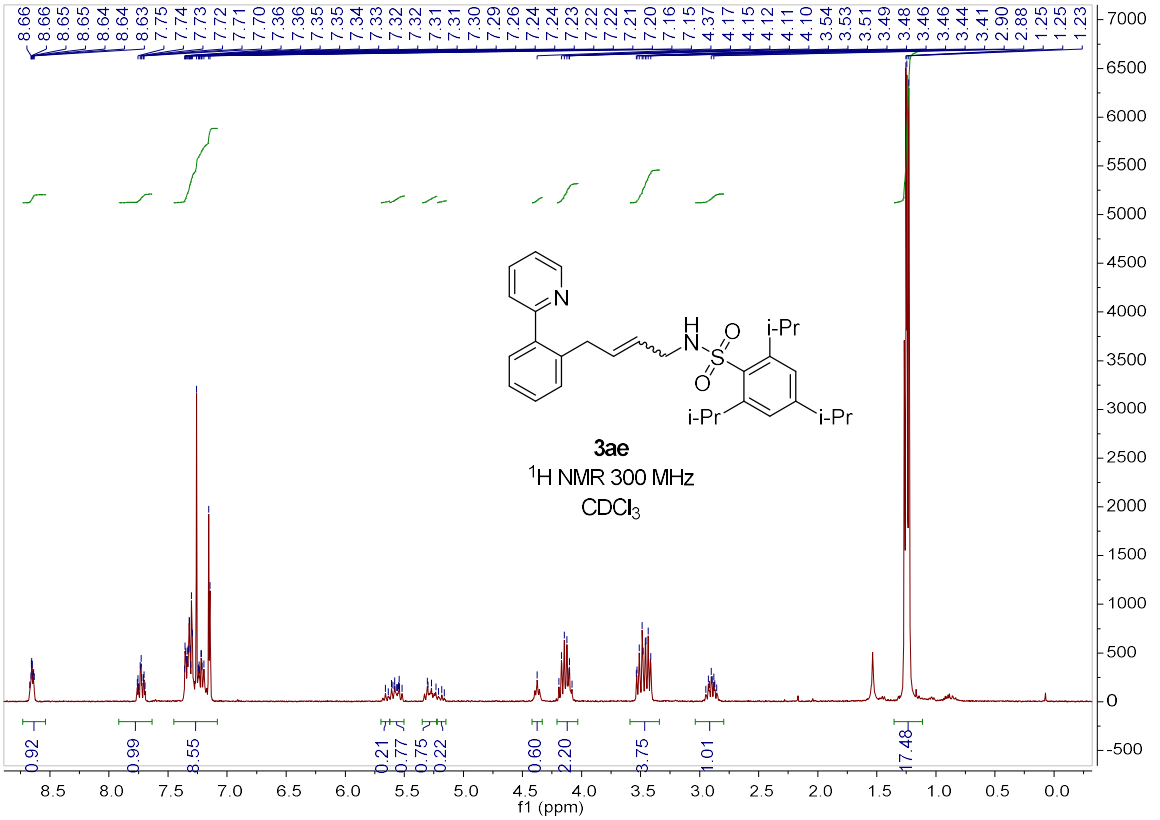
f1 (ppm)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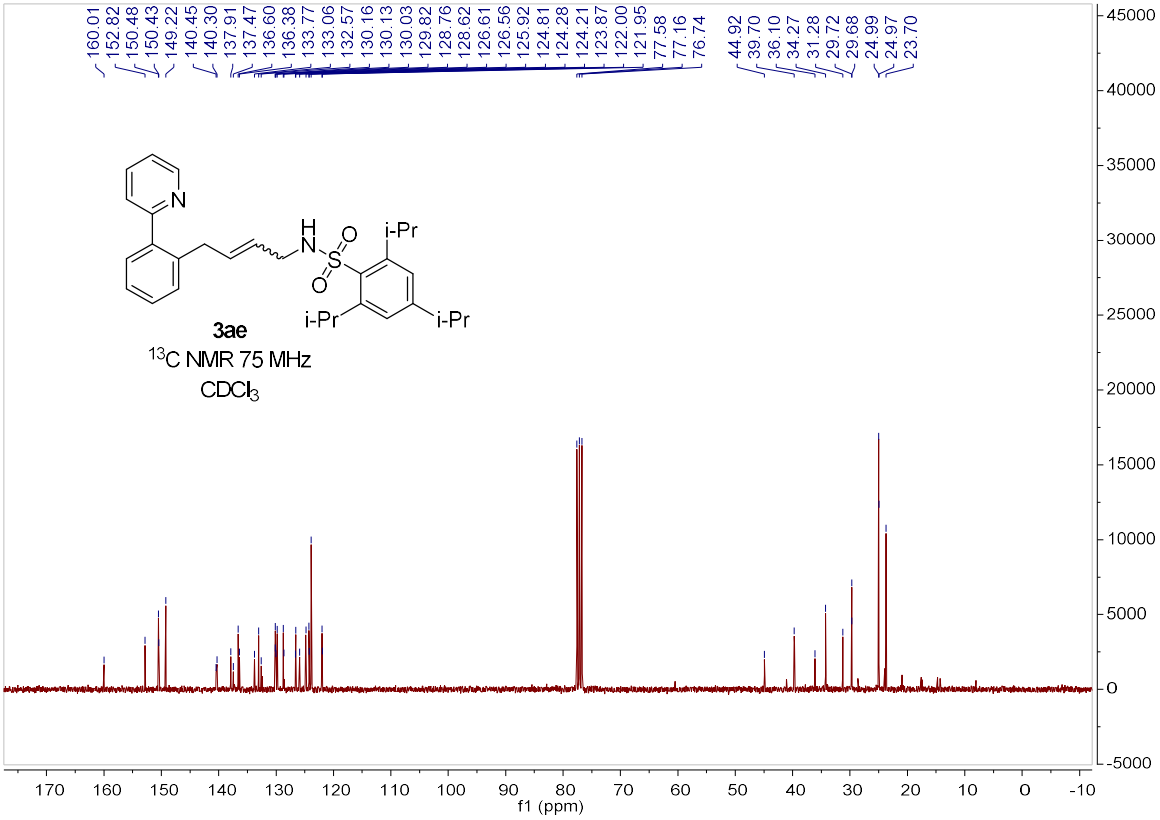
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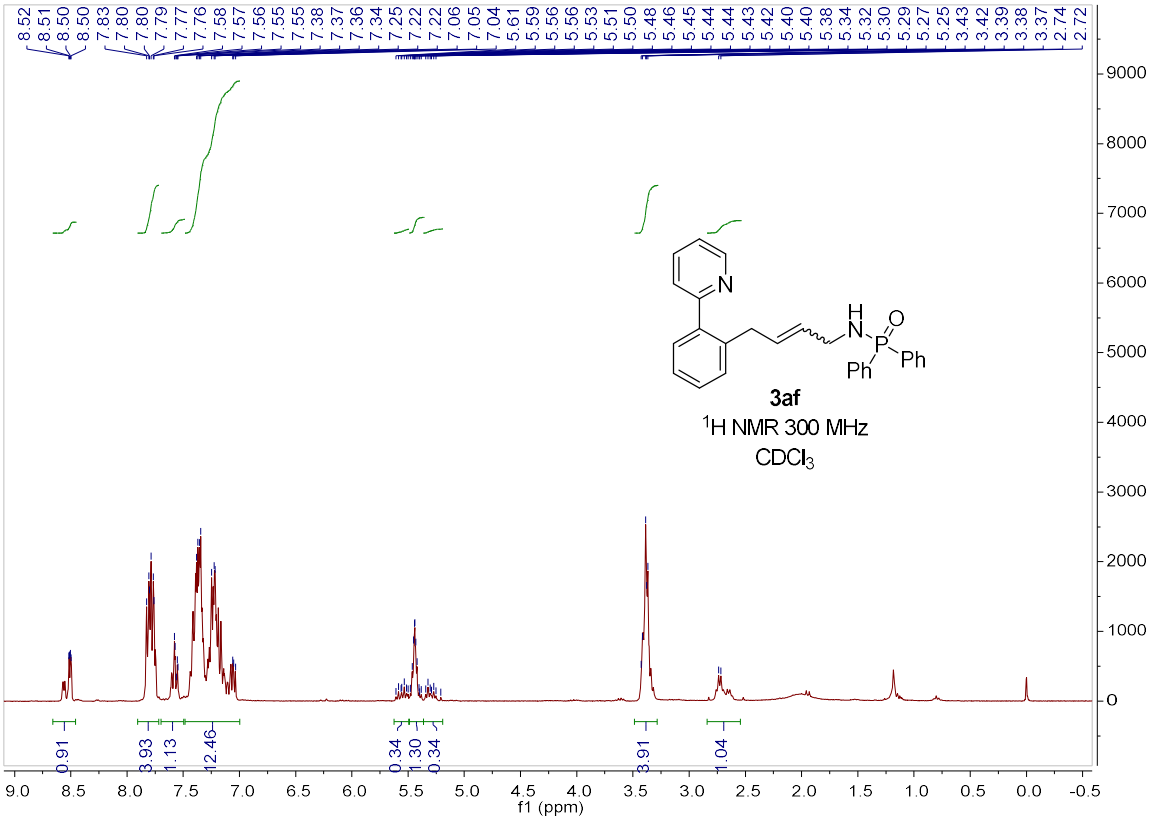
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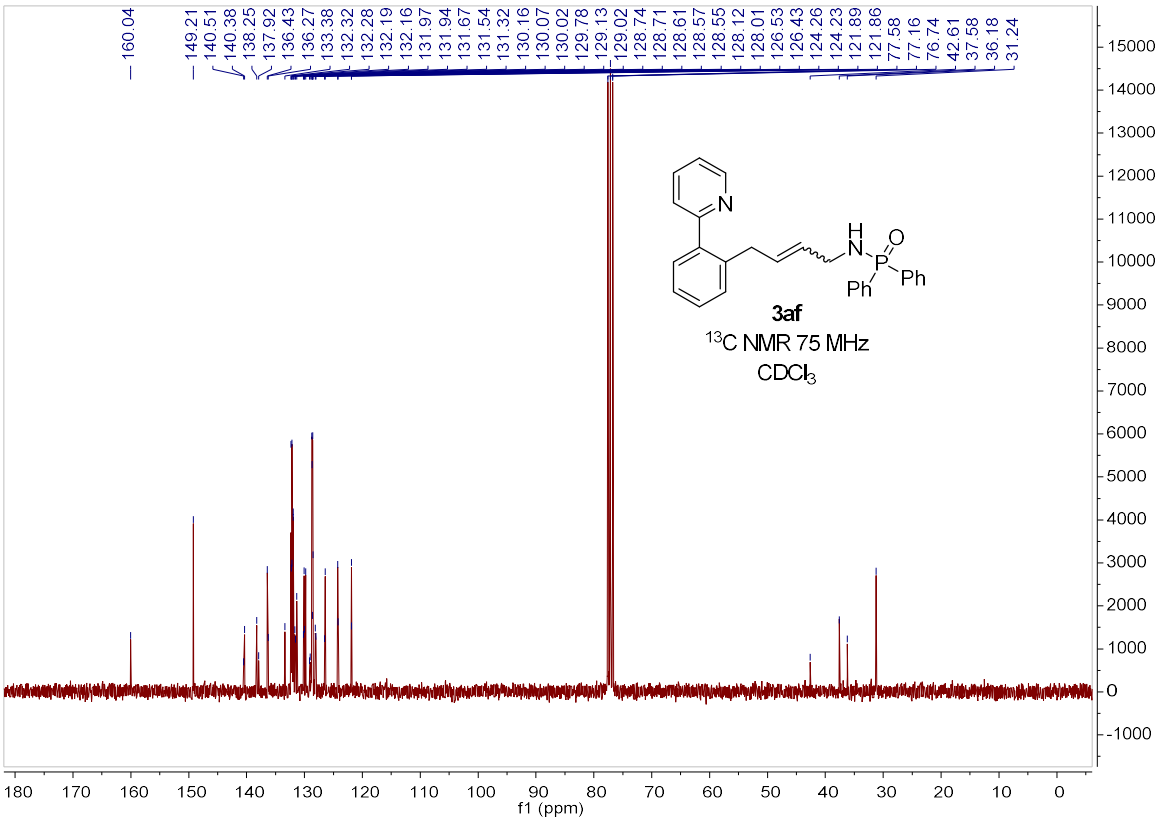
f1 (ppm)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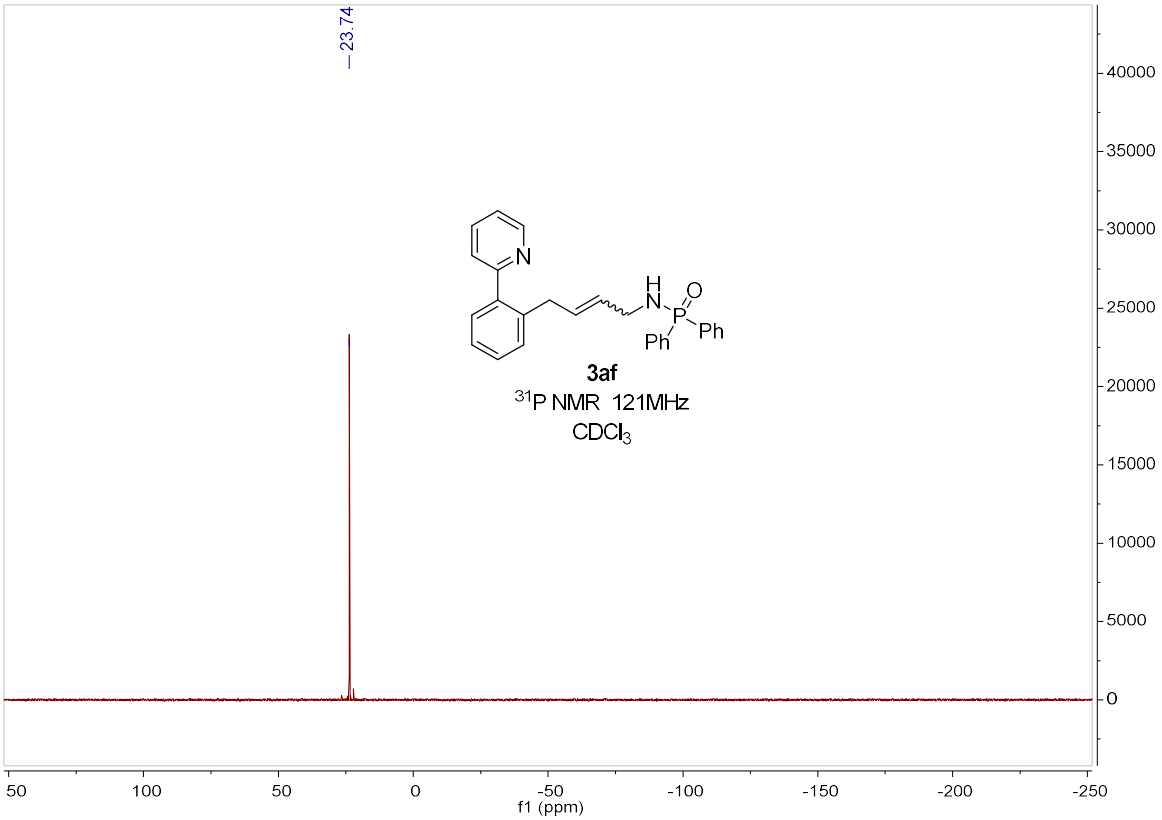
3af
13C NMR 75 MHz
CDCl3
f1 (ppm)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31P NMR 121MHz
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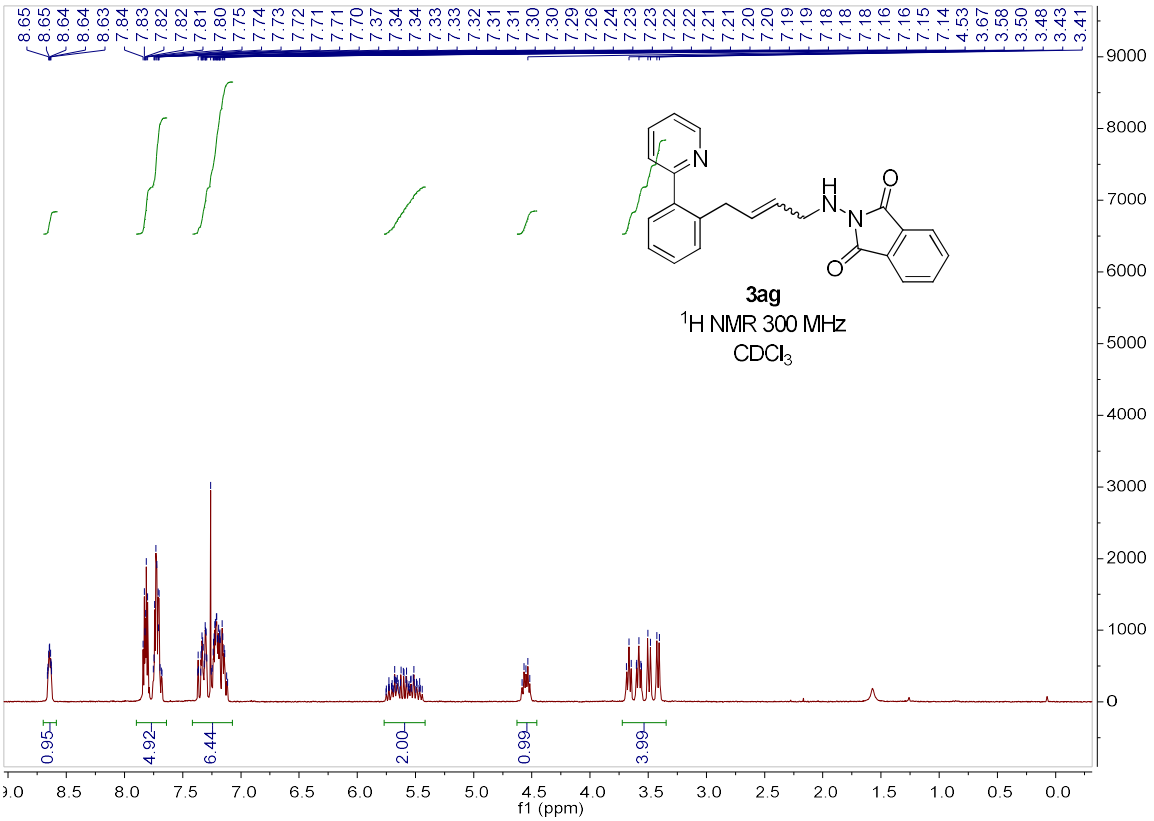
f1 (ppm)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1H NMR 300 MHz
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0.95
4.92
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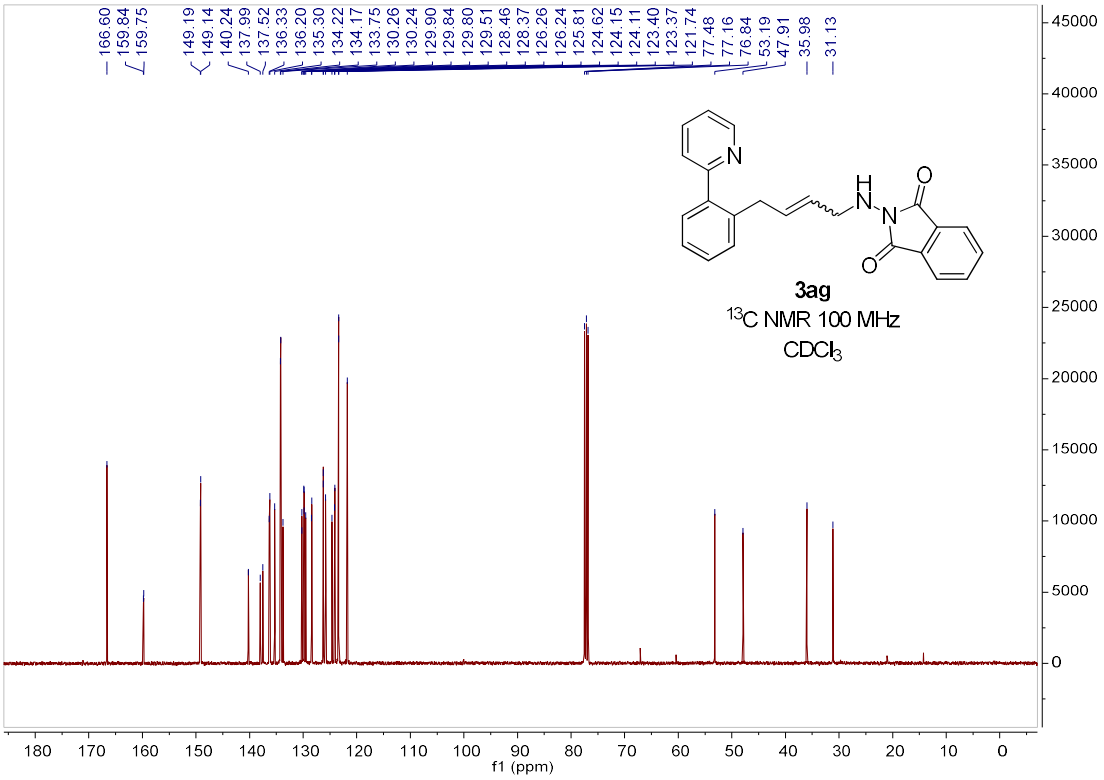
2.00
0.99
3.99
f1 (ppm)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133.75
130.26
130.24
129.90
129.84
129.80
129.51
128.46
128.37
126.26
126.24
125.81
124.62
124.15
124.11
123.40
123.37
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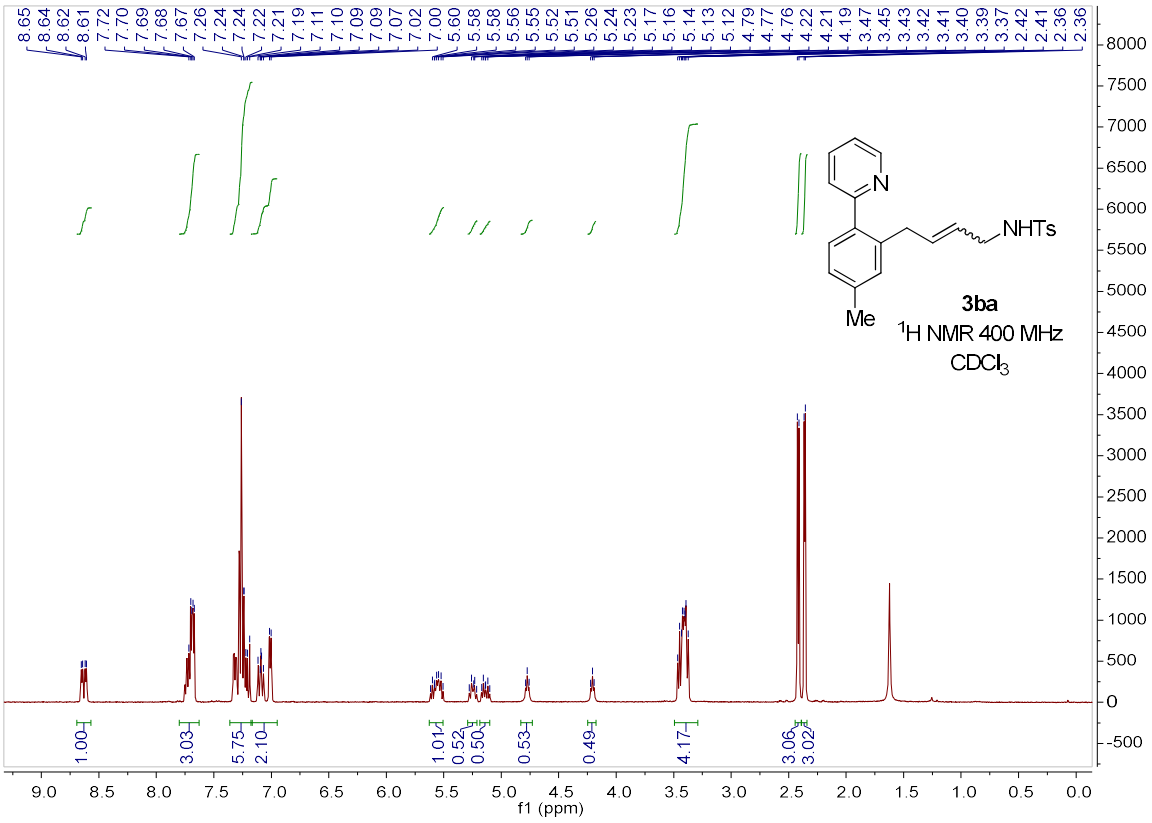
76.84
53.19
47.91
35.98
31.13
3ag
13C NMR 100 MHz
CDCl3
f1 (ppm)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7.11
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7.09
7.09
7.07
7.02
7.00
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5.55
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5.13
5.12
4.79
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4.22
4.21
4.19
3.47
3.45
3.43
3.42
3.41
3.40
3.39
3.37
2.42
2.41
2.36
NHTs
Me
3ba
1H NMR 400 MHz
CDCl3
1.00
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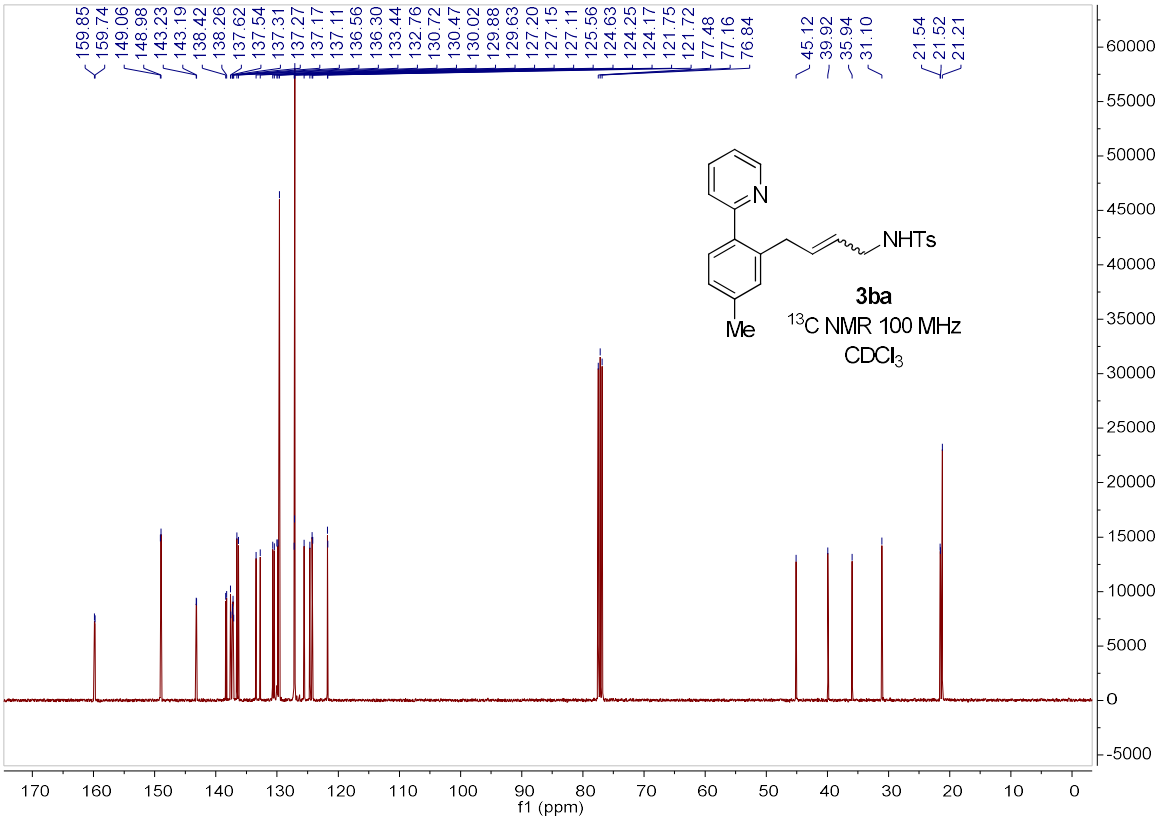
0.49
4.17
3.06
3.02
f1 (ppm)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121.72
77.48
77.16
76.84
45.12
39.92
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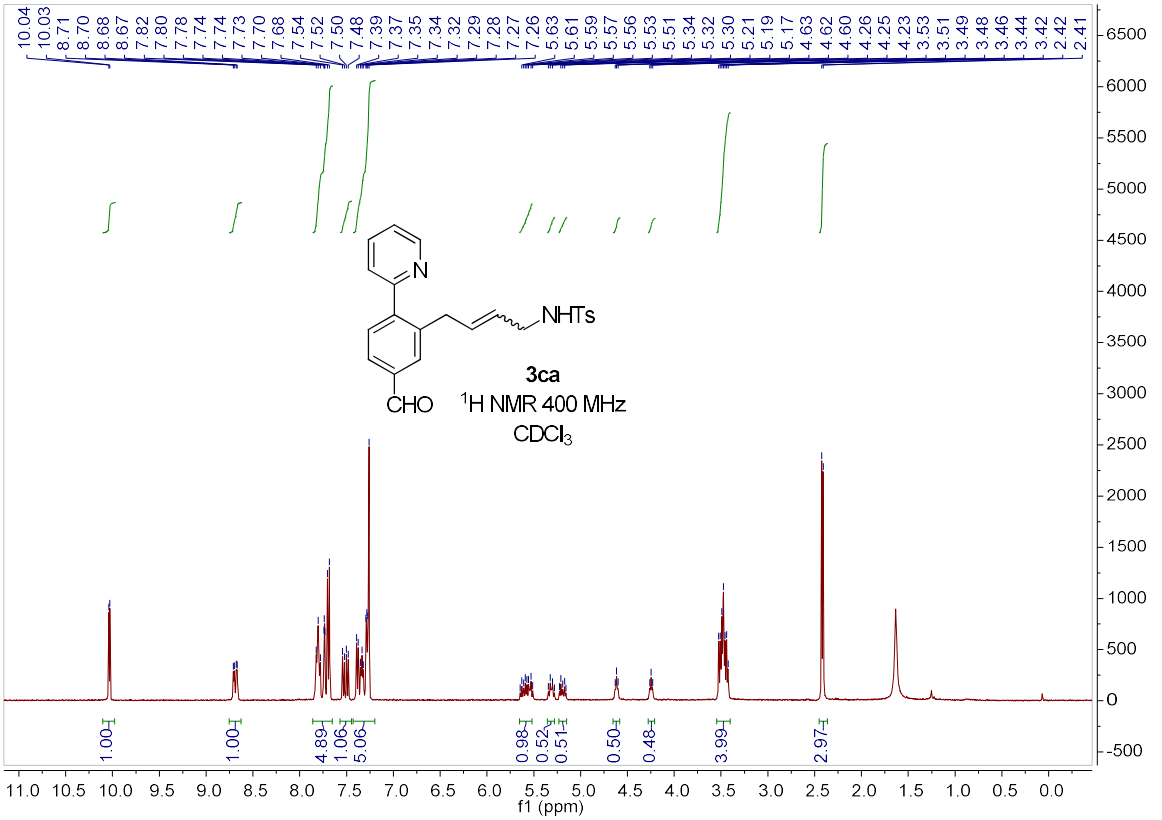
N
NHTs
Me
3ba
13C NMR 100 MHz
CDCl3
f1 (ppm)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7.39
7.37
7.35
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5.30
5.21
5.19
5.17
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4.62
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4.25
4.23
3.53
3.51
3.49
3.48
3.46
3.44
3.42
2.42
2.41
N
NHTs
CHO
3ca
1H NMR 400 MHz
CDCl3
1.00
1.00
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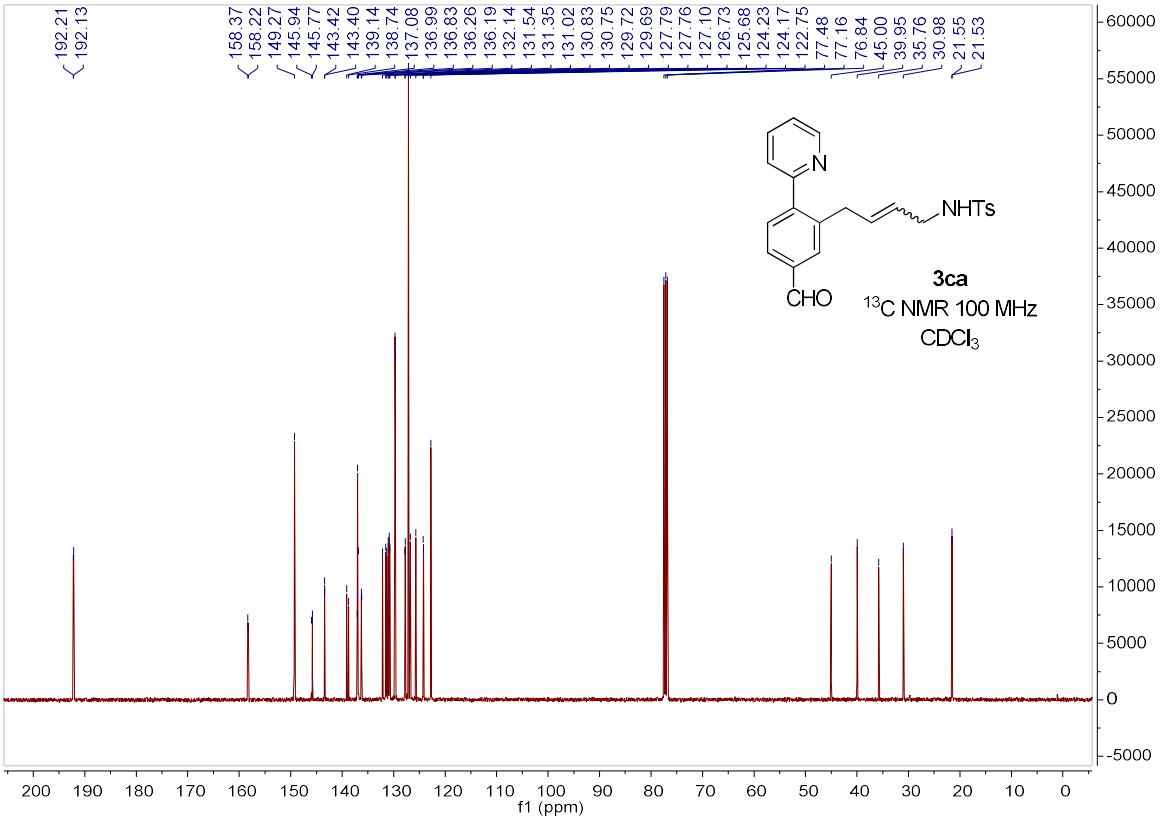
0.52
0.51
0.50
0.48
3.99
2.97
f1 (ppm)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136.83
136.26
136.19
132.14
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131.35
131.02
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124.23
124.17
122.75
77.48
77.16
76.84
45.00
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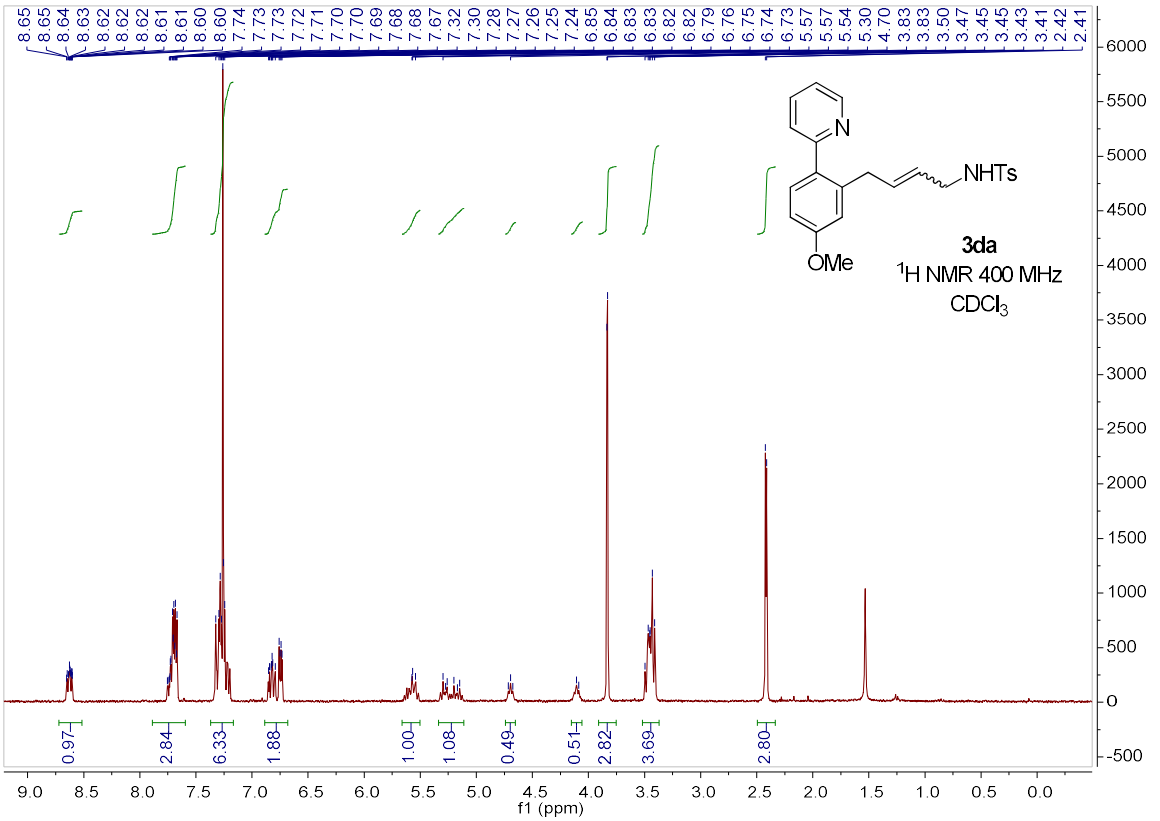
NHTs
CHO
3ca
13C NMR 100 MHz
CDCl3
f1 (ppm)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6.74
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3.45
3.45
3.43
3.41
2.42
2.41
N
NHTs
OMe
3da
1H NMR 400 MHz
CDCl3
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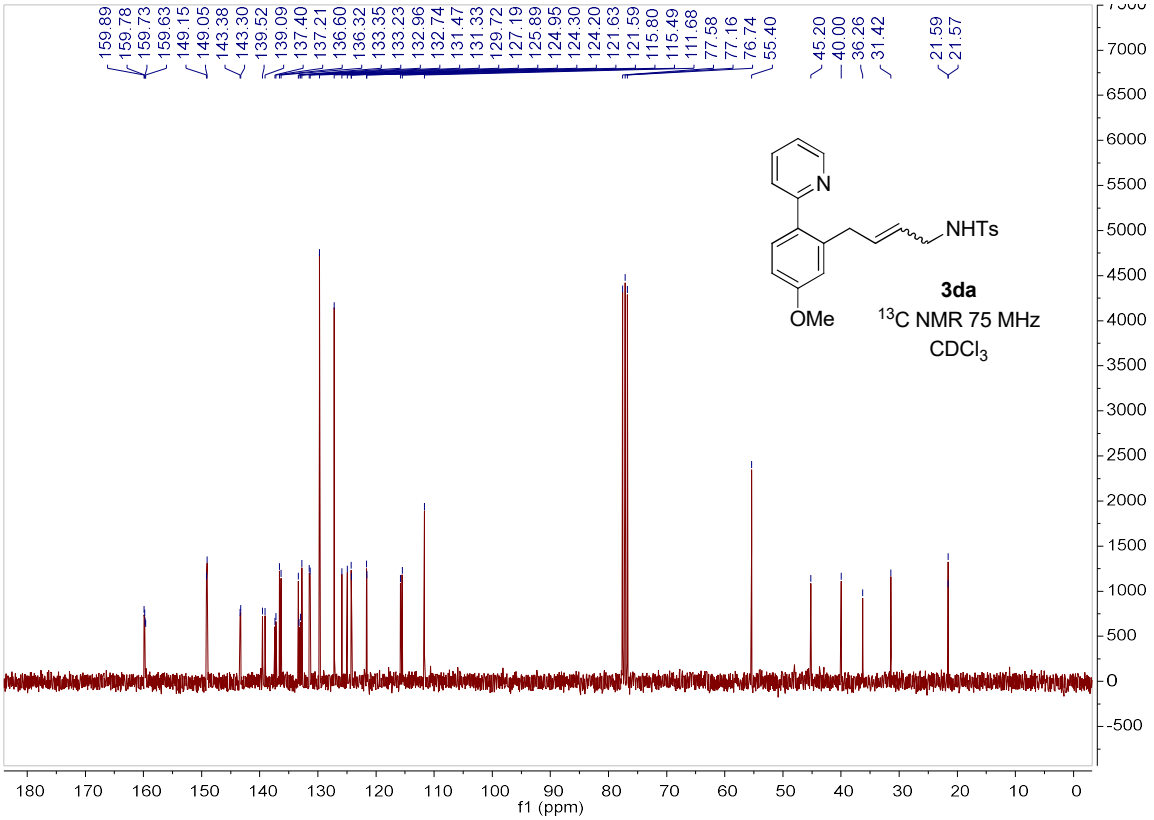
1.88
1.00
1.08
0.49
0.51
2.82
3.69
2.80
f1 (ppm)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131.33
129.72
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125.89
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124.30
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115.80
115.49
111.68
77.58
77.16
76.74
55.40
45.20
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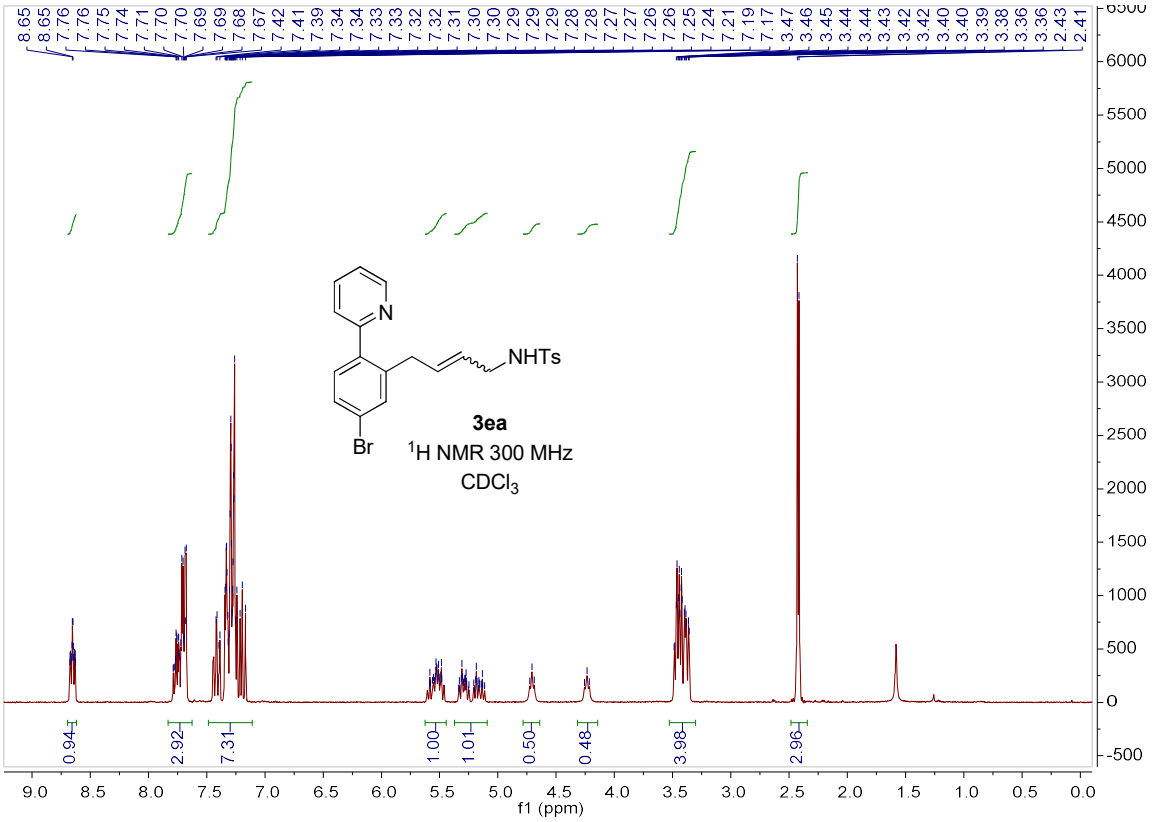
NHTs
OMe
3da
13C NMR 75 MHz
CDCl3
f1 (ppm)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7.19
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3.45
3.44
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3.42
3.40
3.40
3.39
3.38
3.36
3.36
2.43
2.41
N
NHTs
Br
3ea
1H NMR 300 MHz
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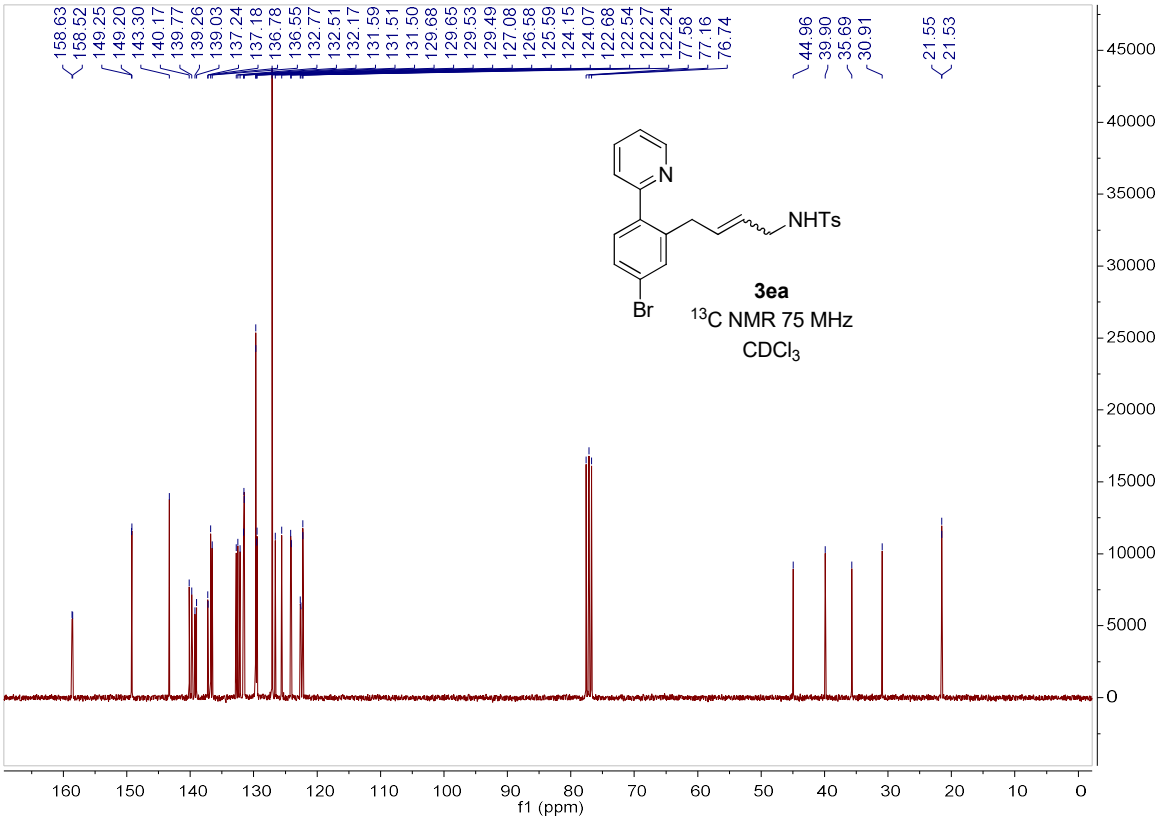
0.48
3.98
2.96
f1 (ppm)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124.15
124.07
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122.54
122.27
122.24
77.58
77.16
76.74
44.96
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21.55
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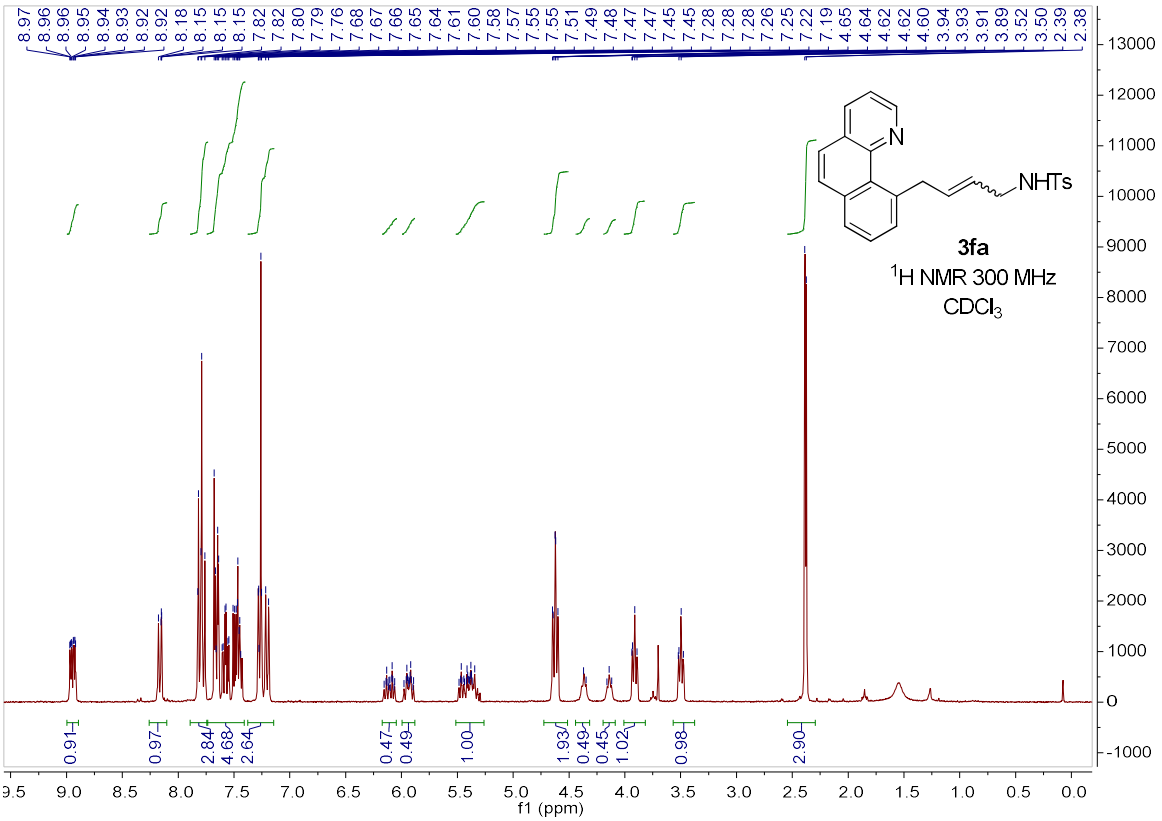
Br
3ea
13C NMR 75 MHz
CDCl3
f1 (ppm)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3.50
2.39
2.38
N
NHTs
3fa
1H NMR 300 MHz
CDCl3
0.91
0.97
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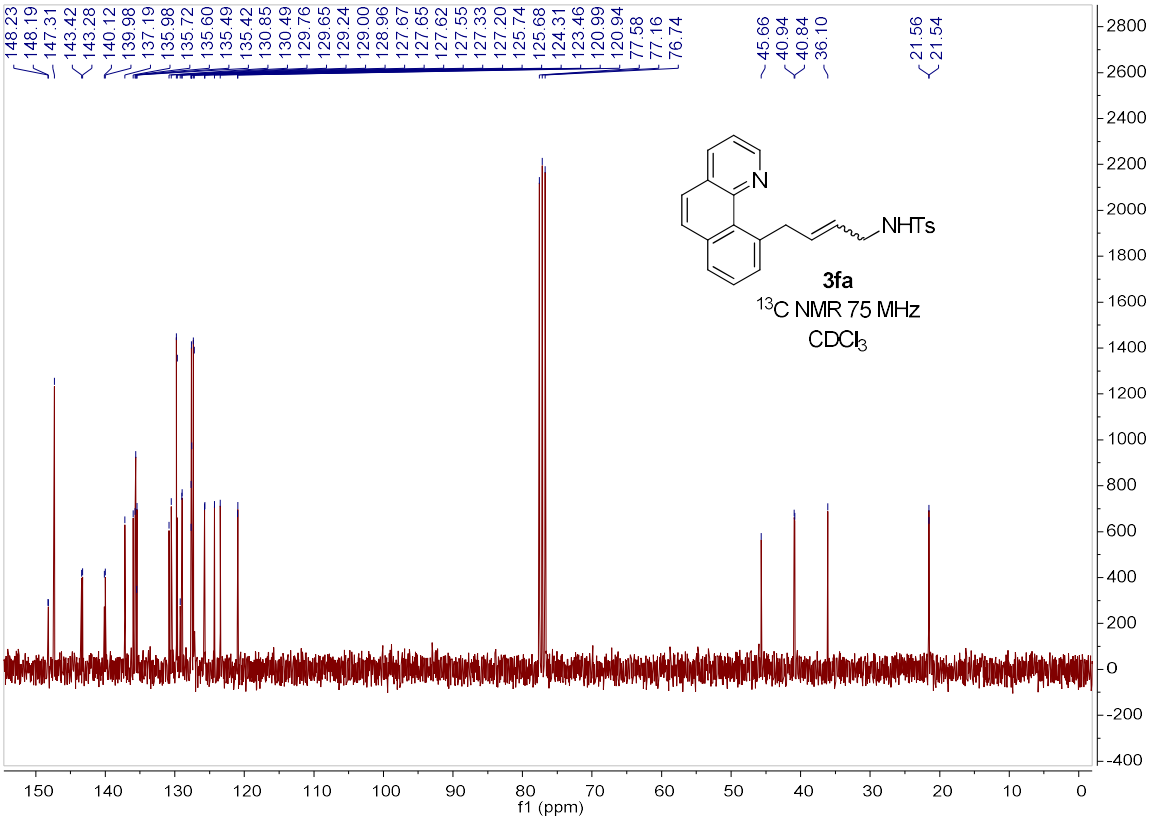
f1 (ppm)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76.74
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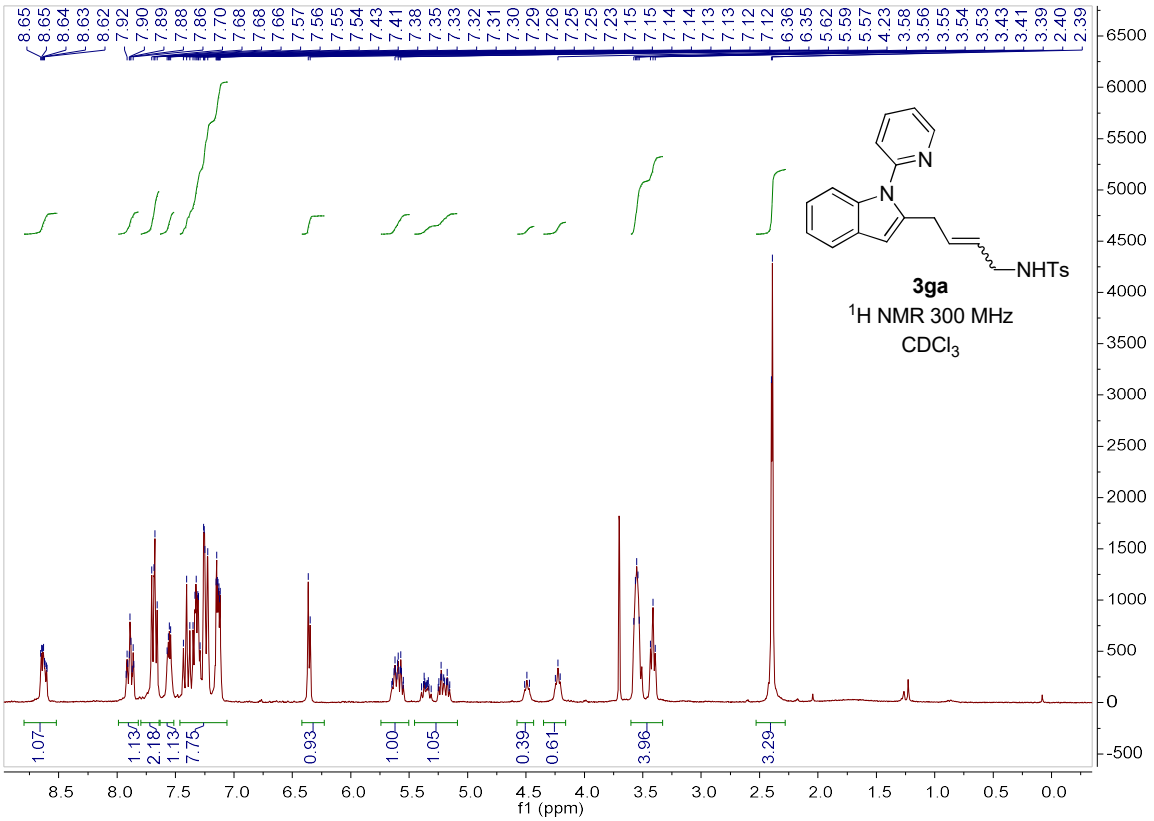
NHTs
3fa
13C NMR 75 MHz
CDCl3
f1 (ppm)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3.43
3.41
3.39
2.40
2.39
N
N
NHTs
3ga
1H NMR 300 MHz
CDCl3
1.07
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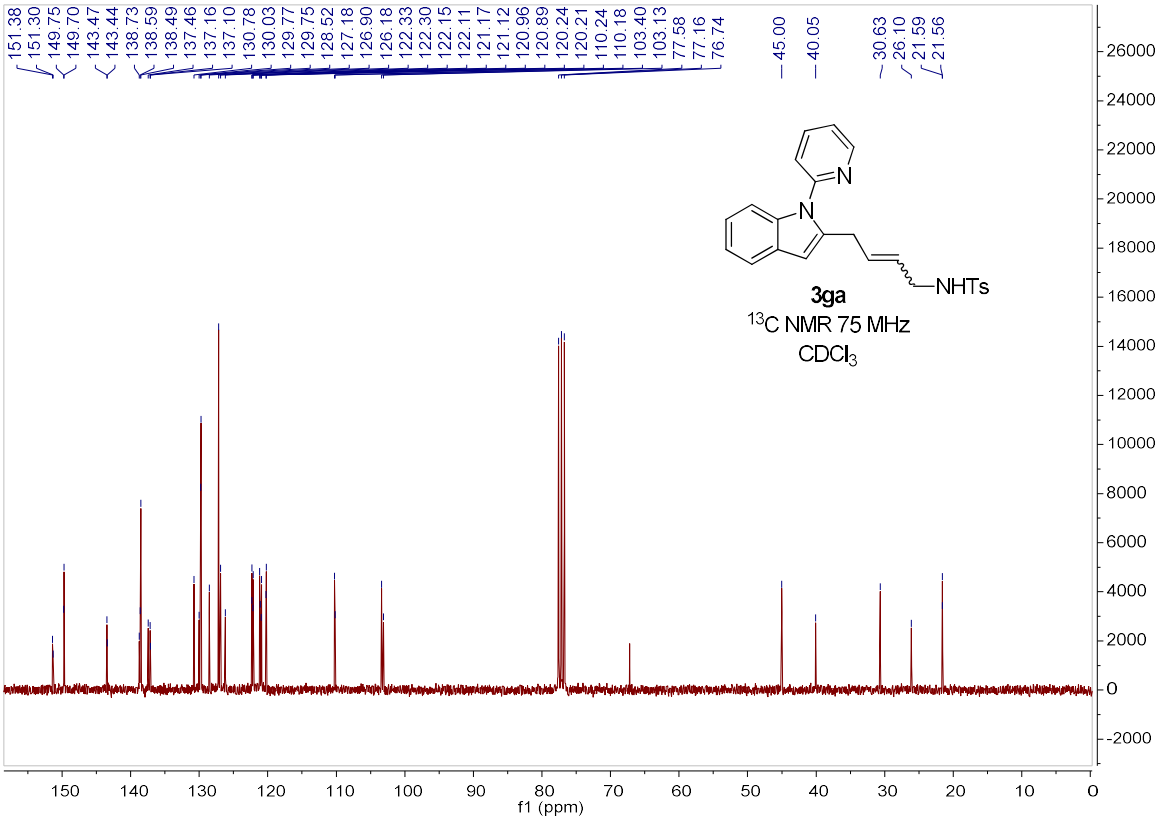
f1 (ppm)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122.11
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120.24
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110.18
103.40
103.13
77.58
77.16
76.74
45.00
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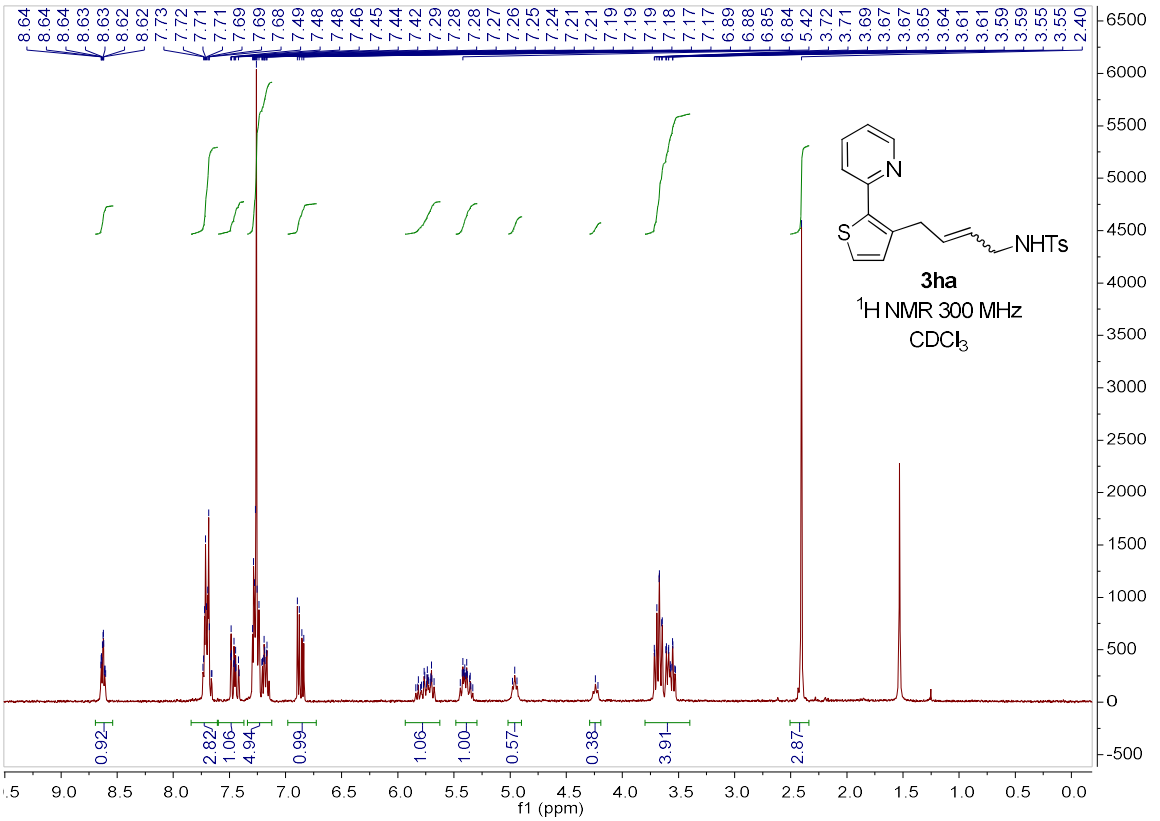
NHTs
3ga
13C NMR 75 MHz
CDCl3
f1 (ppm)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3.59
3.55
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2.40
N
S
NHTs
3ha
1H NMR 300 MHz
CDCl3
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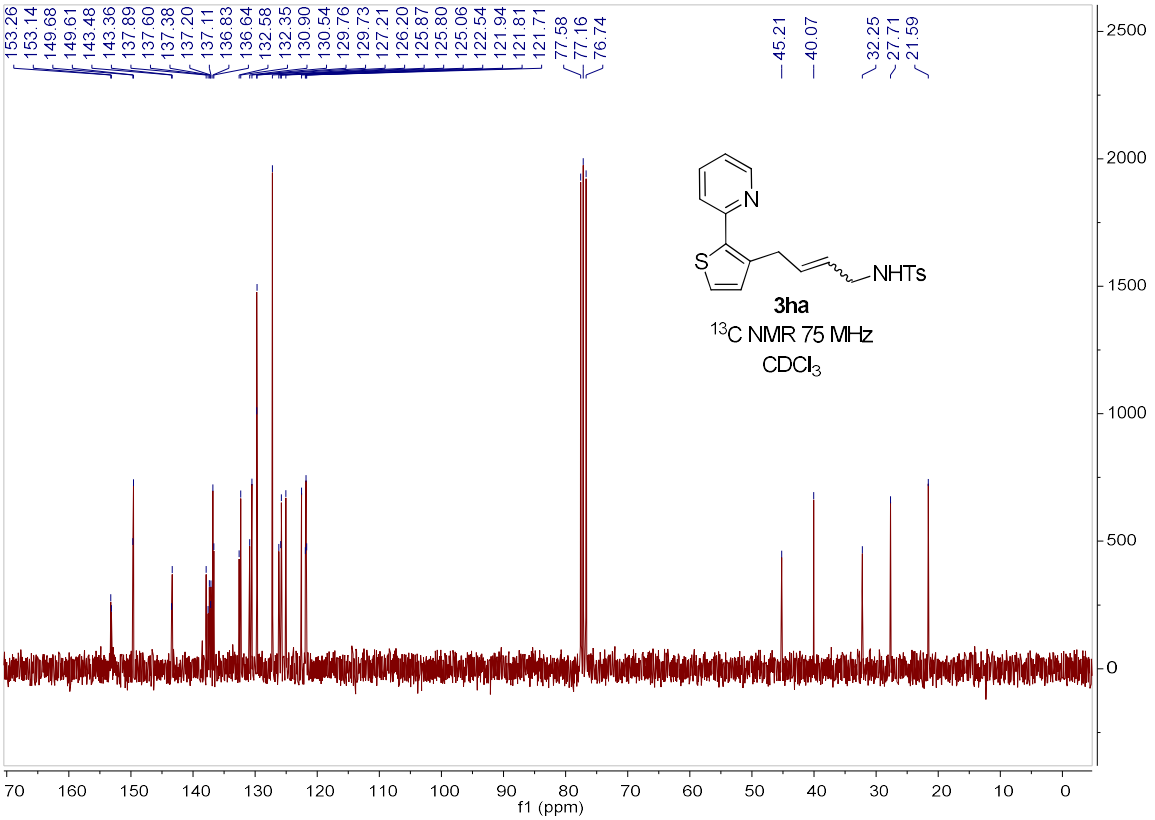
2.87
f1 (ppm)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77.58
77.16
76.74
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S
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3ha
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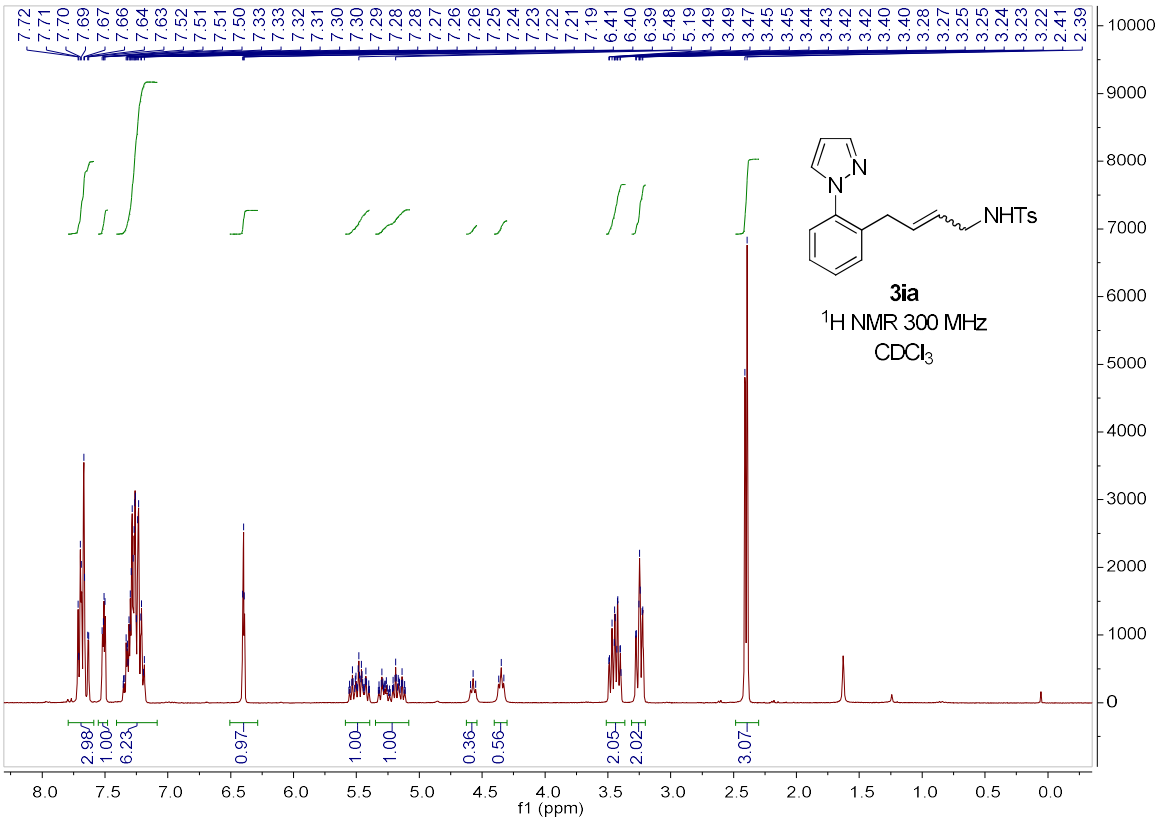
CDCl3
f1 (ppm)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1.00
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N
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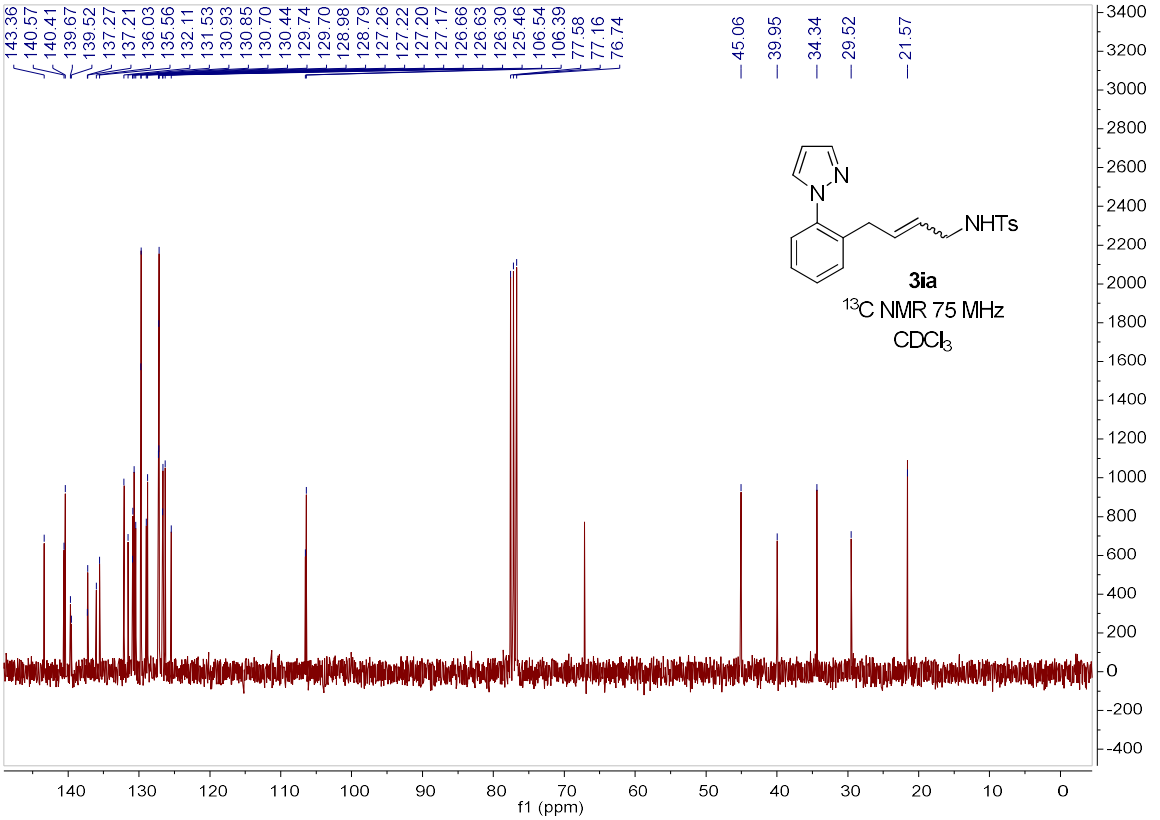
3ia
1H NMR 300 MHz
CDCl3
f1 (ppm)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106.54
106.39
77.58
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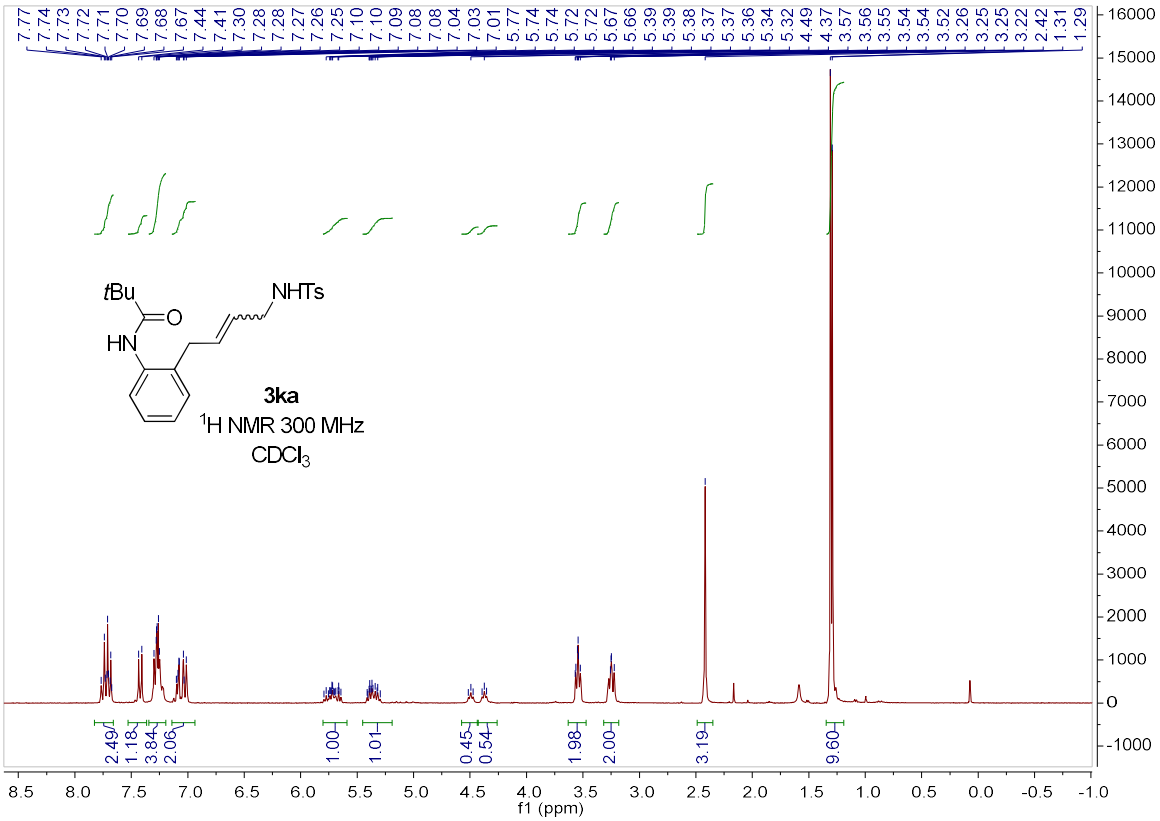
21.57
NHTs
3ia
13C NMR 75 MHz
CDCl3
f1 (ppm)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7.08
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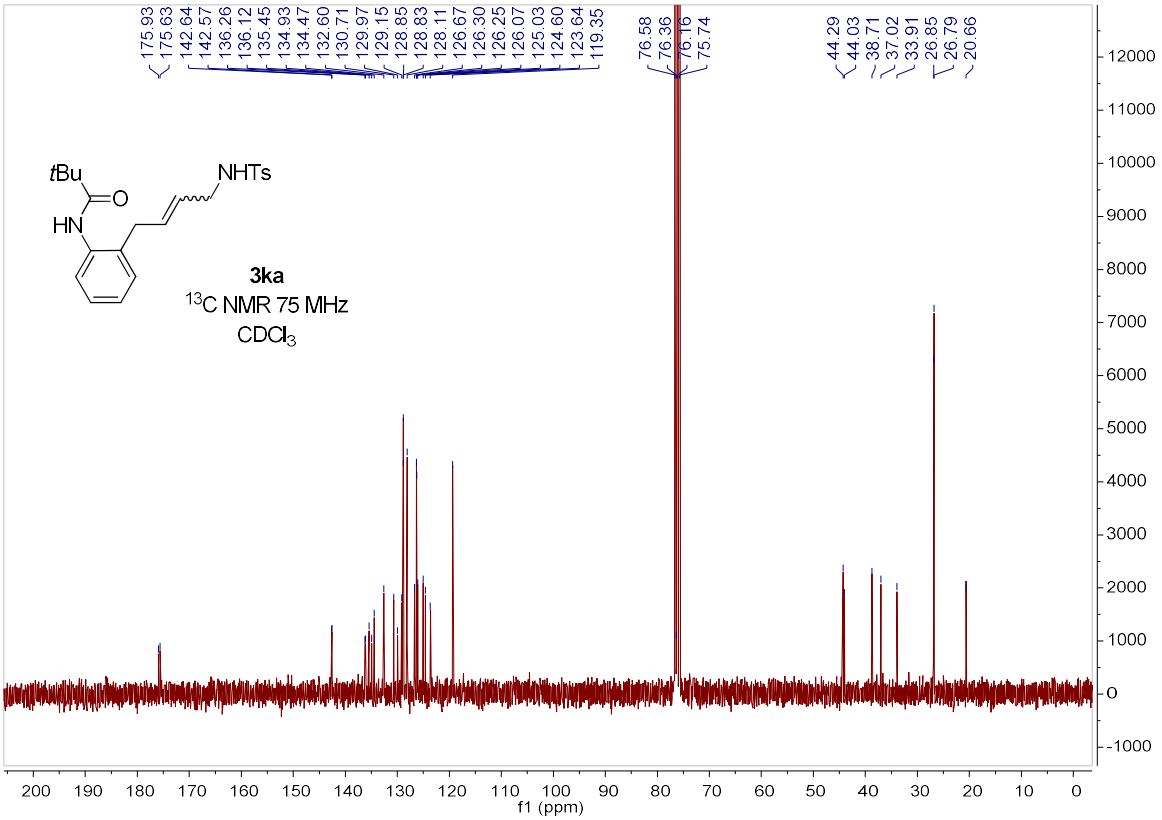
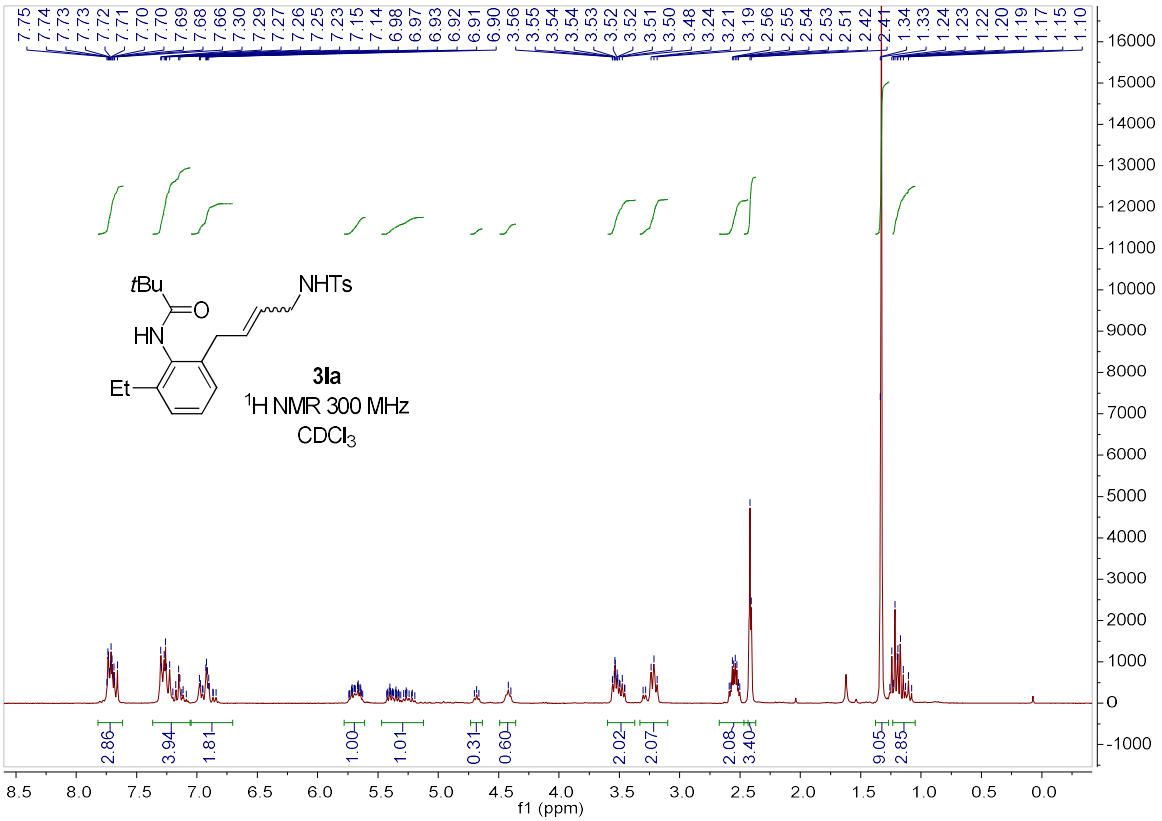
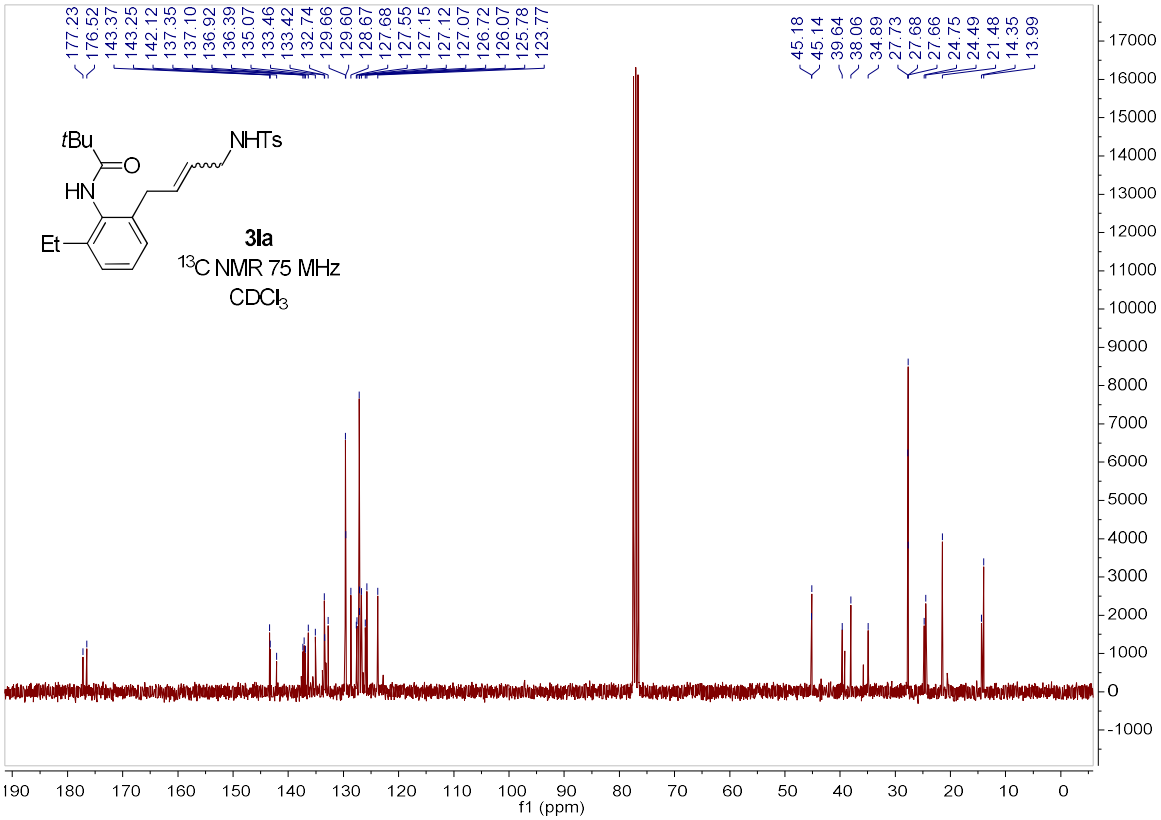
3.52
3.26
3.25
3.25
3.22
2.42
1.31
1.29
tBu
NHTs
HN
O
3ka
1H NMR 300 MHz
CDCl3
2.49
1.18
3.84
2.06
1.00
1.01
0.45
0.54
1.98
2.00
3.19
9.60
f1 (ppm)


175.93
175.63
142.64
142.57
136.26
136.12
135.45
134.93
134.47
132.60
130.71
129.97
129.15
128.85
128.83
128.11
126.67
126.30
126.25
126.07
125.03
124.60
123.64
119.35
76.58
76.36
76.16
75.74
44.29
44.03
38.71
37.02
33.91
26.85
26.79
20.66
tBu
O
HN
NHTs
3ka
13C NMR 75 MHz
CDCl3
f1 (ppm)


7.75
7.74
7.73
7.73
7.72
7.71
7.70
7.70
7.69
7.68
7.66
7.30
7.29
7.27
7.26
7.25
7.23
7.15
7.14
6.98
6.97
6.93
6.92
6.91
6.90
3.56
3.55
3.54
3.54
3.53
3.52
3.52
3.51
3.50
3.48
3.24
3.21
3.19
2.56
2.55
2.54
2.53
2.51
2.42
2.41
1.34
1.33
1.24
1.23
1.22
1.20
1.19
1.17
1.15
1.10
tBu
O
HN
NHTs
Et
3la
1H NMR 300 MHz
CDCl3
2.86
3.94
1.81
1.00
1.01
0.31
0.60
2.02
2.07
2.08
3.40
9.05
2.85
f1 (ppm)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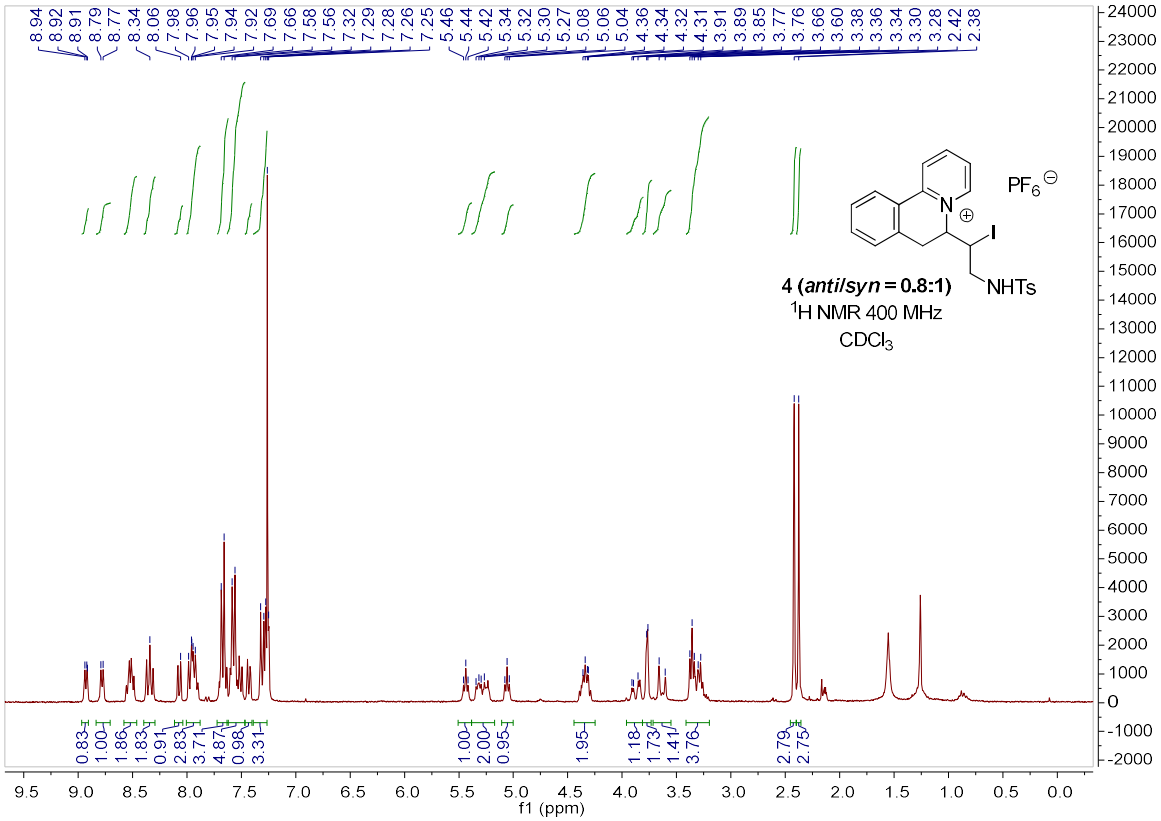
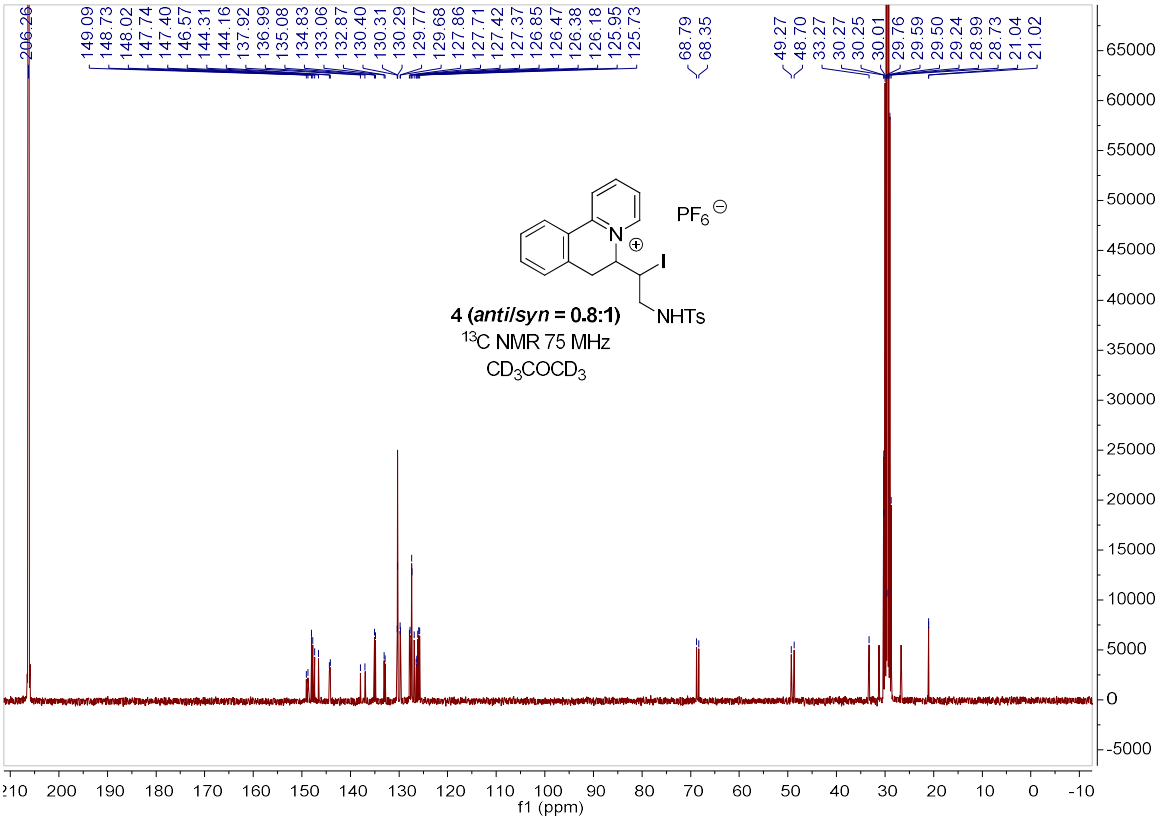
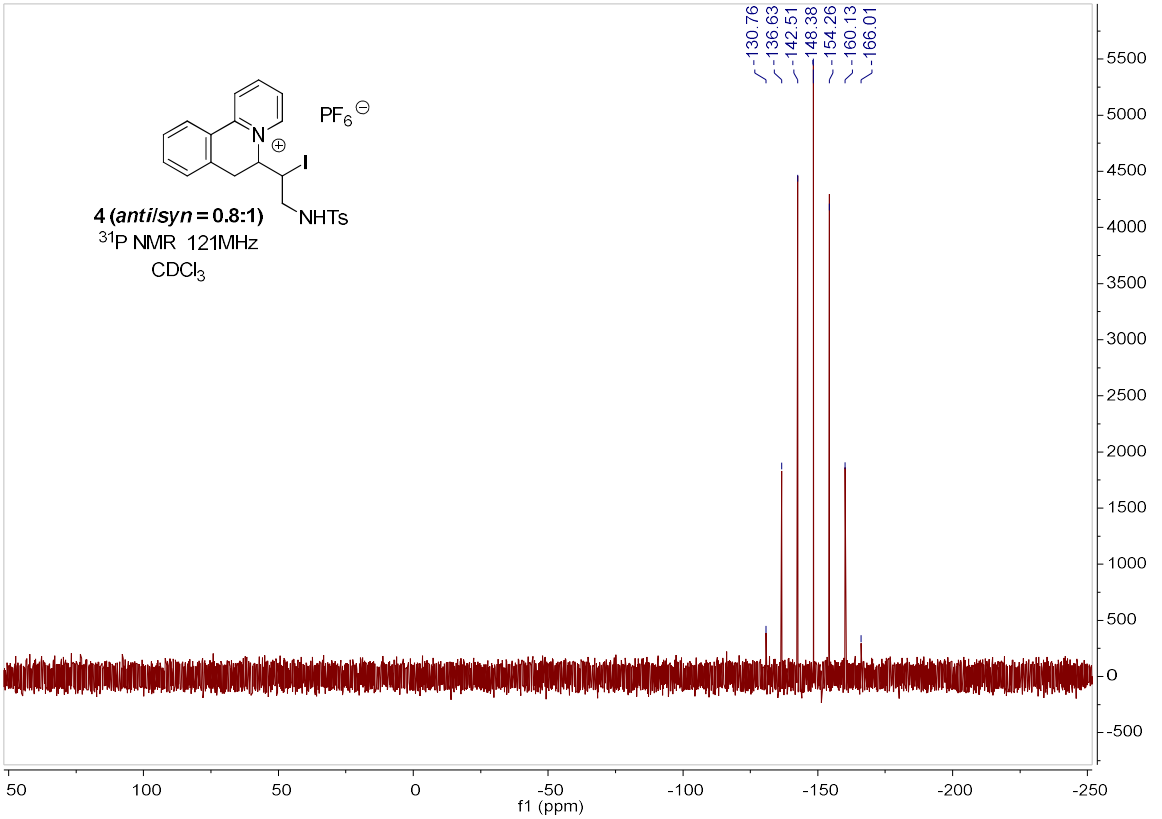
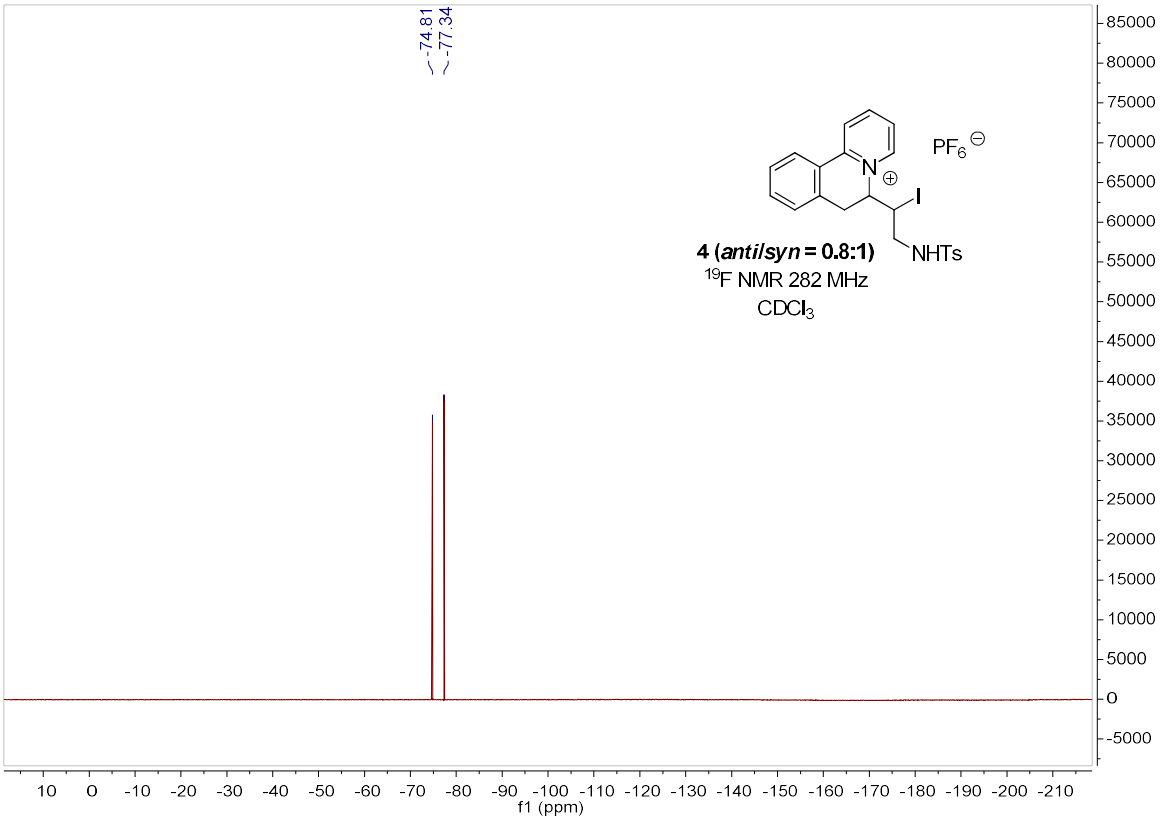
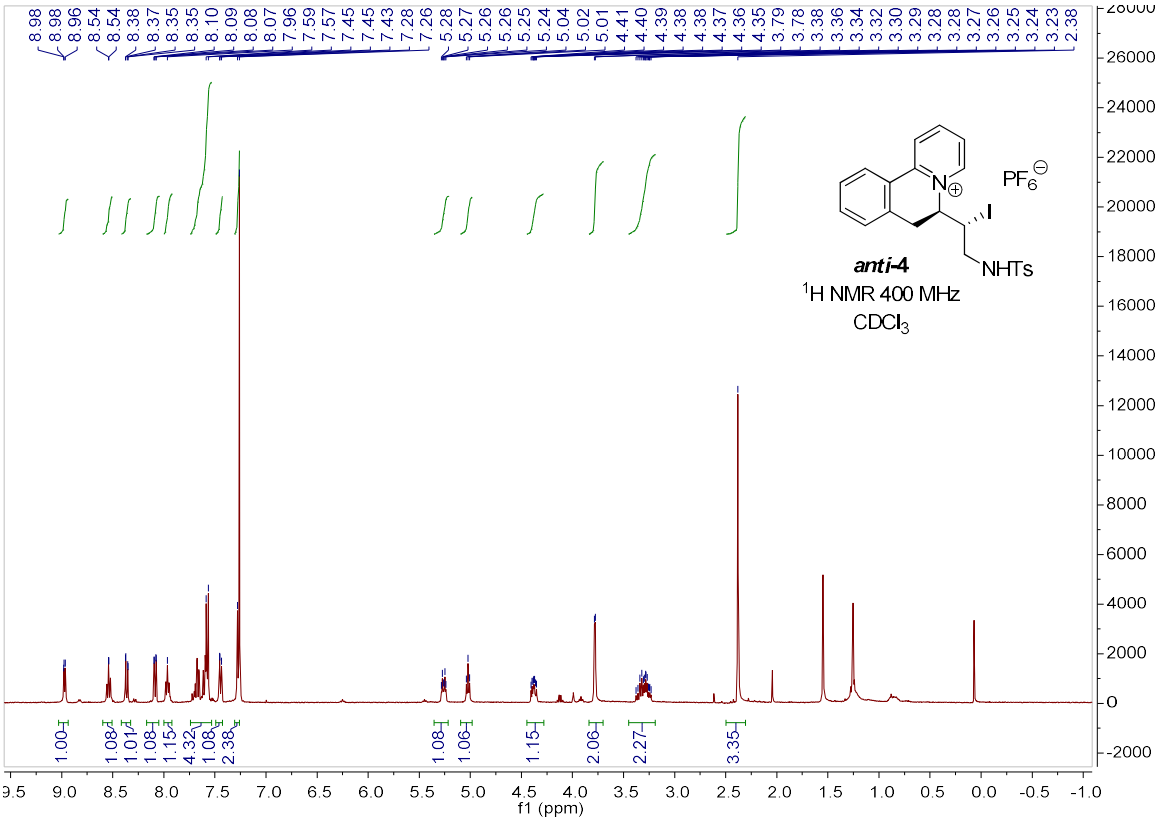
176.52
143.37
143.25
142.12
137.35
137.10
136.92
136.39
135.07
133.46
133.42
132.74
129.66
129.60
128.67
127.68
127.55
127.15
127.12
127.07
126.72
126.07
125.78
123.77
45.18
45.14
39.64
38.06
34.89
27.73
27.68
27.66
24.75
24.49
21.48
14.35
13.99
tBu
NHTs
HN
Et
3la
13C NMR 75 MHz
CDCl3
f1 (ppm)

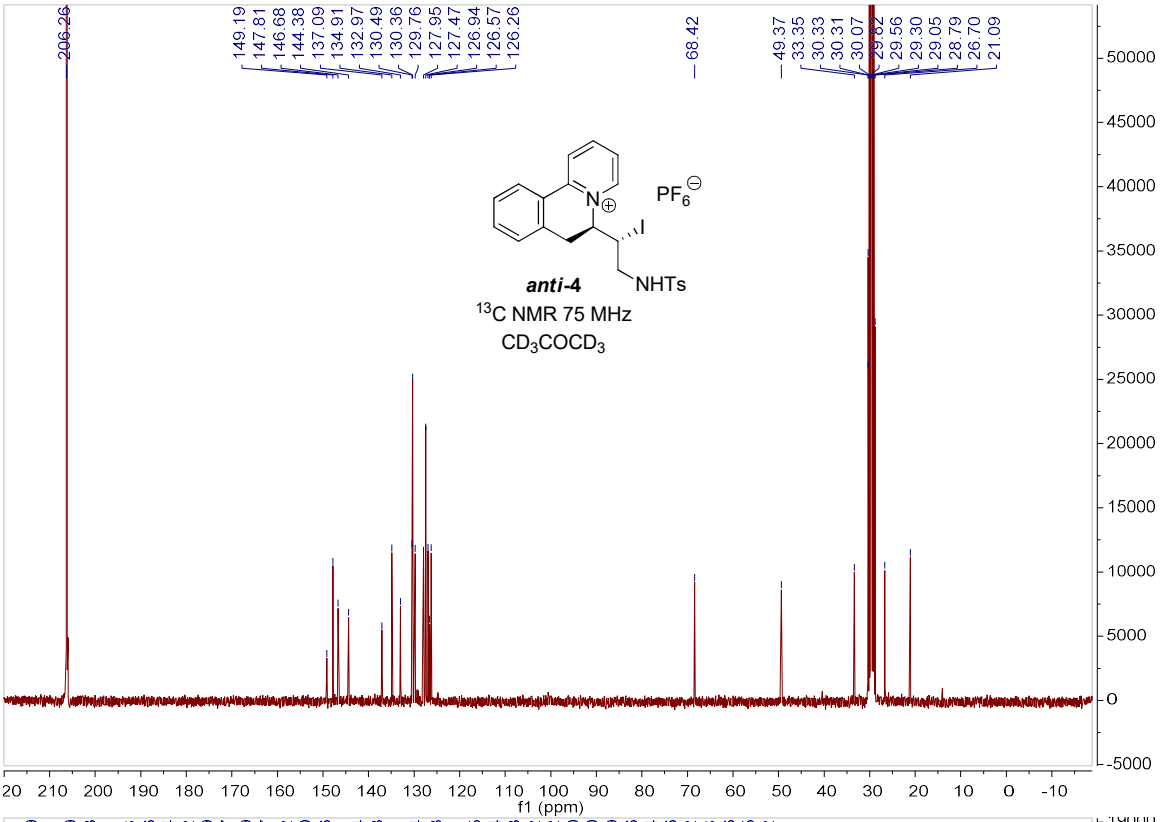

8.94
8.92
8.91
8.79
8.77
8.34
8.06
7.98
7.96
7.95
7.94
7.92
7.69
7.66
7.58
7.56
7.32
7.29
7.28
7.26
7.25
5.46
5.44
5.42
5.34
5.32
5.30
5.27
5.08
5.06
5.04
4.36
4.34
4.32
4.31
3.91
3.89
3.85
3.77
3.76
3.66
3.60
3.38
3.36
3.34
3.30
3.28
2.42
2.38
PF6
N
I
NHTs
4 (anti/syn = 0.8:1)
1H NMR 400 MHz
CDCl3
0.83
1.00
1.86
1.83
0.91
2.83
3.71
4.87
0.98
3.31
1.00
2.00
0.95
1.95
1.18
1.73
1.41
3.76
2.79
2.75
f1 (ppm)

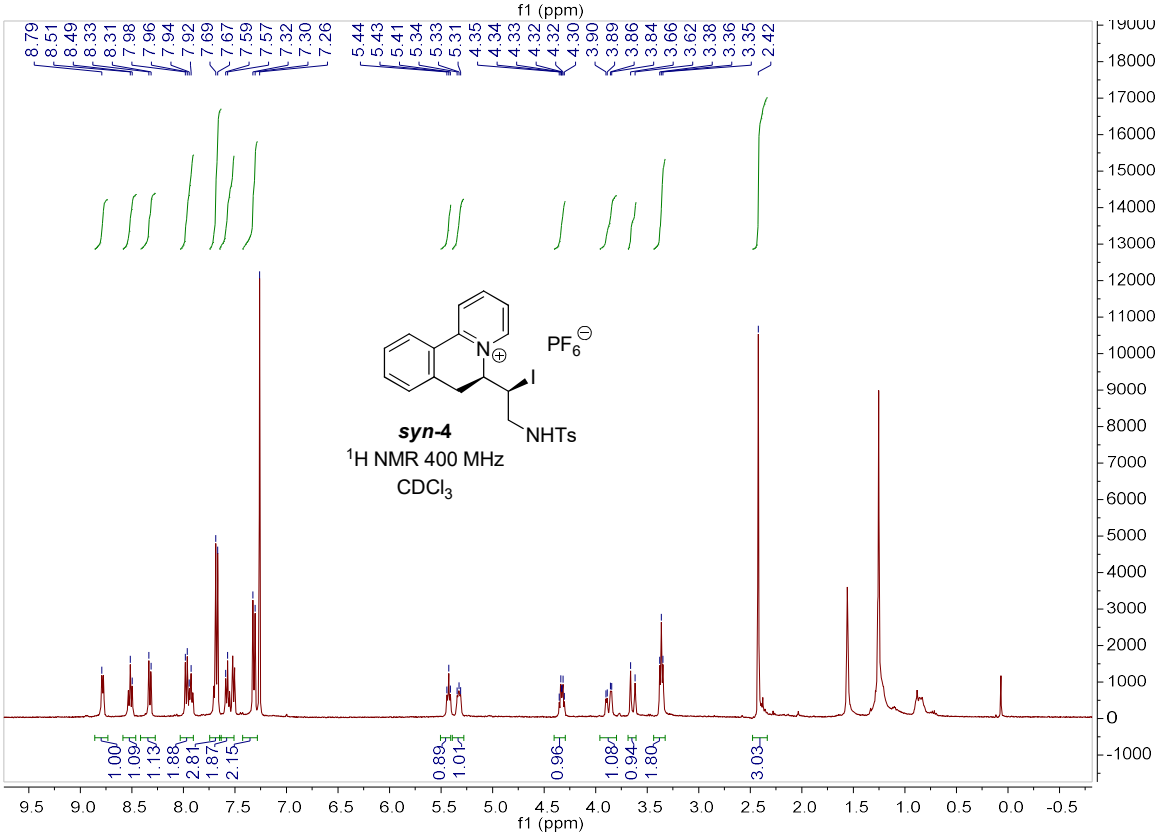

206.26
149.09
148.73
148.02
147.74
147.40
146.57
144.31
144.16
137.92
136.99
135.08
134.83
133.06
132.87
130.40
130.31
130.29
129.77
129.68
127.86
127.71
127.42
127.37
126.85
126.47
126.38
126.18
125.95
125.73
68.79
68.35
49.27
48.70
33.27
30.27
30.25
30.01
29.76
29.59
29.50
29.24
28.99
28.73
21.04
21.02
PF6
N
I
NHTs
4 (anti/syn = 0.8:1)
13C NMR 75 MHz
CD3COCD3
f1 (ppm)

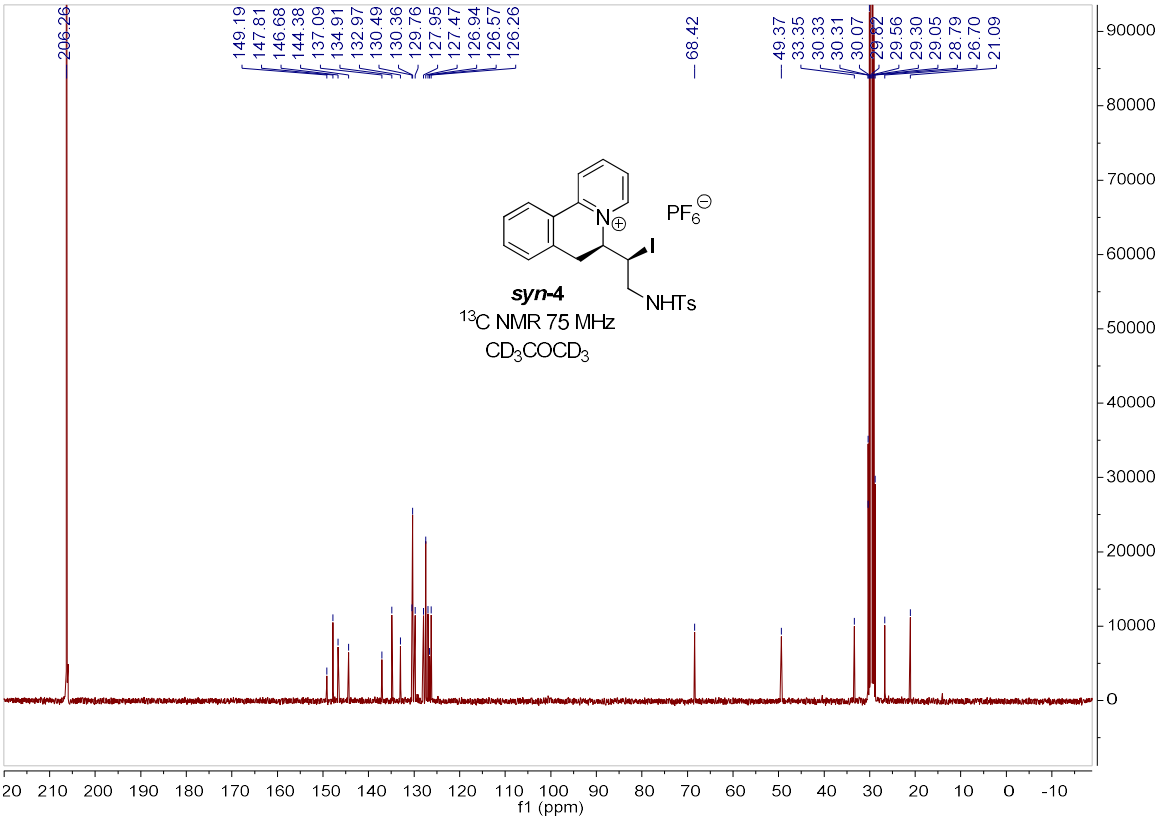

130.76
136.63
142.51
148.38
154.26
160.13
166.01
PF6
N
I
NHTs
4 (anti/syn = 0.8:1)
31P NMR 121MHz
CDCl3
f1 (ppm)


-74.81
-77.34
PF6
I
NHTs
4 (anti/syn = 0.8:1)
19F NMR 282 MHz
CDCl3
f1 (ppm)


PF6
I
NHTs
anti-4
1H NMR 400 MHz
CDCl3
f1 (ppm)


206.26
149.19
147.81
146.68
144.38
137.09
134.91
132.97
130.49
130.36
129.76
127.95
127.47
126.94
126.57
126.26
68.42
49.37
33.35
30.33
30.31
30.07
29.82
29.56
29.30
29.05
28.79
26.70
21.09
PF6
I
NHTs
anti-4
13C NMR 75 MHz
CD3COCD3
f1 (ppm)


8.79
8.51
8.49
8.33
8.31
7.98
7.96
7.94
7.92
7.69
7.67
7.59
7.57
7.32
7.30
7.26
5.44
5.43
5.41
5.34
5.33
5.31
4.35
4.34
4.33
4.32
4.32
4.30
3.90
3.89
3.86
3.84
3.66
3.62
3.38
3.36
3.35
2.42
PF6
I
NHTs
syn-4
1H NMR 400 MHz
CDCl3
1.00
1.09
1.13
1.88
2.81
1.87
2.15
0.89
1.01
0.96
1.08
0.94
1.80
3.03
f1 (ppm)


206.26
149.19
147.81
146.68
144.38
137.09
134.91
132.97
130.49
130.36
129.76
127.95
127.47
126.94
126.57
126.26
68.42
49.37
33.35
30.33
30.31
30.07
29.82
29.56
29.30
29.05
28.79
26.70
21.09
PF6
I
NHTs
syn-4
13C NMR 75 MHz
CD3COCD3
f1 (ppm)