# SUPPORTING INFORMATION

## Stereo- and Regioselective Gold(I)-Catalyzed Hydroamination of 2-(Arylethynyl)pyridines with Anilines†

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## 1. GENERAL INFORMATION

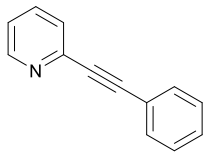
### 1.1. Reagents and methods

All of the commercially available reagents, catalysts, bases, solvents, and eluents were used as purchased, without further purification. 2-(Arylethynyl)pyridines were prepared through Sonogashira cross-coupling of 2-bromopyridine with terminal alkynes and were purified on axially compressed columns, packed with $SiO_2$ 25-40 μm, connected to a solvent delivery system and to a refractive index detector, and eluting with *n*-hexane/EtOAc mixtures. Reaction products **3a-t** were purified by flash chromatography on neutral $Al_2O_3$ (Brockmann activity 1) eluting with *n*-hexane or *n*-hexane/AcOEt mixtures.$^1$H NMR (400.13 MHz), $^{13}$C NMR (100.6 MHz), and $^{19}$F spectra (376.5 MHz) were recorded with a Bruker Avance 400 spectrometer. Splitting patterns are designed as s (singlet), d (doublet), t (triplet), td (triplet of doublets), q (quartet), m (multiplet), or br s (broad singlet). IR spectra were recorded with a Jasco FT/IR-430 spectrometer. Mass spectra were determined with a QP2010 Gas Chromatograph Mass spectrometer (EI ion source). HRMS were recorded with an Orbitrap Exactive Mass spectrometer with ESI source. Melting points were determined with a Büchi B-545 apparatus and are uncorrected. Computational analysis have been performed on a Desktop PC with TITAN suite of programs.

## 2. SYNTHETIC PROCEDURES

### 2.1. Typical procedure for the preparation of 2-(arylethynyl)pyridines (1): synthesis of 2-(phenyethynyl)pyridine (1a).

A flask equipped with a magnetic stirring bar was charged with $PdCl_2(PPh_3)_2$ (49 mg, 0.07 mmol, 0.02 equiv.) and CuI (26.5 mg, 0.14 mmol, 0.04 equiv.) dissolved in diisopropylamine (7 mL) and *N,N*-dimethylformamide (5 mL). The resultant solution was stirred under nitrogen at room temperature for 10 minutes before adding 2-bromopyridine (553 mg, 3.5 mmol, 1.0 equiv.) in diisopropylamine (3 mL) and phenylacetylene (428.5 mg, 461 μl, 4.2 mmol, 1.2 equiv.). Then, stirring was continued at room temperature for an additional hour. After this time, the reaction mixture was diluted with $Et_2O$ and washed with a saturated $NH_4Cl$ solution and with brine. The organic layer was separated, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by chromatography on $SiO_2$ (25-40 μm) eluting with a 85/15 (v/v) *n*-hexane/AcOEt mixture ($R_f$ = 0.25) to obtain 608.5 mg (97% yield) of 2-(phenyethynyl)pyridine **1a**.



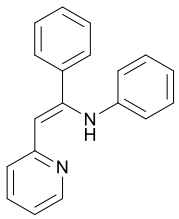

**1a**

**2-(phenylethynyl)pyridine (1a)**[i]: Brown oil (608.5 mg, 97%); IR (neat): 3054, 2919, 2222, 1580, 1490 cm $^{-1}$; $^1$H NMR (400.13 MHz) (DMSO $d_6$): δ = 8.62 (ddd, $J_1$ = 4.8 Hz, $J_2$= 1.8 Hz, $J_3$= 1.0, 1 H), 7.86 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.8 Hz, 1 H), 7.66-7.60 (m, 3 H), 7.48-7.45 (m, 3 H), 7.42 (ddd, $J_1$ = 7.7 Hz, $J_2$= 4.8 Hz, $J_3$= 1.0 Hz, 1 H) ;$^{13}$C NMR (100.6 MHz) (DMSO $d_6$): δ = 150.6, 142.7, 137.2, 132.1, 129.0, 129.3, 127.8, 124.0, 121.9, 89.4, 88.8; MS (EI ion source): *m/z* (%) = 179 (100, [M$^+$]), 151 (14), 126 (12); HRMS: *m/z* [M + H]$^+$ calcd for $C_{13}H_{10}N$: 180.0808; found: 180.0808.

### 2.1. Typical procedure for the preparation of (*Z*)-*N*-(1-aryl-2-(pyridine-2-yl)vinyl)anilines (3): synthesis of (*Z*)-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (3a).

A Carousel Tube Reactor (Radley Discovery Technology) containing a stirring bar was charged with 2-(phenylethynyl)pyridine **1a** (89.6 mg, 0.5 mmol, 1.0 equiv) dissolved in $CH_2Cl_2$ (1.5 mL) and (acetonitrile)[(2-

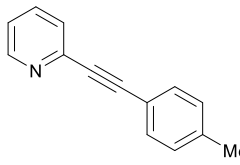
biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (15.4 mg, 0.02 mmol, 0.04 equiv.). Then, aniline **2a** was added (51 mg, 50 μl, 0.55 mmol, 1.1 equiv). The resultant solution was warmed at 80 °C and stirred for 20 hours. After cooling, the volatile materials were evaporated at reduced pressure and the residue was purified by flash chromatography on neutral $Al_2O_3$ (Brockmann activity 1) eluting with *n*-hexane ($R_f$ = 0.21) to obtain 126.5 mg of (*Z*)-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline **3a** (93% yield).



**3a**

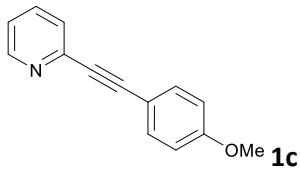
**(*Z*)-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (3a):** Yellow solid (126.5 mg, 93% yield); mp: 83 - 85 °C; IR (KBr): 3357, 3050, 2923, 1626, 1587, 1374 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): δ = 11.61 (br s, 1 H), 8.40 (bd, *J* = 4.5 Hz, 1 H), 7.47 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.6 Hz, 1 H), 7.43-7.40 (m, 2 H), 7.24 - 7.22 (m, 3 H), 7.01-6.97 (m, 3 H), 6.87 - 6.84 (m, 1 H), 6.73 (t, *J* = 7.2 Hz, 1 H), 6.61 (d, *J* = 7.7 Hz, 2 H), 5.52 (s, 1 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): δ = 158.7, 148.5, 147.5, 142.6, 138.3, 136.0, 128.6, 128.5, 128.4, 128.1, 123.1, 121.03, 121.00, 118.6, 103.7; MS (EI ion source): *m/z* (%) = 272 (76 [$M^+$]), 256 (16), 207 (13), 194 (26), 180 (55), 92 (18), 77 (100), 51 (23); HRMS: *m/z* [M + H]$^+$ calcd for $C_{19}H_{17}N_2$: 273.1386; found: 273.1393.

**3. CHARACTERIZATION DATA OF 1b – h, 6a – c, 8, 9**



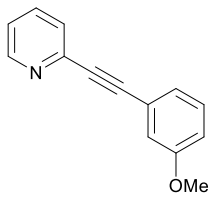
**1b**

**2-(*p*-tolylethynyl)pyridine (1b)**: Brown solid (588.1 mg, 87% yield); mp: 75-76 °C; IR (KBr): 3053, 2975, 2222, 1578, 1507, 1460 cm $^{-1}$; $^{1}$H NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 8.61 (ddd, $J_1$ = 4.8 Hz, $J_2$= 1.6 Hz, $J_3$= 1.1, 1 H), 7.68 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.6 Hz, 1 H), 7.62 (dt, $J_1$ = 7.7 Hz, $J_2$ = 1.1 Hz, 1 H), 7.50 (d, $J$ = 8.1 Hz, 2 H), 7.40 (ddd, $J_1$ = 7.7 Hz, $J_2$= 4.8 Hz, $J_3$= 1.1 Hz, 1 H), 7.27 (d, $J$ = 8.1 Hz, 2 H), 2.35 (s, 3 H); $^{13}$C NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 150.6, 142.9, 139.8, 137.2, 132.1, 130.0, 127.6, 123.8, 118.8, 89.1, 89.0, 21.5; MS (EI ion source): *m/z* (%) = 193 (100, [M$^+$]), 165 (13), 139 (9), 115 (20); HRMS: *m/z* [M + H]$^+$ calcd for $C_{14}H_{12}N$:194.0964; found: 194.0966.



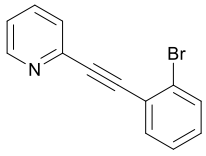
**1c**

**2-((4-methoxyphenyl)ethynyl)pyridine (1c):** Brown oil (651.7 mg, 89% yield); IR (neat): 3052, 2919, 2219, 1605, 1580, 1028 cm $^{-1}$; $^{1}$H NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 8.59 (bd, $J$ = 4.2 Hz .1 H), 7.83 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.7 Hz, 1 H), 7.60 (d, $J$ = 7.7 Hz, 1 H), 7.57 (d, $J$ = 8.8 Hz, 2 H), 7.38 ( ddd, $J_1$ = 7.7 Hz, $J_2$= 4.7 Hz, $J_3$= 0.9 Hz, 1 H), 7.01 (d, $J$ = 8.8 Hz, 2 H), 3.81 (s, 3 H); $^{13}$C NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 160.5, 150.5, 143.1, 137.2, 133.8, 132.5, 132.0, 129.3, 129.1, 127.5, 123.6, 115.0, 113.7, 89.2, 88.4, 55.8; MS (EI ion source): *m/z* (%) = 209 (100, [M$^+$]), 194 (44), 166 (21), 140 (35); HRMS: *m/z* [M + H]$^+$ calcd for $C_{14}H_{12}NO$: 210.0913; found: 210.0915.



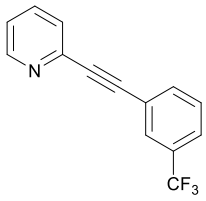
**1d**

**2-((3-methoxyphenyl)ethynyl)pyridine (1d):** Brown oil (724.7 mg, 99% yield); IR (neat): 3052, 2938, 2210 1240, 1042 cm$^{-1}$; $^{1}$H NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 8.61 (ddd, $J_1$ = 4.9 Hz, $J_2$= 1.8 Hz, $J_3$= 1.0, 1 H), 7.85 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.8 Hz, 1 H), 7.65 (dt, $J_1$ = 7.7 Hz, $J_2$ = 0.9 Hz, 1 H) 7.42 (ddd, $J_1$ = 7.7 Hz, $J_2$= 4.9 Hz, $J_3$= 1.0 Hz, 1 H), 7.37 (t, $J$ = 8.0 Hz, 1 H), 7.19 (dt, $J_1$ = 7.7 Hz, $J_2$ = 1.0 Hz, 1 H) 7.17-7.16 (m, 1 H), 7.05 (ddd, $J_1$ = 8.4 Hz, $J_2$= 2.6 Hz, $J_3$= 0.9 Hz, 1 H ), 3.83 (m, 3 H); $^{13}$C NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 159.7, 150.6, 142.7, 137.2, 130.5, 127.8, 124.5, 124.0, 122.9, 116.8, 116.4, 89.2, 88.7, 55.7; MS (EI ion source): *m/z* (%) = 209 (100, [M$^+$]), 178 (15), 140 (24); HRMS: *m/z* [M + H]$^+$ calcd for $C_{14}H_{12}NO$: 210.0913; found: 210.0916.



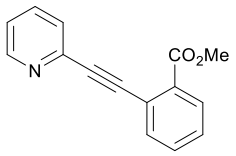

**1e**

**2-((2-bromophenyl)ethynyl)pyridine (1e)**: Brown oil (541.7 mg, 60% yield); IR (neat): 3056, 2919, 2224, 1580, 1470 $cm^{-1}$; $^{1}H$ NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 8.64 (bd, $J$ = 4.3 Hz, 1 H), 7.88 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.7 Hz, 1 H), 7.78 (dd, $J_1$ = 8.0 Hz, $J_2$ = 0.8 Hz, 1 H), 7.73 (dd, $J_1$ = 7.7 Hz, $J_2$ = 1.7 Hz, 1 H), 7.67 (dt, $J_1$ = 7.7 Hz, $J_2$ = 0.9 Hz, 1 H), 7.49-7.38 (m, 3 H); $^{13}C$ NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 150.7, 142.4, 137.3, 134.3, 133.1, 131.6, 128.4, 128.0, 125.4, 124.4, 123.9, 93.4, 78.1; MS (EI ion source): *m/z* (%) = 259 (93 [$^{81}$ Br $M^+$]), 257 ( 100 [$^{79}$ Br $M^+$]), 178 (77), 151 (43); HRMS: *m/z* [$^{81}$Br M + H] $^+$ calcd for $C_{13}H_9BrN$: 259.9892; found: 259.9895; [$^{79}$Br M + H] $^+$ calcd for $C_{13}H_9BrN$: 257.9913; found: 257.9917.



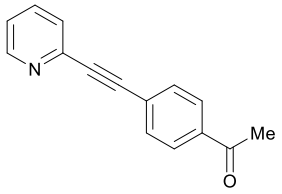

**1f**

**2-((3-(trifluoromethyl)phenyl)ethynyl)pyridine (1f):** Brown solid (522.5 mg, 60% yield); mp: 40 – 42 °C; IR (KBr): 3047, 2923, 2215, 1609, 1582, 1489, 1338 $cm^{-1}$; $^{1}H$ NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = (ddd, $J_1$ = 4.9 Hz, $J_2$= 1.8 Hz, $J_3$= 1.0, 1 H), 8.0 (s, 1 H), 7.93 (d, $J$ = 7.8 Hz, 1 H), 7.89 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.8 Hz, 1 H), 7.83 (d, $J$ = 7.8 Hz, 1 H), 7.73-7.69 (m, 2 H), 7.45 (ddd, $J_1$ = 7.7 Hz, $J_2$ = 4.9 Hz, $J_3$= 1.0 Hz, 1 H); $^{13}C$ NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 150.7, 142.2, 137.3, 136.0, 130.6, 130.2 (q, $J_{CF}$ = 32.3 Hz), 128.6 (q, $J_{CF}$ = 3.8 Hz), 128.1, 126.4 (q, $J_{CF}$ = 3.8 Hz), 124.4, 123.6 (q, $J_{CF}$ = 271 Hz), 123.0, 90.7, 87.0; $^{19}$ F NMR (376.5 MHz) (DMSO $d_6$): $\delta$ = -61.5; MS (EI ion source): *m/z* (%) = 247 (100, [$M^+$]), 178 (8), 151 (8); HRMS: *m/z* [M + H]$^+$ calcd for $C_{14}H_9F_3N$: 248.0682; found: 248.0685.



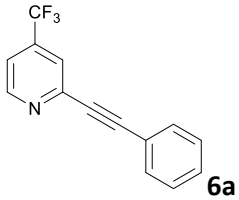

**1g**

**methyl 2-(pyridin-2-ylethynyl)benzoate (1g):** Brown solid (773.1 mg, 93% yield); IR (neat): 3061, 2950, 2219, 1727, 1581, 1486 $cm^{-1}$**;** $^{1}H$ NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 8.64 (bd, $J$= 4.3 Hz, 1 H), 7.95 (dd, $J_1$ = 7.8 Hz, $J_2$= 1.0 Hz, 1 H), 7.87 (td, $J_1$ = 7.8 Hz, $J_2$= 1.7 Hz, 1 H), 7.76 (dd, $J_1$ = 7.6 Hz, $J_2$= 0.8 Hz, 1 H), 7.69-7.63 (m, 2 H), 7.58 (td, $J_1$ = 7.7 Hz, $J_2$= 1.1 Hz, 1 H), 7.44.7.41 (m, 1 H), 3.90 (s, 3 H); $^{13}C$ NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 166.2, 150.7, 142.9, 137.3, 134.5, 132.8, 132.5, 130.7, 129.8, 128.0, 124.1, 121.9, 93.7, 87.5, 52.8; MS (EI ion source): *m/z* (%) = 237 (43, [$M^+$]), 208 (50), 180 (100), 151 (22). HRMS: *m/z* [M + H]$^+$ calcd for $C_{15}H_{12}NO_2$: 238.0863; found: 238.0864.



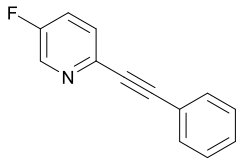

**1h**

**1-(4-(pyridin-2-ylethynyl)phenyl)ethanone (1h):** Yellow solid (644.4 mg, 83% yield); mp: 112 - 114 °C ; IR (KBr): 3052, 2911, 2215, 1674, 1599, 1263 cm $^{-1}$; $^{1}$H NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 8.64 (ddd, $J_1$ = 4.9 Hz, $J_2$= 1.8 Hz, $J_3$= 1.1, 1 H), 8.03 (d, $J$ = 8.3 Hz, 2 H), 7.89 (td, $J_1$ = 7.7 Hz, $J_2$= 1.8 Hz, 1 H), 7.76 (d, $J$ = 8.3 Hz, 2 H ), 7.71 (dt, $J_1$ = 7.7 Hz, $J_2$= 1.1 Hz, 1 H), 7.46 (ddd, $J_1$ = 7.7 Hz, $J_2$= 4.9 Hz, $J_3$= 1.1 Hz, 1 H), 2.62 (s, 3 H); $^{13}$C NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 197.8, 150.8, 137.4, 137.2, 132.4, 129.0, 128.1, 126.4, 124.4, 92.0, 87.9, 27.3; MS (EI ion source): *m/z* (%) = 221 (67, [M$^+$]), 206 (100), 178 (38), 151 (23); HRMS: *m/z* [M + H]$^+$ calcd for $C_{15}H_{12}NO$: 222.0913; found: 222.0917.



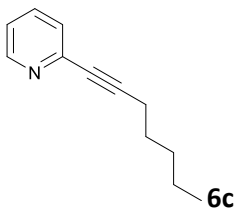

**6a**

**2-(phenylethynyl)-4-(trifluoromethyl)pyridine (6a)**: Brown oil (426.4 mg, 98% yield); IR (neat): 2927, 1564, 1404, 1337 cm $^{-1}$; 1H NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 8.82 (d, $J$ = 5.0 Hz, 1 H), 7.78-7.75 (m, 1 H), 7.66 - 7.62 (m, 2 H) 7.50 -7.38 (m, 4 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): 151.1, 144.9, 138.8 (q, $J_{CF}$ = 34 Hz), 132.3, 129.6, 128.6, 122.8 (q, $J_{CF}$ = 4 Hz), 122.6 (q, $J_{CF}$ = 272 Hz), 121.7, 118.2 (q, $J_{CF}$ = 4 Hz), 91.1, 87.6; $^{19}$F NMR (376.5 MHz) ($CDCl_3$): $\delta$ = -64.9; HRMS: *m/z* [M + H]$^+$ calcd for $C_{14}H_9F_3N$: 248.0682; found: 248.0685.




**6b**

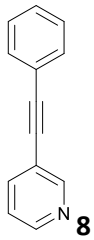
**5-fluoro-2-(phenylethynyl)pyridine (6b)**: Brown solid (354.3 mg, 79% yield); mp: 128 - 129 °C; IR (KBr): 2918, 1577, 1493, 1467 cm$^{-1}$; $^{1}$H NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 8.47 (d, $J$ = 2.8 Hz 1 H), 7.62-7.51 (m, 3 H), 7.44-7.43 (m, 4 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 158.7 (d, $J_{CF}$ = 260 Hz), 139.7 (d, $J$ = 4 Hz), 138.8 (d, $J_{CF}$ = 24 Hz), 132.12, 129.19, 128.5, 128.3 (d, $J_{CF}$ = 4 Hz), 123.3 (d, $J_{CF}$ = 19 Hz), 122.2, 87.1, 87.7. $^{19}$F NMR (376.5 MHz) ($CDCl_3$): $\delta$ = -124.9; HRMS: *m/z* [M + H]$^+$ calcd for $C_{13}H_9FN$: 198.0714; found: 198.0712.




**6c**

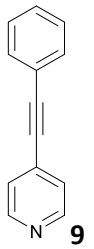
**2-(hept-1-yn-1-yl)pyridine (6c)**: Brown oil (1.013 g, 92% yield); IR (neat): 2956, 2931, 2858, 1582, 1561, 1463, 1427 cm$^{-1}$; $^{1}$H NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 8.54 (ddd, $J_1$ = 4.8 Hz, $J_2$= 1.8 Hz, $J_3$= 0.9, 1 H), 7.58 (td, $J_1$

= 7.7 Hz, $J_2$ = 1.8 Hz, 1 H), 7.36 (dt, $J_1$ = 7.8 Hz, $J_2$ = 1.3 Hz, 1 H), 7.18 (ddd, $J_1$ = 7.7 Hz, $J_2$= 4.8 Hz, $J_3$= 1.3 Hz, 1 H), 2.44 (t, $J$ = 7.1 Hz, 2 H), 1.65 (quintet, $J$ = 7.7 Hz, 2 H), 1.50-1.31 (m, 4 H), 0.92 (t, $J$ = 7.1 Hz, 3 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 144.1, 136.1, 126.9, 122.3, 91.3, 80.4, 31.2, 28.32, 22.3, 19.4, 14.0; HRMS: *m/z* [M + H]$^+$ calcd for $C_{12}H_{16}N$: 174.1272; found: 174.1272.




**8**

**3-(phenylethynyl)pyridine (8)**: wax (269.4 mg, 88% yield); IR (KBr): 3053, 2918, 2222, 1580, 1460 cm $^{-1}$;$^1$H NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 8.79 (bd, $J$ = 1.5 Hz, 1H), 8.57 (dd, $J_1$ = 4.9 Hz, $J_2$ = 1.6 Hz, 1 H), 7.83 (dt, $J_1$ = 7.8 Hz, $J_2$ = 1.8 Hz, 1 H), 7.61-7.54 (m, 2 H), 7.43 -7.36 (m, 3 H), 7.31 (ddd, $J_1$ = 7.9 Hz, $J_2$ = 4.9 Hz, $J_3$ = 0.8 Hz 1 H), $^{13}$C NMR (100.6 MHz) ($CDCl_3$): 152.4, 148.7, 138.6, 131.8, 128.9, 128.6, 123.2, 122.7, 120.6, 92.8, 86.1; HRMS: *m/z* [M + H]$^+$ calcd for $C_{13}H_{10}N$: 180.0808; found: 180.0806.



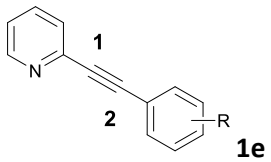

**9**

**4-(phenylethynyl)pyridine (9)**: Orange solid (269.4 mg, 88% yield); mp: 92 - 93 °C; IR (KBr): 3390, 2917, 1590, cm $^{-1}$;$^1$H NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 8.63 (dd, $J_1$ = 6.0 Hz, $J_2$ = 1.4 Hz, 2 H), 7.62-7.54 (m, 2 H), 7.45 -7.36 (m, 5 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): 149.9, 132.0, 131.6,129.3, 128.6, 125.7, 122.2, 94.21, 86.8; HRMS: *m/z* [M + H]$^+$ calcd for $C_{13}H_{10}N$: 180.0808; found: 180.0808.

### 3.1 Additional NMR data of compounds 1a - h

Attribution of $^{1}H$ NMR and $^{13}C$ NMR signals of compounds **1a - h** (and of the corresponding pyridinium salts **1a'- h'** generated in situ within an NMR tube using a solution of DMSO $d_6$ /DCl/$D_2O$) has been performed by homonuclear 2D NMR experiments (Cosy and Noesy) and heteronuclear 2D NMR experiments (HSQC and HMBC). $\delta_{C2}$-$\delta_{C1}$ of each compound is reported in Table 1 and Table 2.

**Table 1.** $\delta_{C2}$-$\delta_{C1}$ of compounds **1a- h**

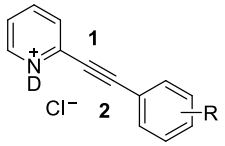



**1e**

| Compound | $\delta_{C1}$ (ppm) | $\delta_{C2}$ (ppm) | $\delta_{C2-C1}$(ppm) |
|---|---|---|---|
| **1a** | 88.6 | 89.2 | 0.6 |
| **1b** | 88.1 | 89.5 | 1.5 |
| **1c** | 87.6 | 89.5 | 1.9 |
| **1d** | 88.4 | 89.1 | 0.7 |
| **1e** | 92.8 | 87.6 | -5.2 |
| **1f** | 89.9 | 87.3 | -2.6 |
| **1g** | 93.3 | 87.9 | -5.4 |
| **1h** | 91.5 | 88.1 | -2.4 |
| **6** | 86.6 | 92.7 | 6.1 |

Experiments were performed using a solution of alkyne (25 mg) in DMSO $d_6$ (0.7 mL).

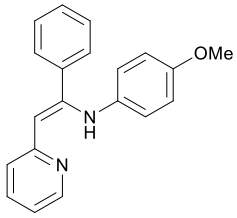
**Table 2**. $\delta_{C2}$-$\delta_{C1}$ of compounds **1a'- h'**




| Compound | $\delta_{C1}$ (ppm) | $\delta_{C2}$ (ppm) | $\delta_{C2-C1}$ (ppm) |
|---|---|---|---|
| **1a'** | 81.0 | 100.4 | 18.6 |
| **1b'** | 81.3 | 100.5 | 19.2 |
| **1c'** | 80.3 | 101.8 | 21.5 |
| **1d'** | 80.5 | 100.6 | 20.1 |
| **1e'** | 84.4 | 99.1 | 14.7 |
| **1f'** | 81.6 | 98.4 | 16.8 |
| **1g'** | 85.1 | 99.1 | 14.0 |
| **1h'** | 83.4 | 98.7 | 15.3 |
| **6'** | 83.3 | 96.3 | 13.0 |

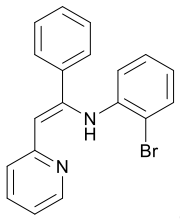
Experiments were performed by adding a solution of DCl/$D_2O$ (0.1 mL) to a solution of alkyne (25 mg) in DMSO $d_6$ (0.7 mL).

**4. CHARACTERIZATION DATA OF COMPOUND 3b – t, 6a – g, 4a, 5a**



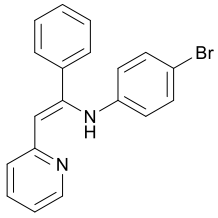

**3b**

**(*Z*)-4-methoxy-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (3b):** Yellow oil (125.7 mg, 83% yield); IR (neat): 3362, 3054, 2950, 1629, 1033 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.58 (br s, 1 H), 8.50 (bd, *J* = 4.9 Hz, 1 H), 7.56 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.8 Hz, 1 H), 7.51-7.46 (m, 2 H), 7.34-7.29 (m, 3 H), 7.10 (d, *J* = 8.2 Hz, 1 H), 6.94 (ddd, $J_1$ = 7.6 Hz, $J_2$= 4.9 Hz, $J_3$= 1.1 Hz, 1 H), 6.72-6.65 (m, 4 H), 5.56 (s, 1 H), 3.73 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 159.1, 154.7, 149.5, 147.5, 138.4, 136.0, 135.9, 128.4, 128.3, 128.2, 123.1, 122.8, 118.2, 114.0, 102.1, 55.5; MS (EI ion source): *m/z* (%) = 302 (84 [$M^+$]), 281 (37), 253 (15), 207 (83), 135 (26), 92 (30), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{20}H_{19}N_2O$: 303.1492; found: 303.1499.




**3c**

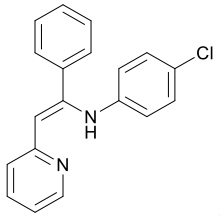
**(*Z*)-2-bromo-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (3c):** Yellow oil (62.1 mg, 35 % yield); IR (neat): 3322, 3013, 2919, 1620, 1580, 1377 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 12.03 (br s, 1 H), 8.57 (bd, *J* = 5.0 Hz, 1 H), 7.61 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.8 Hz 1 H), 7.56 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.5 Hz 1 H), 7.53-7.49 (m, 2 H), 7.37-7.34 (m, 3 H), 7.16 (d, *J*= 8.0 Hz, 1 H) 7.02 (ddd, $J_1$ = 7.7 Hz, $J_2$ = 5.0 Hz, $J_3$ = 1.0 Hz 1 H), 6.87-6.83 (m, 1 H), 6.68 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.8 Hz, 1 H), 6.31 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.3 Hz 1 H), 5.78 (s, 1 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 158.0, 147.6, 147.2, 141.0, 138.0, 136.2, 132.7, 128.6, 128.5, 127.8, 127.1, 123.1, 122.0, 121.5, 119.1, 114.7, 105.9; MS (EI ion source): *m/z* (%) = 352 ( 12 [$^{81}Br$ $M^+$]), 350 (13 [$^{79}Br$ $M^+$]), 271 (100), 207 (48), 135 (22), 73 (52); HRMS: *m/z* [$^{81}Br$ M + H] $^+$ calcd for $C_{19}H_{16}BrN_2$: 353.0471; found: 353.0479; [$^{79}Br$ M + H] $^+$ calcd for $C_{19}H_{16}BrN_2$: 351.0491; found: 351.0499.




**3d**

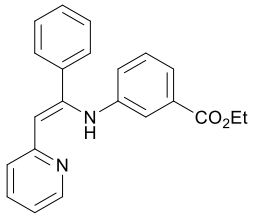
**(*Z*)-4-bromo-N-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (3d):** Yellow oil, (131.4 mg, 75% yield): IR (neat): 3326, 3010, 2922, 1620, 1585, 1360 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.62 (br s, 1 H), 8.40 (bd, *J* = 5.0 Hz, 1 H), 7.49 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.8 Hz, 1 H), 7.40-7.36 (m, 2 H), 7.26-7.23 (m, 3 H), 7.08 (d, *J* = 8.8 Hz, 2

H ), 7.02 (d, *J* = 8.0 Hz, 1 H), 6.88 (ddd, $J_1$ = 7.6 Hz, $J_2$ = 5.0 Hz, $J_3$ = 1.0 Hz, 1 H), 6.46 (d, *J* = 8.8 Hz 2 H), 5.54 (s, 1 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): δ = 158.5, 147.9, 147.5, 141.7, 137.9, 136.2, 131.5, 128.64, 128.59, 128.0, 123.3, 122.3, 118.9, 113.4, 104.4; MS (EI ion source): *m/z* (%) = 352 ( 37 [$^{81}$Br $M^+$]), 350 (43 [$^{79}$Br $M^+$]), 271 (41), 207 (55), 135 (32), 73 (100); HRMS: *m/z* [$^{81}$Br M + H] $^+$calcd for $C_{19}H_{16}N_2Br$: 353.0471; found: 353.0470. [$^{79}$Br M + H] $^+$ calcd for $C_{19}H_{16}N_2Br$: 351.0491; found: 351.0490.



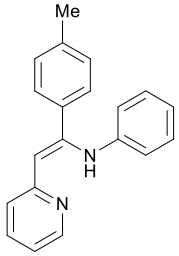

**3e**

**(*Z*)-4-chloro-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (3e):** Yellow oil, (75.9 mg, 49% yield)**:** IR (neat): 3342, 3026, 2948, 1628, 1589, 1358 $cm^{-1}$; $^1$H NMR (400.13 MHz) ($CDCl_3$): δ = 11.62 (br s, 1 H), 8.40 (bd, *J* = 5.0 Hz, 1 H), 7.48 (td, $J_1$ = 7.7 Hz $J_2$ = 1.7 Hz 1 H), 7.39-7.37 (m, 2 H), 7.25-7.23 (m, 3 H), 7.01 (d, *J* = 8.0 Hz, 1 H ), 6.93 (d, *J* = 8.8 Hz, 2 H), 6.87 (ddd, $J_1$ = 7.7 Hz, $J_2$ = 5.0 Hz, $J_3$ = 1.0 Hz, 1 H), 6.51 (d, *J* = 8.8 Hz 2 H), 5.53 (s, 1 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$)**:** δ = 158.5, 148.1, 147.5, 141.2, 137.9, 136.2, 128.61, 128.60, 128.56, 128.0, 126.0, 123.2, 122.0, 118.8, 104.2; MS (EI ion source): *m/z* (%) = 306 (58 [$M^+$]), 271 (21), 214 (44), 111 (41), 75 (75), 51 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{19}H_{15}ClN_2$: 307.0952; found: 307.0999.



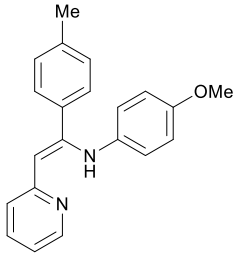

**3f**

**(*Z*)-ethyl 3-(1-phenyl-2-(pyridin-2-yl)vinylamino)benzoate (3f):** Yellow oil, (125.9 mg, 73% yield)**:** IR (neat): 3346, 3053, 2948, 1728, 1626, 1589, 1377 $cm^{-1}$; $^1$H NMR (400.13 MHz) (DMSO $d_6$): δ = 11.61 (br s, 1 H), 8.57 (bd, *J* = 5.0 Hz, 1 H), 7.75 (td, $J_1$ = 7.6 Hz $J_2$ = 1.8 Hz 1 H), 7.49-7.46 (m, 2 H), 7.40-7.33 (m, 5 H), 7.23-7.19 (m, 2 H), 7.13 (ddd, $J_1$ = 7.6 Hz, $J_2$ = 5.0 Hz, $J_3$ = 1.0 Hz, 1 H), 6.89 (dd, $J_1$ = 8.3 Hz, $J_2$ = 2.3 Hz, 1 H), 5.85 (s, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (100.6 MHz) (DMSO $d_6$): δ = 165.9, 158.0, 148.0, 147.0, 143.0, 137.7, 137.2, 130.8, 129.5, 129.1 (2C), 127.9, 124.9, 124.0, 121.8, 120.6, 120.0, 105.8, 61.0, 14.5; HRMS: *m/z* [M + H]$^+$ calcd for $C_{22}H_{20}N_2O_2$: 345.1603.; found: 345.1600.



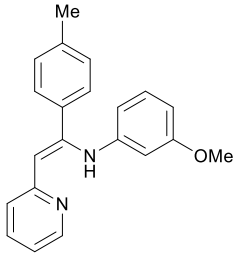

**3g**

**(*Z*)-*N*-(2-(pyridin-2-yl)-1-p-tolylvinyl)aniline (3g):** Yellow solid (121.7 mg, 85% yield); mp: 90 - 92 °C; IR (KBr): 3364, 3012, 2914, 1621, 1587, 1370 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): δ = 11.59 (br s, 1 H), 8.39 (bd, *J* = 4.5 Hz, 1 H), 7.46 (td, $J_1$ = 7.8 Hz, $J_2$ = 1.8 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H ), 7.02-6.98 (m, 3 H), 6.86-6.83 (m, 1 H), 6.73 (t, *J* = 7.2 Hz, 1 H), 6.63 (d, *J* = 8.0 Hz, 2 H), 5.50 (s, 1 H), 2.27 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): δ = 158.9, 148.6, 147.5, 142.7, 138.3, 136.0, 135.4, 129.2, 128.6, 128.0, 123.0, 121.0, 120.9, 118.4, 103.2, 21.4; MS (EI ion source): *m/z* (%) = 286 (100 [$M^+$]), 270 (20), 208 (37), 207 (52), 194 (70), 92 (17), 77 (73); HRMS: *m/z* [M + H]$^+$ calcd for $C_{20}H_{19}N_2$: 287.1543; found: 287.1547.



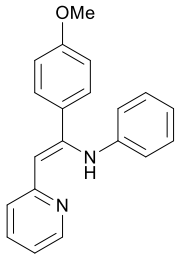

**3h**

**(*Z*)-4-methoxy-*N*-(2-(pyridin-2-yl)-1-*p*-tolylvinyl)aniline (3h):** Yellow wax (155.7 mg, 98% yield); IR (neat): 3352, 3012, 1619, 1587, 1365, 1245, 1024 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): δ = 11.45 (br s, 1 H), 8.36 (bd, *J* = 5.0 Hz, 1 H), 7.44 (td, $J_1$ = 7.6 Hz, $J_2$= 1.8 Hz, 1 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.02 (d, *J* = 8.0 Hz, 2 H), 6.98 (d, *J* = 8.0 Hz, 1 H) 6.82 (ddd, $J_1$ = 7.6 Hz, $J_2$= 5.0 Hz, $J_3$= 1.1 Hz 1 H), 6.62-6.56 (m, 4 H), 5.44 (s, 1 H), 3.63 (s, 3 H), 2.26 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): δ = 159.1, 154.6, 149.5, 147.4, 138.1, 136.0, 135.9, 135.5, 129.0, 128.2, 123.1, 122.7, 118.0, 114.0, 101.7, 55.5, 21.4; MS (EI ion source): *m/z* (%) = 316 (21 [$M^+$]), 281 (13), 224 (100), 207 (28), 181 (8), 92 (20); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{21}N_2O$: 317.1648; found: 317.1653.



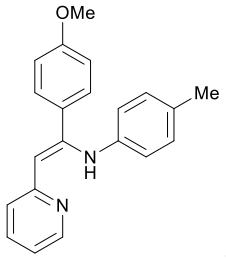

**3i**

**(*Z*)-3-metossi-*N*-(2-(piridin-2-il)-1-*p*-tolilvinil)aniline (3i):** Yellow solid (148.5 mg, 94% yield); mp: 88 - 90 °C; IR (KBr): 3342, 3012, 2950, 1630, 1588, 1370, 1035 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): δ = 11.70 (br s, 1 H), 8.51 (bd, *J* = 4.6 Hz, 1 H), 7.57 (td, $J_1$ = 7.6 Hz, $J_2$= 1.6 Hz, 1 H ), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.2 Hz, 1 H), 7.01 (t, *J* = 8.2 Hz, 1 H), 6.99-6.94 (m, 1 H), 6.41 (dd, $J_1$ = 8.2 Hz, $J_2$= 2.3 Hz, 1 H), 6.36 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1 H), 6.26 (bt, *J* = 2.0 Hz, 1 H), 5.61 (s, 1 H), 3.60 (s, 3 H), 2.38 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): δ = 160.0, 158.7, 148.4, 147.5, 144.0, 138.3, 136.0, 135.5, 129.3, 129.2, 127.9, 123.0, 118.5, 113.5, 106.9, 106.4, 103.4, 55.0, 21.4; MS (EI ion source): *m/z* (%) = 316 (54 [$M^+$]), 300 (34), 281 (30), 224 (45), 207 (79), 92 (40), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{21}N_2O$: 317.1648; found: 317.1655.



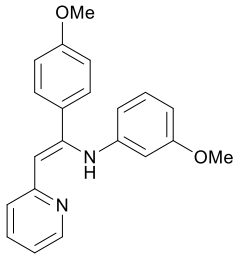

**3j**

**(*Z*)-*N*-(1-(4-methoxyphenyl)-2-(pyridin-2-yl)vinyl)aniline (3j):** Yellow solid; (125.5 mg, 83% yield); mp: 131-132 °C; IR (neat): 3344, 3008, 2967, 1617, 1590, 1365, 1245, 1024 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.70 (br s, 1 H), 8.50 (bd, *J* = 5.0 Hz, 1 H), 7.57 (td, $J_1$ = 7.8 Hz, $J_2$= 1.6 Hz, 1 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.14-7.10 (m, 3 H), 6.95 (ddd, $J_1$ = 7.6 Hz, $J_2$= 5.0 Hz, $J_3$= 1.1 Hz 1 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 6.87-6.83 (m, 1 H), 6.75 (d, $J_1$= 7.6 Hz, 2 H), 5.59 (s, 1 H), 3.84 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 159.8, 158.9, 148.2, 147.5, 142.8, 136.0, 130.7, 129.3, 128.6, 122.9, 121.0, 120.9, 118.3, 113.9, 102.8, 55.4; MS (EI ion source): *m/z* (%) = 302 (88 [$M^+$]), 286 (32), 223 (42), 210 (87), 167 (34), 92 (22), 77 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{20}H_{19}N_2O$: 303.1492; found 303.1500.




**3k**

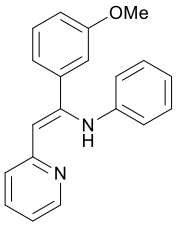
**(*Z*)-*N*-(1-(4-methoxyphenyl)-2-(pyridin-2-yl)vinyl)-4-methylaniline (3k):** Yellow solid (106.1 mg, 67% yield); mp**:** 128 - 129 °C; IR (KBr): 3343, 3010, 1620, 1580, 1368, 1275, 1075 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.65 (br s, 1 H), 8.50 (bd, *J* = 4.4 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 1 H), 7.46 (d, *J* = 8.3 Hz, 2 H), 7.10 (d, *J* = 7.8 Hz, 1 H), 6.94 (d, *J* = 7.8 Hz, 3 H), 6.88 (d, *J* = 8.3 Hz, 2 H), 6.67 (d, *J* = 7.8 Hz, 2 H), 5.56 (s, 1 H), 3.48 (s, 3 H), 2.26 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 159.7, 159.0, 148.6, 147.4, 140.1, 135.9, 130.7, 130.4, 129.4, 129.2, 122.8, 121.3, 118.1, 113.8, 102.1, 55.3, 20.7; MS (EI ion source): *m/z* (%) = 316 (100 [$M^+$]), 281 (32), 224 (88), 207 (76), 182 (28), 92 (25), 73 (96); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{21}N_2O$: 317.1648; found: 317.1655.




**3l**

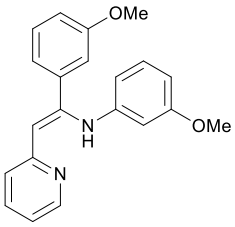
**(*Z*)-3-methoxy-*N*-(1-(4-methoxyphenyl)-2-(pyridin-2-yl)vinyl)aniline (3l):** Yellow oil (163.0 mg 98% yield); IR (neat): 3360, 3010, 2955, 1631, 1588, 1370, 1275, 1035 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.74 (br s, 1 H), 8.52 (bd, *J* = 4.8 Hz, 1 H), 7.57 (td, $J_1$ = 7.9 Hz, $J_2$ = 1.7 Hz, 1 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 7.05 (t, *J* = 8.1 Hz, 1 H), 6.98-6.94 (m, 1 H), 6.91 (d, *J* = 8.6 Hz, 2 H), 6.45 (dd, $J_1$ = 8.2 Hz, $J_2$ = 2.1 Hz, 1 H), 6.40 (bd, *J* = 8.1 Hz, 1 H), 6.32 (bt, *J* = 2.1 Hz, 1 H), 5.63 (s, 1 H), 3.85 (s, 3 H), 3.65 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 159.9, 159.8, 158.7, 148.0, 147.4, 144.0, 136.0, 130.7, 129.2 (2C), 122.9, 118.4,

113.8, 113.5, 106.8, 106.5, 103.1, 55.3, 55.0; MS (EI ion source): *m/z* (%) = 332 (8 [$M^+$]), 281 (25), 267 (10), 253 (31), 207 (65), 193 (12), 92 (31), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{21}N_2O_2$: 333.1598; found: 333.1604.



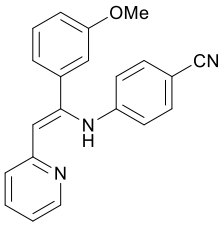

**3m**

**(*Z*)-*N*-(1-(3-methoxyphenyl)-2-(pyridin-2-yl)vinyl)aniline (3m):** Yellow solid (136.3 mg, 90% yield); mp**:** 81 - 82 °C; IR (KBr): 3341, 3010**,** 2950, 1621, 1604, 1378, 1218, 1042 cm$^{-1}$; $^1$H NMR (400.13 MHz) ($CDCl_3$): δ = 11.59 (br s, 1 H), 8.40 (bd, *J* = 4.7 Hz, 1 H), 7.47 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.5 Hz, 1 H ), 7.14 (t, *J* = 8.0 Hz, 1 H), 7.03-6.95 (m, 5 H), 6.88-6.83 (m, 1 H), 6.77 (dd, $J_1$= 8.1 Hz, $J_2$= 2.2 Hz 1 H), 6.73 (t, *J* = 7.4 Hz, 1 H), 6.63 (d, *J* = 8.0 Hz, 2 H), 5.54 (s, 1 H), 3.66 (s, 3 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): δ = 159.6, 158.7, 148.4, 147.5, 142.6, 139.8, 136.0, 129.5, 128.6, 123.1, 121.1, 120.9, 120.7, 118.6, 114.2, 113.4, 103.5, 55.4; MS (EI ion source): *m/z* (%) = 302 (100 [$M^+$]), 281 (27), 224 (32), 210 (60), 195 (27), 92 (29), 77 (73); HRMS: *m/z* [M + H]$^+$ calcd for $C_{20}H_{19}N_2O$: 303.1492; found: 303.1499.



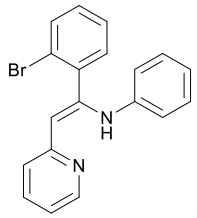

**3n**

**(*Z*)-4-methoxy-*N*-(1-(3-methoxyphenyl)-2-(pyridin-2-yl)vinyl)aniline (3n):** Yellow oil; (124.6 mg 75% yield); IR (neat): 3362, 3004, 2935, 1626, 1590, 1378, 1037 cm$^{-1}$; $^1$H NMR (400.13 MHz) ($CDCl_3$): δ = 11.45 (br s, 1 H), 8.38 (bd, *J* = 4.8 Hz, 1 H), 7.46 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.8 Hz, 1 H ), 7.12 (t, *J*= 7.8 Hz, 1 H), 6.98 (t, *J* = 7.8 Hz, 2 H), 6.95-6.92 (m, 1 H), 6.86-6.81 (m, 1 H), 6.75 (dd, $J_1$ = 8.0 Hz, $J_2$ = 2.6 Hz, 1 H ), 6.64-6.56 (m, 4 H), 5.48 (s, 1 H), 3.66 (s, 3 H), 3.63 (s, 3 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): δ = 159.5, 159.0, 154.7, 149.4, 147.5, 139.8, 136.0, 135.9, 129.3, 123.1, 122.8, 120.9, 118.2, 114.1, 114.0, 113.7, 102.0, 55.6, 55.4; MS (EI ion source): *m/z* (%) = 332 (100 [$M^+$]), 316 (18), 254 (26), 240 (72), 184 (26), 167 (25), 92 (39), 73 (41); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{21}N_2O_2$: 333.1598; found: 333.1603.



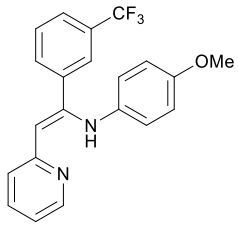

**3o**

**(*Z*)-4-(1-(3-methoxyphenyl)-2-(pyridin-2-yl)vinylamino)benzonitrile (3o):** Yellow wax, (31.3 mg, 19% yield); IR (neat): 3332, 3036, 2950, 2210, 1620, 1580, 1368, 1267, 1037; $^{1}$H NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 12.02 (br s,, 1 H), 8.55 (bd, *J* = 4.7 Hz, 1 H), 7.64 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.7 Hz, 1 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.17 (d, *J* = 8.0 Hz, 1 H), 7.09-7.03 (m, 3 H), 6.94 (m, 1 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 5.78 (s, 1 H), 3.81 (s, 3 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 159.9, 157.7, 147.6, 146.7, 146.1, 138.9, 136.5, 132.9, 130.0, 123.8, 120.2, 120.0, 119.7, 119.3, 114.4, 113.2, 107.0, 102.4, 55.4; MS (EI ion source): *m/z* (%) = 327( 24 [$M^+$]), 281 (41), 253 (18), 207 (89), 135 (17), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{18}N_3O$: 328.1444; found: 328.1452.



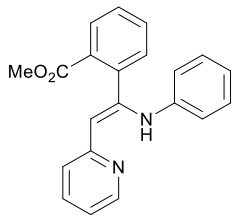

**3p**

**(*Z*)-*N*-(1-(2-bromophenyl)-2-(pyridin-2-yl)vinyl)aniline (3p):** Yellow oil (131.4 mg, 75% yield); IR (neat): 3343, 3023, 2956, 1620, 1580, 1377 cm$^{-1}$; $^{1}$H NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.98 (br s, 1 H), 8.54 (bd, *J* = 4.9 Hz, 1 H), 7.60-7.55 (m, 2 H), 7.52 (dd, $J_1$ = 7.6 Hz $J_2$ = 1.7 Hz, 1 H), 7.34 (td, $J_1$ = 7.6 Hz $J_2$ = 1.2 Hz, 1 H), 7.22 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.7 Hz, 1 H), 7.11-7.06 (m, 3 H), 6.97 (ddd, $J_1$ = 7.6 Hz, $J_2$ = 4.9 Hz $J_3$ = 1.1 Hz, 1 H), 6.87-6.83 (m, 1 H), 6.69-6.67 (m, *J* = 7.1, 2 H), 5.33 (s, 1 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 158.7, 147.5, 147.1, 141.7, 139.1, 136.0, 133.3, 131.4, 129.7, 128.7, 127.5, 123.0, 122.9, 121.4, 120.4, 118.4, 101.9; MS (EI ion source): *m/z* (%) = 352 ( 10 [$^{81}$Br $M^+$]), 350 (8 [$^{79}$Br $M^+$]), 271 (100), 207 (64), 135 (18), 73 (55); HRMS: *m/z* [$^{81}$Br M + H] $^+$ calcd for $C_{19}H_{16}BrN_2$: 353.0471; found: 353.0480; [$^{79}$Br M + H] $^+$ calcd for $C_{19}H_{16}BrN_2$: 351.0491; found: 351.0501.



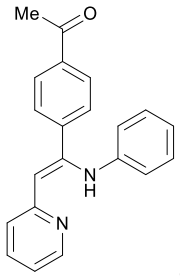

**3q**

**(*Z*)-4-methoxy-*N*-(2-(pyridin-2-yl)-1-(3-(trifluoromethyl)phenyl)vinyl)aniline (3q):** Yellow oil (146.3 mg 79% yield); IR (neat): 3354, 3008, 2928, 1621, 1590, 1245, 1170, 1037 cm$^{-1}$; $^{1}$H NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.44 (br s, 1 H), 8.39 (bd, *J* = 4.9 Hz, 1 H), 7.69 (br s, 1 H), 7.51-7.44 (m, 3 H), 7.28 (t, *J* = 7.8 Hz, 1 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 6.88 (ddd, $J_1$ = 7.6 Hz, $J_2$ = 4.9 Hz, $J_3$ = 0.9 Hz, 1 H), 6.58 (br s, 4 H), 5.48 (s, 1 H), 3.63 (s, 3 H); $^{13}$C NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 158.6, 155.0, 147.9, 147.5, 139.3, 136.1, 135.4, 131.7, 130.8 (q, $J_{CF}$ = 32 Hz), 128.7, 124.9-124.8 (m, 2C), 124.1 (q, $J_{CF}$ = 273 Hz), 123.5, 123.1, 118.7, 114.7, 103.0, 55.6; $^{19}$F NMR (376.5 MHz) ($CDCl_3$): $\delta$ = -62.6; MS (EI ion source): *m/z* (%) = 370 (100 [$M^+$]), 355 (15), 278 (46), 248 (19), 184 (29), 92 (39), 78 (53); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{18}F_3N_2O$: 371.1366; found: 371.1373.



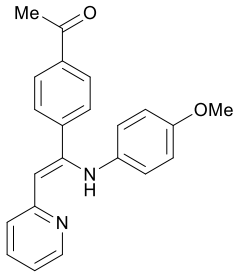

**3r**

**(*Z*)-methyl 2-(1-(phenylamino)-2-(pyridin-2-yl)vinyl)benzoate (3r):** Yellow oil (131.0 mg, 79% yield); IR (neat): 3342, 3056, 2948, 1728, 1626, 1589 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11 95 (br s, 1 H), 8.51 (bd, *J* = 4.9 Hz, 1 H), 7.76 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.0 Hz 1 H), 7.57-7.52 (m, 1 H), 7.50-7.39 (m, 3 H), 7.10-7.02 (m, 3 H), 6.94 (ddd, $J_1$ = 7.6 Hz, $J_2$ = 4.9 Hz, $J_3$ = 1.1 Hz, 1 H), 6.89-6.82 (m, 1 H), 6.74 (d, *J* = 7.6 Hz, 2 H), 5.28 (s, 1 H), 3.75 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 168.7, 158.8, 147.7, 147.4, 141.6, 138.4, 135.9, 131.5, 131.4, 130.3, 129.6, 128.6, 128.2, 122.7, 121.4, 120.8, 118.2, 101.5, 55.4; MS (EI ion source): *m/z* (%) = 330( 40 [$M^+$]), 271 (100), 238 (44), 207 (39), 135 (29), 73 (43); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{19}N_2O_2$: 331.1441; found: 331.1447.



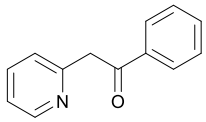

**3s**

**(*Z*)-1-(4-(1-(phenylamino)-2-(pyridin-2-yl)vinyl)phenyl)ethanone (3s):** Yellow solid (72.1 mg 46% yield); mp: 112 - 114 °C; IR (KBr): 3344 3012, 2948, 1678, 1626, 1596, 1368, 1263 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.68 (br s, 1 H), 8.53 (bd, *J* = 5.0 Hz, 1 H), 7.93 (d, *J* = 8.5 Hz, 2 H), 7.64-7.58 (m, 3 H), 7.18-7.09 (m, 3 H), 7.00 (ddd, $J_1$ = 7.6 Hz, $J_2$= 5.0 Hz, $J_3$= 1.0 Hz, 1 H), 6.86 (t, *J* = 7.4 Hz, 1 H), 6.71 (d, *J* = 7.6 Hz, 2 H), 5.70 (s, 1 H), 2.62 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 197.7, 158.3, 147.6, 147.3, 143.2, 142.3, 136.7, 136.2, 128.8, 128.6, 128.2, 123.4, 121.4, 121.1, 119.1, 105.1, 26.7; MS (EI ion source): *m/z* (%) = 314 (20 [$M^+$]), 281 (36), 253 (16), 207 (69), 135 (18), 96 (15), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{21}H_{19}N_2O$: 315.1492; found: 315.1498.



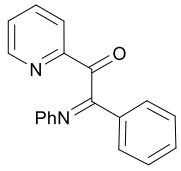

**3t**

**(*Z*)-1-(4-(1-(4-methoxyphenylamino)-2-(pyridin-2-yl)vinyl)phenyl)ethanone (3t):** Yellow oil (153.4 mg, 89% yield); IR (neat): 3353, 3003, 2950, 1680, 1626, 1580, 1274, 1037 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 11.53 (br s, 1 H), 8.50 (bd, *J* = 4.3 Hz, 1 H), 7.90 (d, *J* = 8.2 Hz, 2 H), 7.60-7.57 (m, 3 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 6.99-6.96 (m, 1 H), 6.71-6.66 (m, 4 H), 5.63 (s, 1 H), 3.72 (s, 3 H), 2.60 (s, 3 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 197.7, 158.6, 155.0, 148.2, 147.6, 143.3, 136.6, 136.1, 135.6, 128.45, 128.39, 123.3, 123.1, 118.8, 114.1, 103.5, 55.5, 26.7; MS (EI ion source): *m/z* (%) = 344 (24 [$M^+$]), 281 (40), 207 (86), 135 (18), 96 (14), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{22}H_{21}N_2O_2$: 345.1598; found: 345.1605.



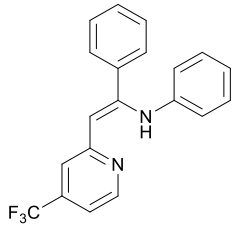

**4a**

**1-phenyl-2-(pyridin-2-yl)ethanone (4a):** known compound; lit mp: 52 - 54[ii]; mp 55 – 57.



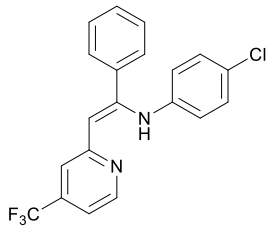

**5a**

**2-phenyl-2-(phenylimino)-1-(pyridin-2-yl)ethanone (5a)**: yellow solid, mp :123 - 124 °C; IR (KBr): 3059, 2940, 1686, 1622 1579, 1445, 1231, 1194 $cm^{-1}$; $^1H$ NMR (400.13 MHz) ($CDCl_3$): $\delta$ = 8.61 (bd, *J* = 4.8 Hz , 1 H), 7.89 (d, *J* = 6.8 Hz, 2 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.73 (td, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1 H), 7.52-7.43 (m, 3 H), 7.39-7.36 (m, 1 H), 7.10 (t, *J* = 7.6 Hz, 2 H), 6.91 (t, *J* = 7.2 Hz, 1 H) 6.86 (d, *J* = 6.8 Hz, 2 H); $^{13}C$ NMR (100.6 MHz) ($CDCl_3$): $\delta$ = 198.4, 167.1, 152.4, 149.7, 149.6, 136.9, 135.2, 131.4, 128.7, 128.4, 128.1, 127.5, 124.2, 122.3, 120.1; MS (EI ion source): m/z (%) = 286 ( 12 [$M^+$]), 180 (100), 77 (45).



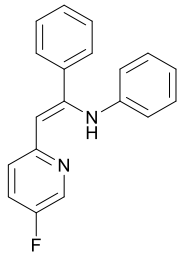

**7a**

**(*Z*)-*N*-(1-phenyl-2-(4-(trifluoromethyl)pyridin-2-yl)vinyl)aniline** (**7a**): Yellow solid (163.3 mg, 96% yield); mp**:** 76 - 77 °C; IR (KBr): 3398, 2926, 1633, 1134 $cm^{-1}$; $^1H$ NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 11.39 (br s, 1 H), 8.76 (d, *J* = 5.3 Hz, 1 H), 7.69 (s, 1 H), 7.51-7.43 (m, 2 H), 7.42-7.34 (m, 4 H), 7.10 (t, *J* = 7.8 Hz, 2 H), 6.85 (t, *J* = 7.3 Hz, 1 H), 6.69 (d, *J* = 7.7 Hz, 2 H), 5.90 (s, 1 H); $^{13}C$ NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 159.7, 149.7, 149.6, 142.0, 137.7, 137.2 (q, $J_{CF}$ = 33.0 Hz), 129.3, 129.2, 129.0, 128.3, 123.5 (q, $J_{CF}$ = 273.6 Hz), 122.1, 121.4, 118.9 (q, $J_{CF}$ = 3.8 Hz), 113.9 (q, $J_{CF}$ = 3.4 Hz), 103.1. $^{19}F$ NMR (376.5 MHz) (DMSO $d_6$): $\delta$ = -63.6; HRMS: *m/z* [M + H]$^+$ calcd for $C_{20}H_{16}F_3N_2$: 341.1260; found: 341.1254.



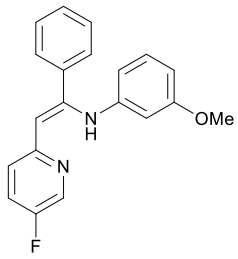

**7b**

**(*Z*)-4-chloro-*N*-(1-phenyl-2-(4-(trifluoromethyl)pyridin-2-yl)vinyl)aniline** (**7b**): Wax (185.1 mg, 99% yield); IR (neat): 3061, 1624, 1549, 1332, 1171 $cm^{-1}$; $^1H$ NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 11.38 (br s, 1 H), 8.77 (d, *J* = 5.2 Hz, 1 H), 7.71 (s, 1 H), 7.49-7.37 (m, 6 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 6.69 (d, *J* = 8.8 Hz, 2 H), 5.96 (s, 1 H); $^{13}C$ NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 159.4, 149.6, 149.0, 141.0, 137.3 (q, $J_{CF}$ = 33.0 Hz), 137.2, 129.5, 129.1, 129.0, 128.2, 125.9, 123.5 (q, $J_{CF}$ = 273.3 Hz), 122.7, 119.0 (q, $J_{CF}$ = 3.8 Hz), 114.2 (q, $J_{CF}$ = 3.2 Hz), 103.1. $^{19}F$ NMR (376.5 MHz) (DMSO $d_6$): $\delta$ = -63.6; HRMS: *m/z* [M + H]$^+$ calcd for $C_{20}H_{16}ClF_3N_2$: 375.0870; found: 375.0866.



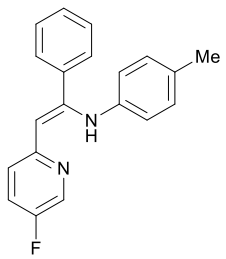
**7c**

**(*Z*)-*N*-(2-(5-fluoropyridin-2-yl)-1-phenylvinyl)aniline (7c):** Yellow solid (124.7 mg 86% yield); mp**:** 128 - 129 °C; IR (neat): 3390, 2927, 1624, 1596, 1477, 1385, 1230 $cm^{-1}$; $^{1}H$ NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 11.06 (br s, 1 H), 8.54 (bd, $J$ = 2.9 Hz, 1 H), 7.69 (td, $J_1$ = 8.8 Hz, $J_2$ = 3.1 Hz, 1 H), 7.49-7.33 (m, 6 H), 7.11-7.05 (m, 2 H), 6.80 (dt, $J_1$ = 7.2, $J_2$ = 0.9 Hz, 1 H), 6.64 (d, $J$ = 7.6 Hz, 2 H), 5.83 (s, 1 H); $^{13}C$ NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 156.3 (d, $J_{CF}$ = 249.0 Hz), 155.2 (d, $J_{CF}$ = 3.5 Hz), 146.9 (d, $J_{CF}$ = 2.1 Hz), 142.6, 138.1, 135.5 (d, $J_{CF}$ = 24.2 Hz),129.4, 129.1, 129.0, 128.8, 125.2 (d, $J_{CF}$ = 4.3 Hz), 124.5 (d, $J_{CF}$ = 19.3 Hz), 121.4, 120.7. 104.1. $^{19}F$ NMR (376.5 MHz) (DMSO $d_6$): $\delta$ = -131.8; HRMS: *m/z* $[M + H]^+$ calcd for $C_{19}H_{16}FN_2$: 291.1292; found: 291.1289.



**7d**

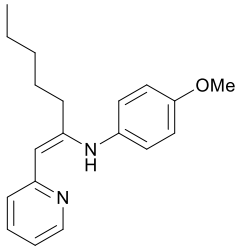
(***Z*)-*N*-(2-(5-fluoropyridin-2-yl)-1-phenylvinyl)-3-methoxyaniline** (7d): Yellow solid (153.6 mg, 96% yield); 90% yield); mp**:** 88 - 89 °C; IR (neat): 3390, 2926, 1627, 1596, 1478, 1230, 1140 $cm^{-1}$; $^{1}H$ NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 11.05 (br s, 1 H), 8.55 (bd, $J$ = 2.8 Hz, 1 H), 7.70 (td, $J_1$ = 9.0 Hz, $J_2$ = 3.0 Hz, 1 H), 7.50-7.34 (m, 6 H), 6.98 (t, $J$ = 8.1 Hz, 1 H), 6.37 (dd, $J_1$ = 8.0 Hz, $J_2$ = 2.1 Hz, 1 H), 6.26 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.6 Hz, 1 H), 6.13 (t, $J$ = 2.1 Hz, 1 H), 5.83 (s, 1 H), 3.52 (s, 3 H); $^{13}C$ NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 160.0, 156.4 (d, $J_{CF}$ = 250.0 Hz), 155.7 (d, $J_{CF}$ = 3.6 Hz),146.7 (d, $J_{CF}$ = 2.0 Hz), 143.8, 138.2, 135.5 (d, $J_{CF}$ = 24.3 Hz), 129.8, 129.0, 128.0, 125.2 (d, $J_{CF}$ = 4.2 Hz), 124.7 (d, $J_{CF}$ = 19.0 Hz), 113.1, 107.0, 106.3, 104.3, 55.1. $^{19}F$ NMR (376.5 MHz) (DMSO $d_6$): $\delta$ = -131.7; HRMS: *m/z* $[M + H]^+$ calcd for $C_{20}H_{18}FN_2O$: 321.1398; found: 321.1394.



**7e**

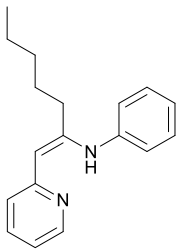
**(*Z*)-*N*-(2-(5-fluoropyridin-2-yl)-1-phenylvinyl)-4-methylaniline (7e):** Yellow solid (135.3 mg, 89% yield); mp**:** 143 – 144 °C; IR (neat): 3398, 3024, 1624, 1478, 1386, 1230, 1084 $cm^{-1}$; $^{1}H$ NMR (400.13 MHz) (DMSO $d_6$): $\delta$ = 11.00 (br s, 1 H), 8.52 (bd, $J$ = 2.8 Hz, 1 H), 7.68 (td, $J_1$ = 8.9 Hz, $J_2$ = 3.1 Hz, 1 H), 7.47-7.31 (m, 6 H), 6.89 (d, $J$ = 8.1 Hz, 2 H), 6.55 (d, $J$ = 8.3 Hz, 2 H), 5.77 (s, 1 H), 2.14 (s, 3 H); $^{13}C$ NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 156.2 (d, $J_{CF}$ = 249.0 Hz), 155.4 (d, $J_{CF}$ = 3.6 Hz),147.4 (d, $J_{CF}$ = 1.7 Hz), 140.0, 138.1, 135.5 (d, $J_{CF}$ = 24.1

Hz),130.5, 129.6, 128.92, 128.88, 128.1, 125.0 (d, $J_{CF}$ = 4.3 Hz), 124.6 (d, $J_{CF}$ = 18.9 Hz), 121.1, 103.2, 20.6. $^{19}$F NMR (376.5 MHz) (DMSO $d_6$): $\delta$ = -132.2; HRMS: *m/z* [M + H]$^+$ calcd for $C_{20}H_{18}FN_2$: 305.1449; found: 305.1446.



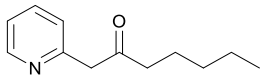

**7f**

**(*Z*)-4-methoxy-*N*-(1-(pyridin-2-yl)hept-1-en-2-yl)aniline (7f):** wax (145.9 mg, 79% NMR yield); $^1$H NMR (400.13 MHz) (DMSO $d_6$) (selected signals): $\delta$ = 11.34 (br s, 1 H), 8.36 (bd, *J* = 4.3 Hz, 1 H), 7.57 (td, $J_1$ = 7.7 Hz, $J_2$ = 1.7 Hz, 1 H), 7.06 (d, *J* = 8.8, 2 H), 7.01 (d, *J* = 8.2, 1 H), 6.91 (d, *J* = 8.8, 2 H), 6.67-6.62 (m, 1 H), 6.54-6.49 (m, 1 H), 5.21 (s, 1 H), 2.33 (d, *J* = 7.6, 2 H), 1.40-1.34 (m, 2 H), 1.22-1.14 (m, 4H), 0.80-0.69 (m, 3 H) ; $^{13}$C NMR (100.6 MHz) (DMSO $d_6$): $\delta$ = 159.6, 156.3, 152.2, 147.3, 136.4, 134.1, 126.0, 122.3, 122.1, 121.8, 117.5, 114.7, 55.7, 32.7, 31.3, 27.9, 22.2, 14.2.




**7g**

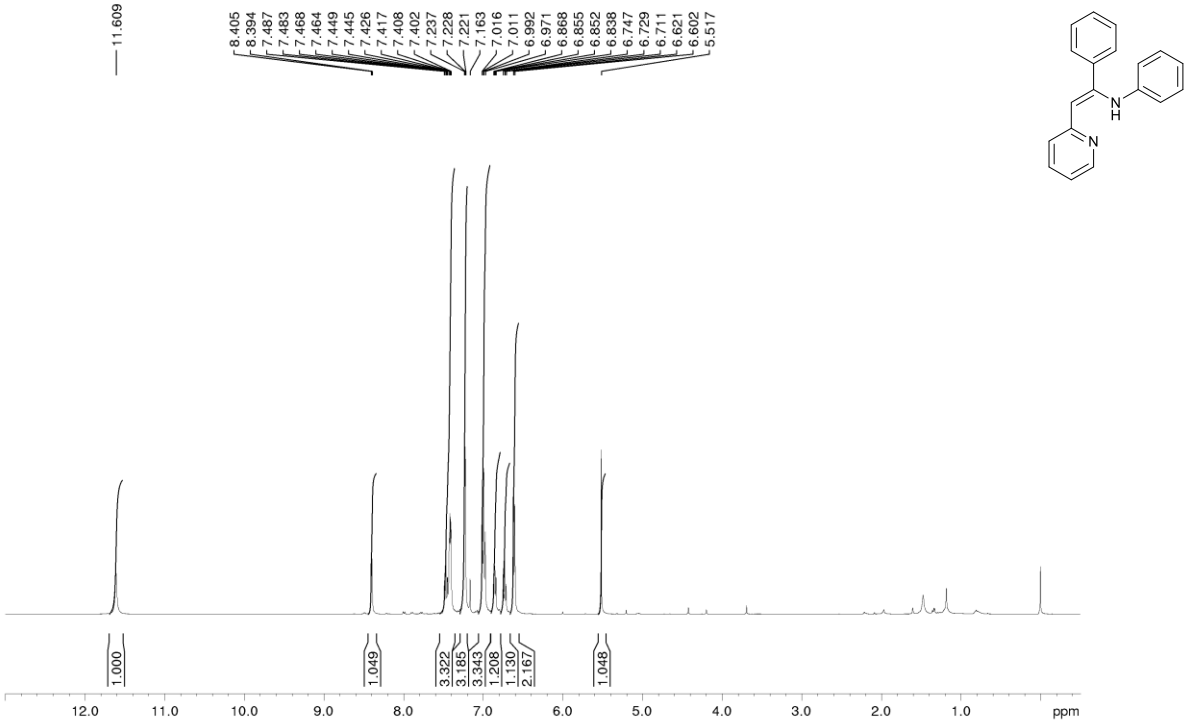
**(*Z*)-*N*-(1-(pyridin-2-yl)hept-1-en-2-yl)aniline (7g):** oil (63.9 mg, 48 % NMR yield); $^1$H NMR (400.13 MHz) (DMSO $d_6$) (selected signals): $\delta$ = 11.63 (br s, 1 H), 8.40 (bd, *J* = 4.2 Hz, 1 H), 5.30 (s, 1 H).



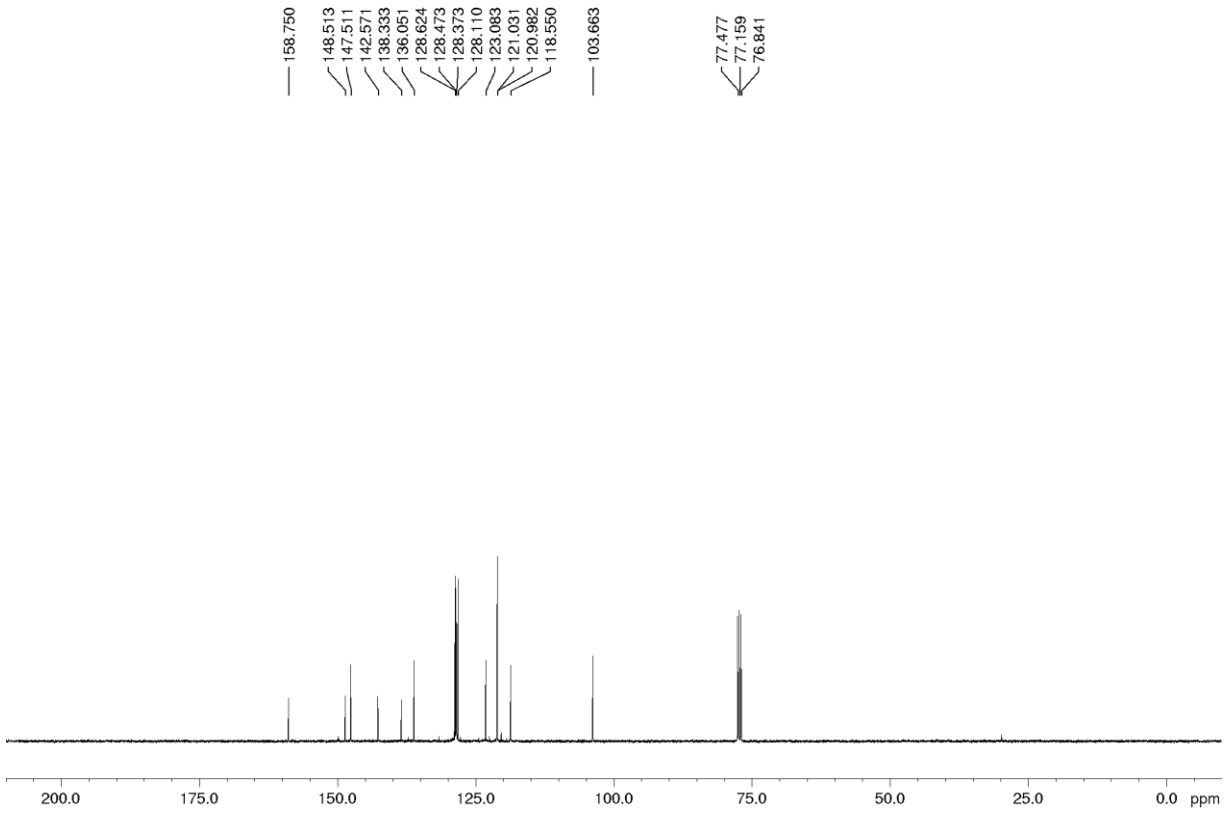

**1-(pyridin-2-yl)heptan-2-one** (**4b**): known compound; yellow oil. lit mp: 52 - 54[iii]; mp 55 - 57.

**$^{1}$H, $^{13}$C, $^{19}$F NMR SPECTRA OF COMPOUNDS 3a – t, 5a, 7a -g**

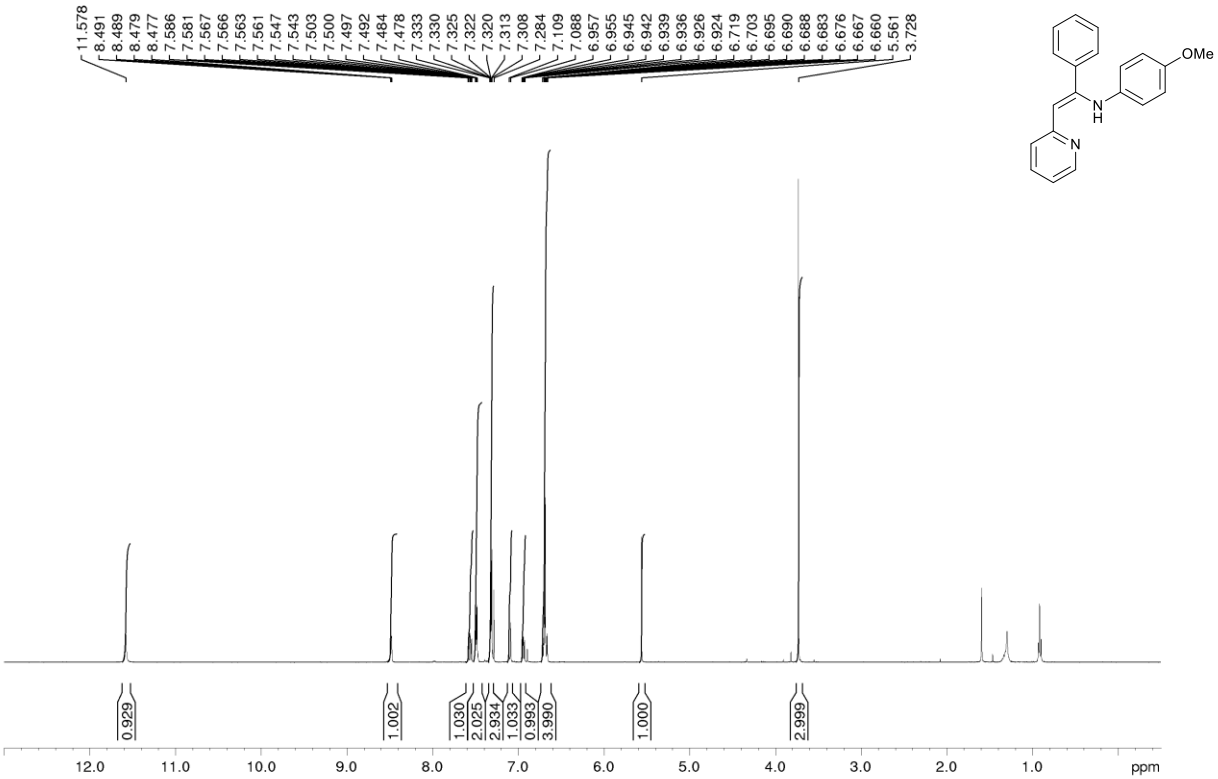
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (**3a**)



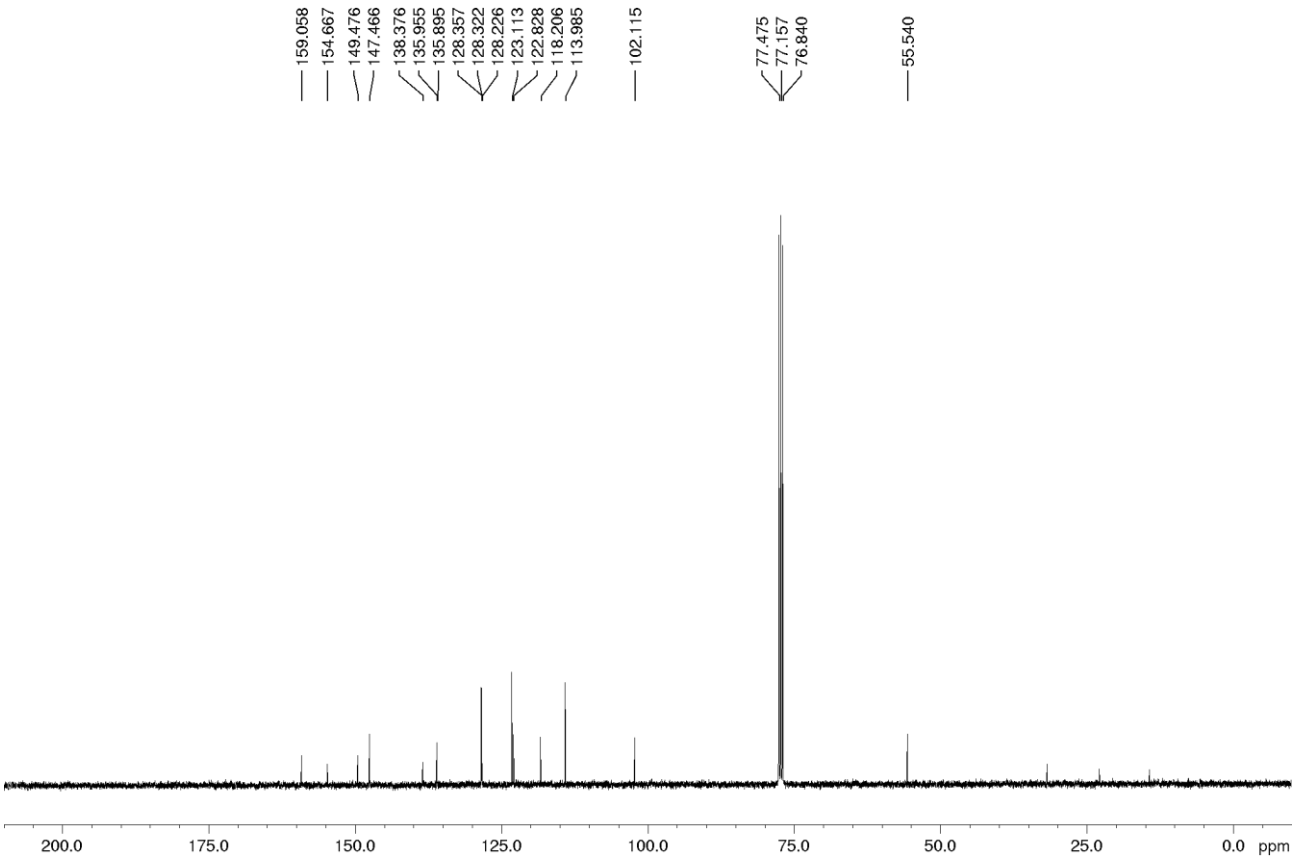

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



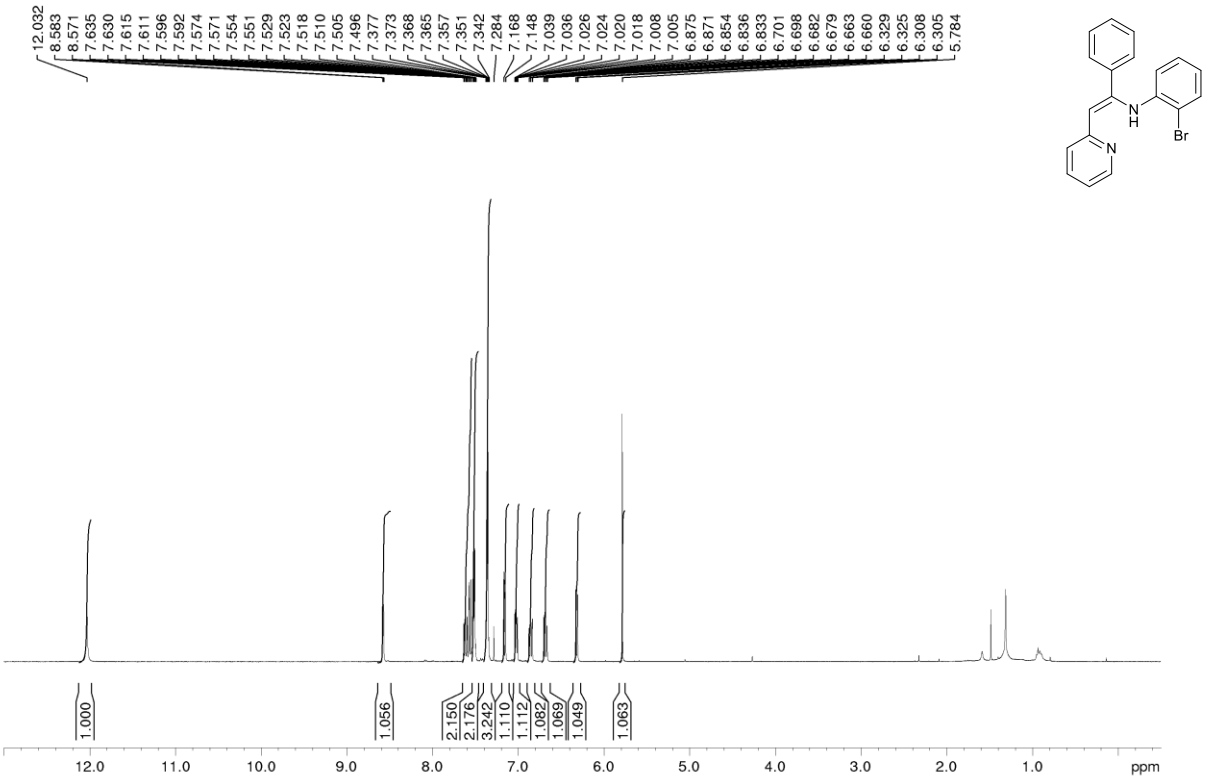
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-4-methoxy-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (**3b**)



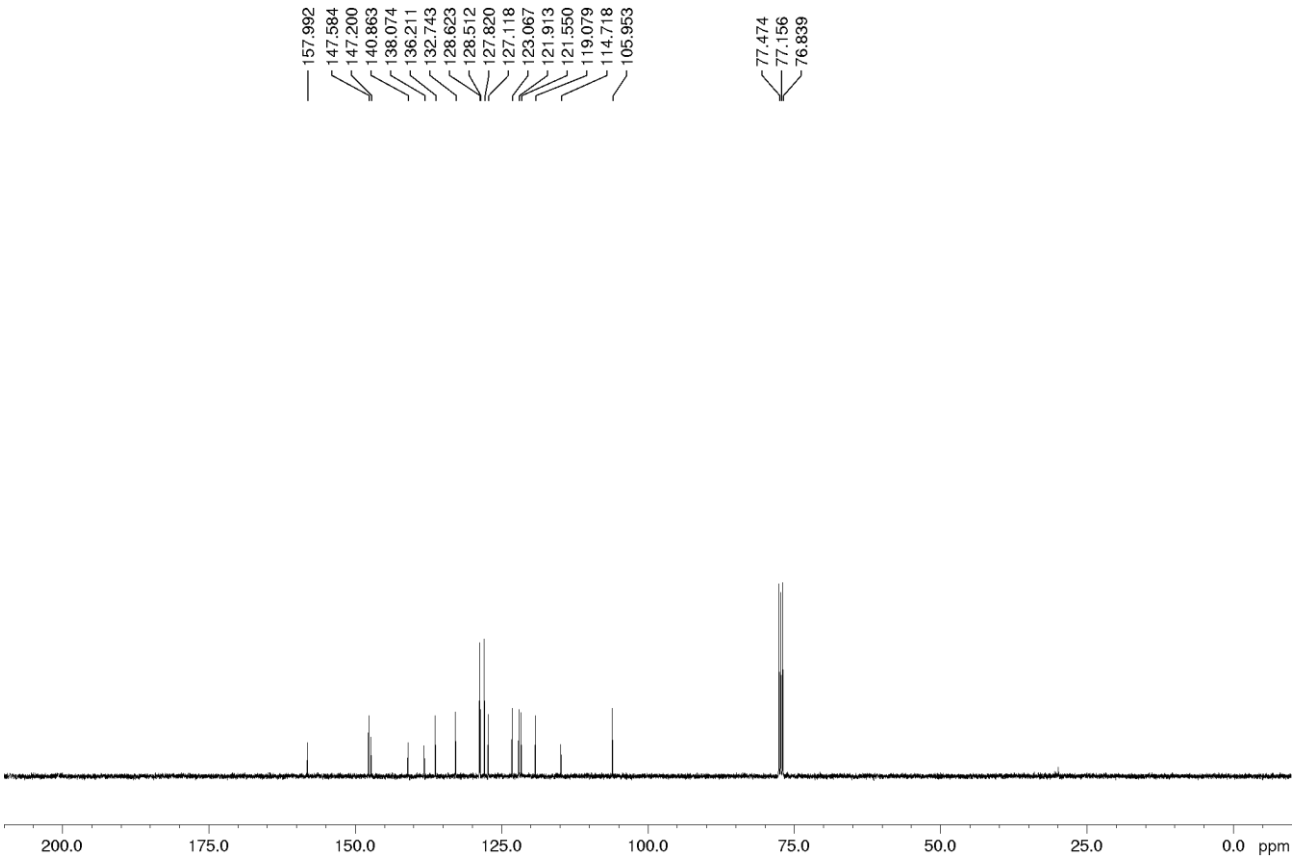

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



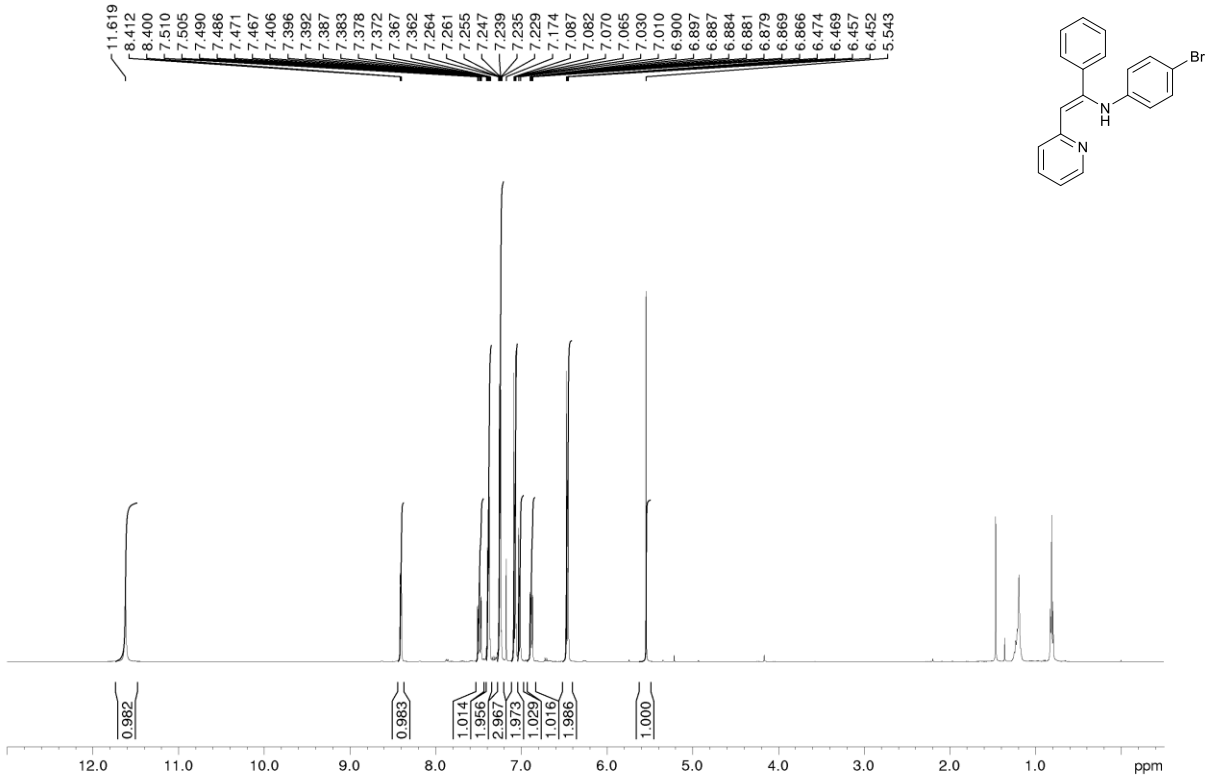
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-2-bromo-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (**3c**)



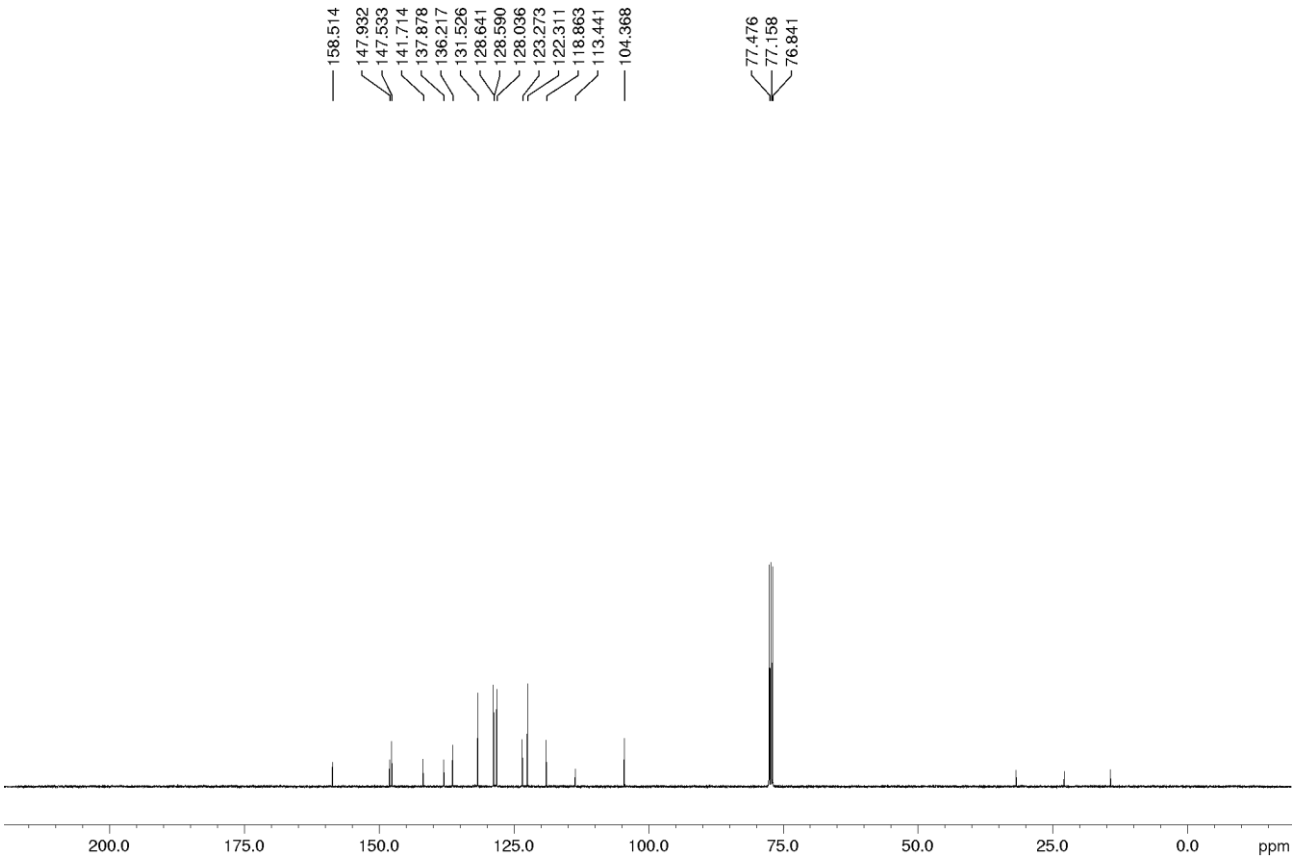

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



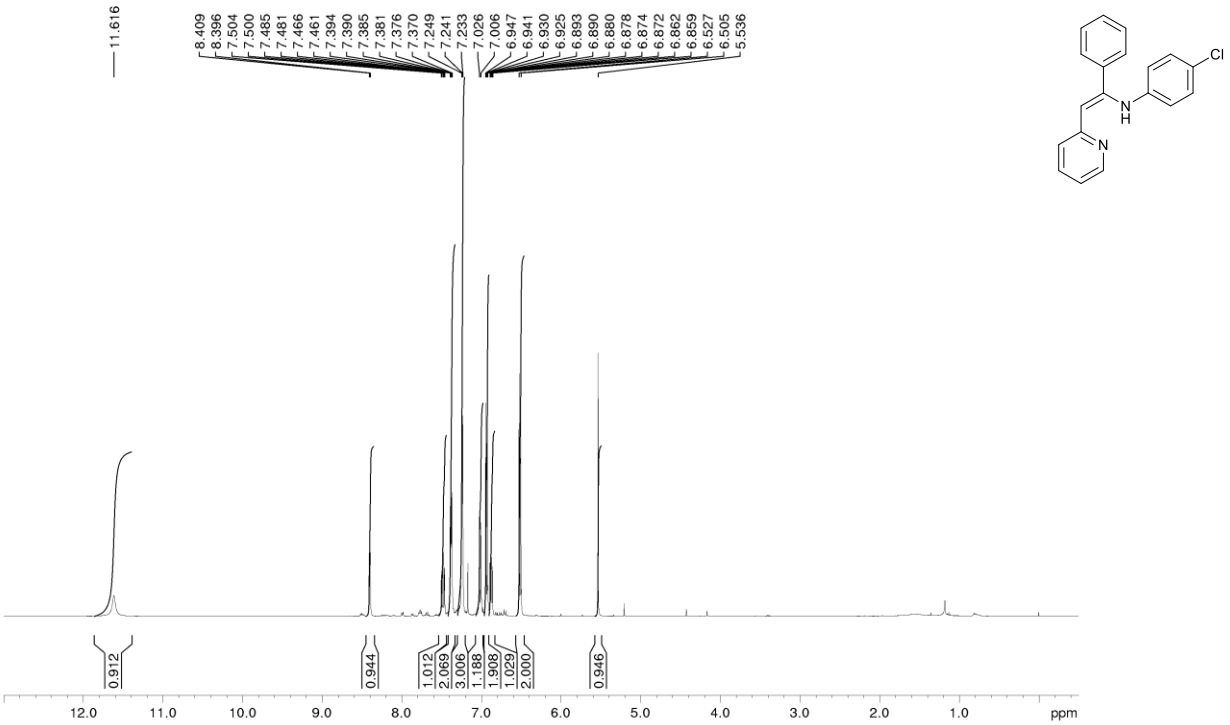
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-4-bromo-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (**3d**)



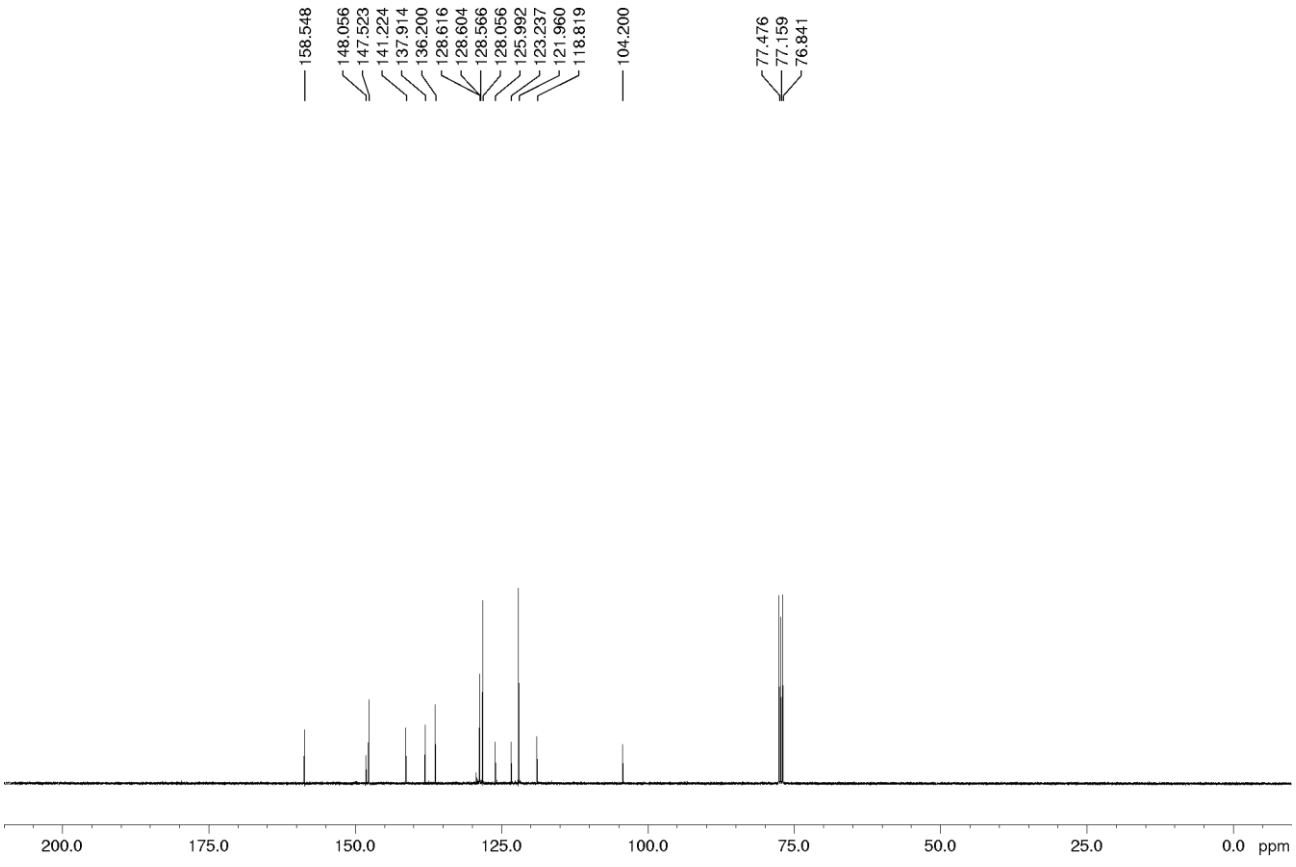

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



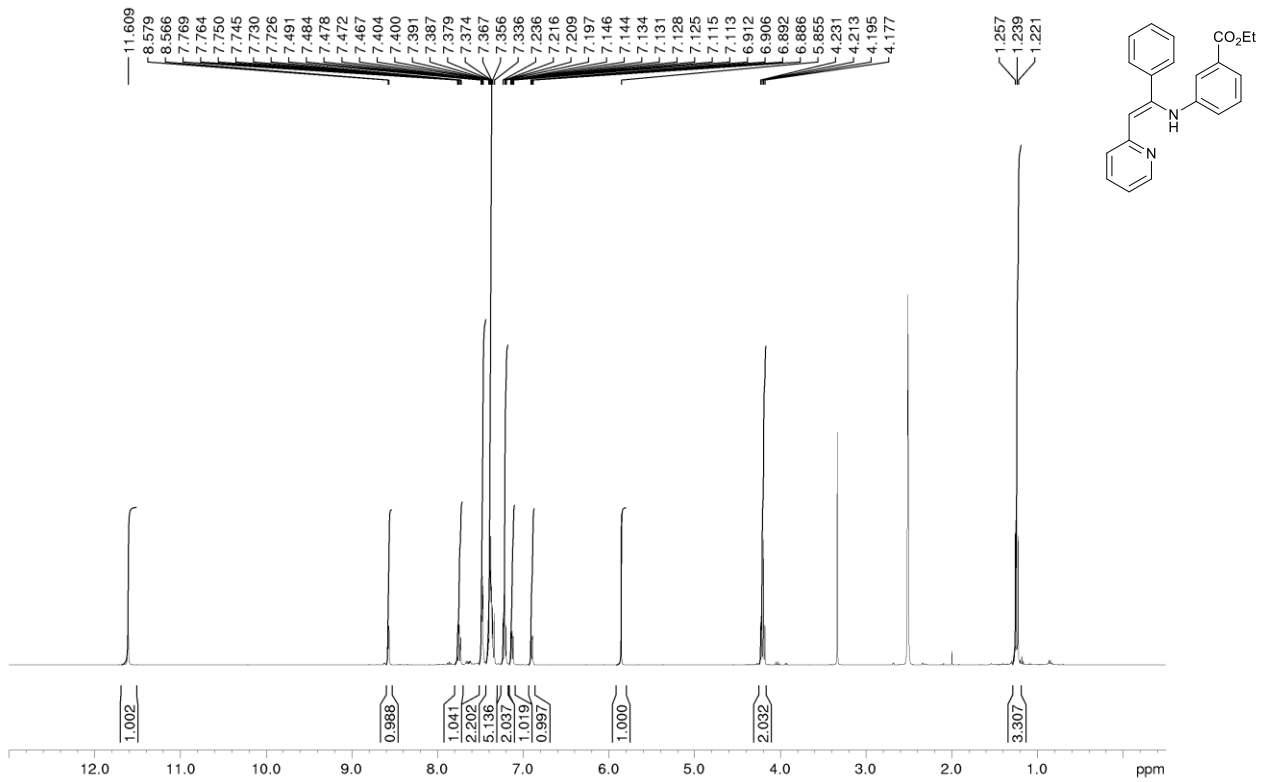
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-4-chloro-*N*-(1-phenyl-2-(pyridin-2-yl)vinyl)aniline (**3e**)



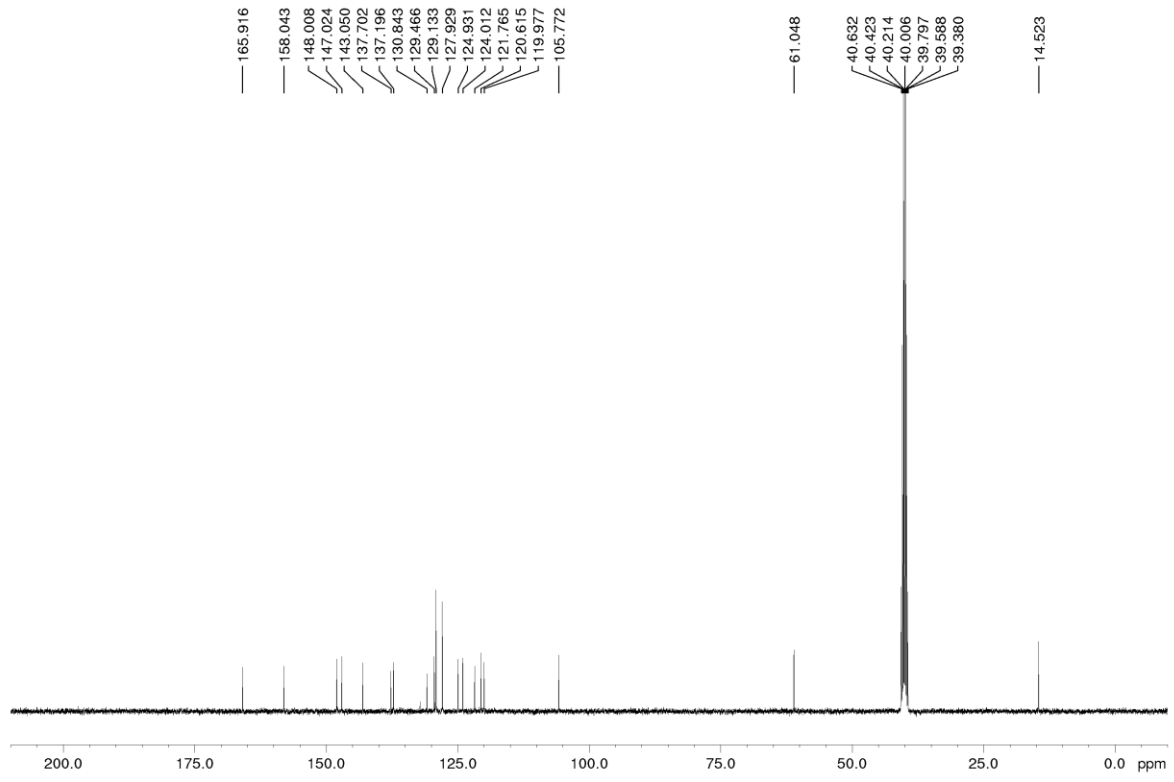

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



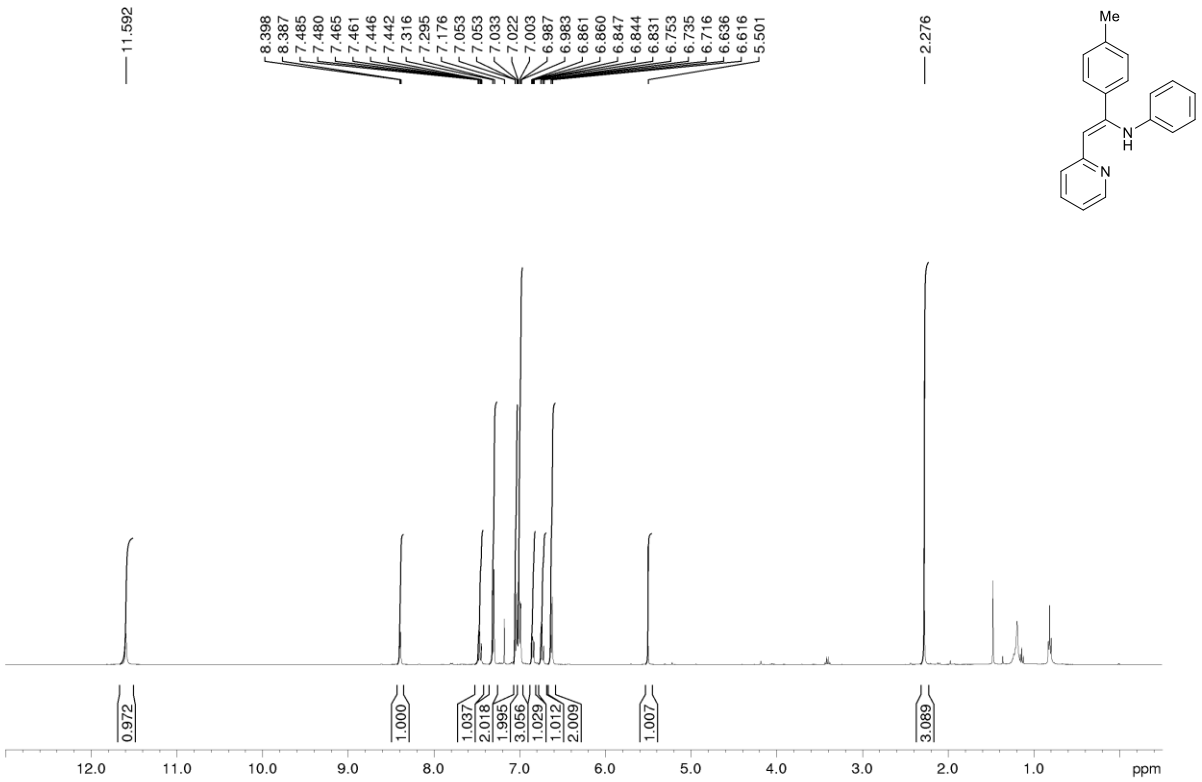
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$:** (*Z*)-ethyl 3-(1-phenyl-2-(pyridin-2-yl)vinylamino)benzoate (**3f**)



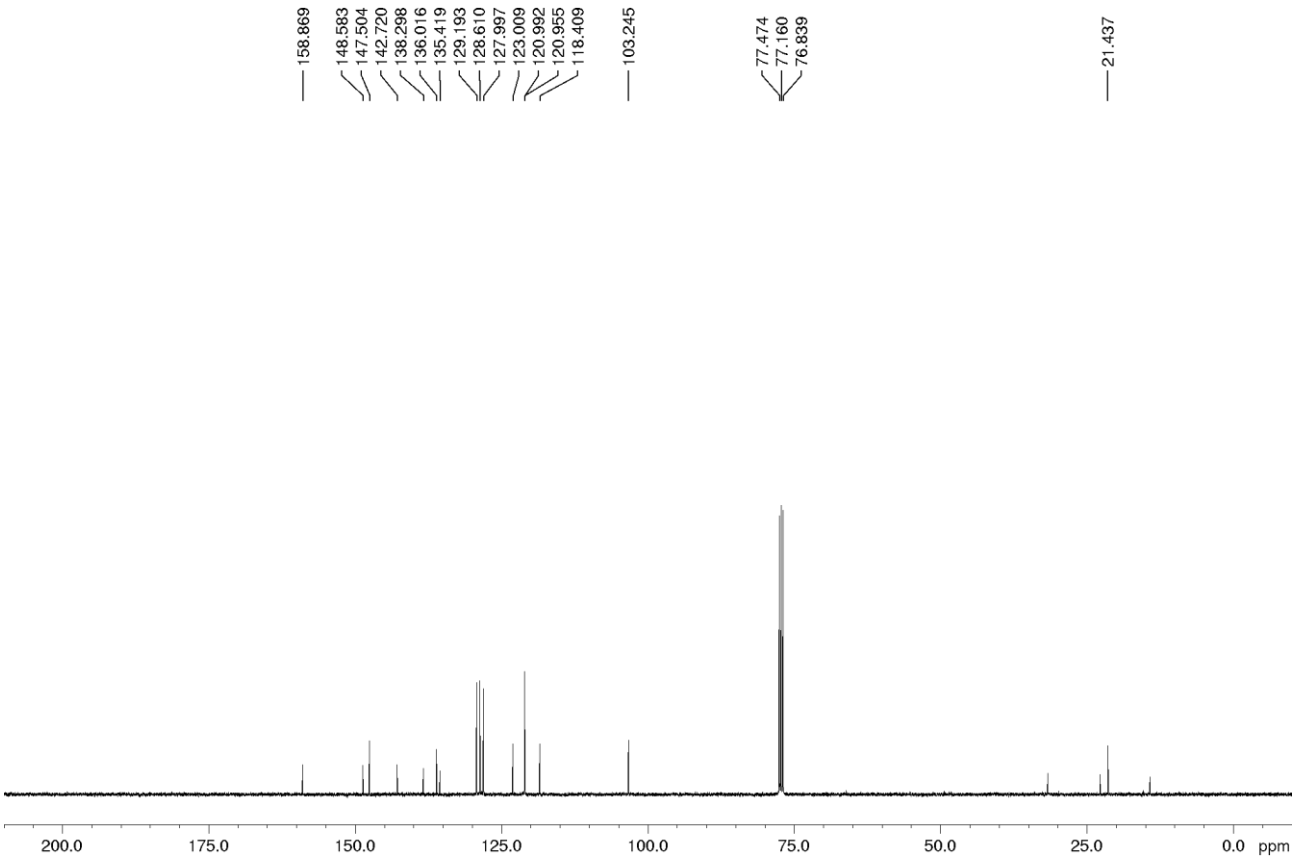

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



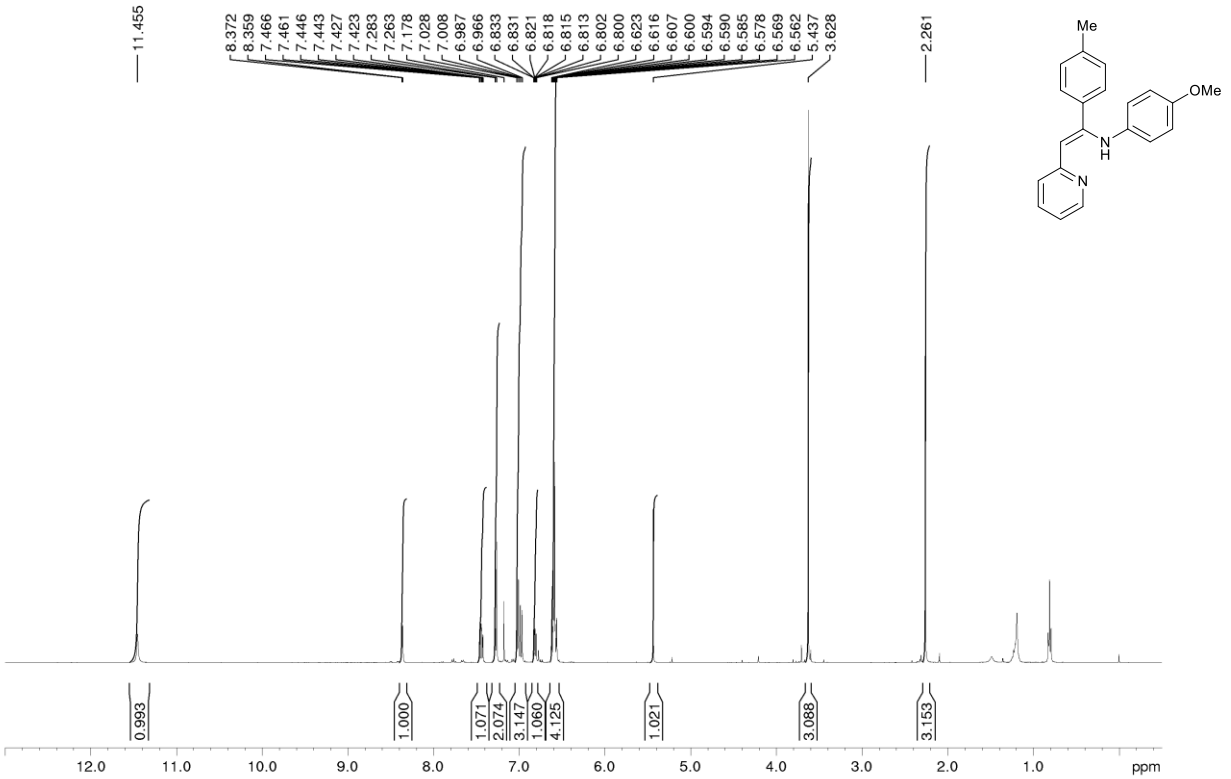
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-*N*-(2-(pyridin-2-yl)-1-*p*-tolylvinyl)aniline (**3g**)



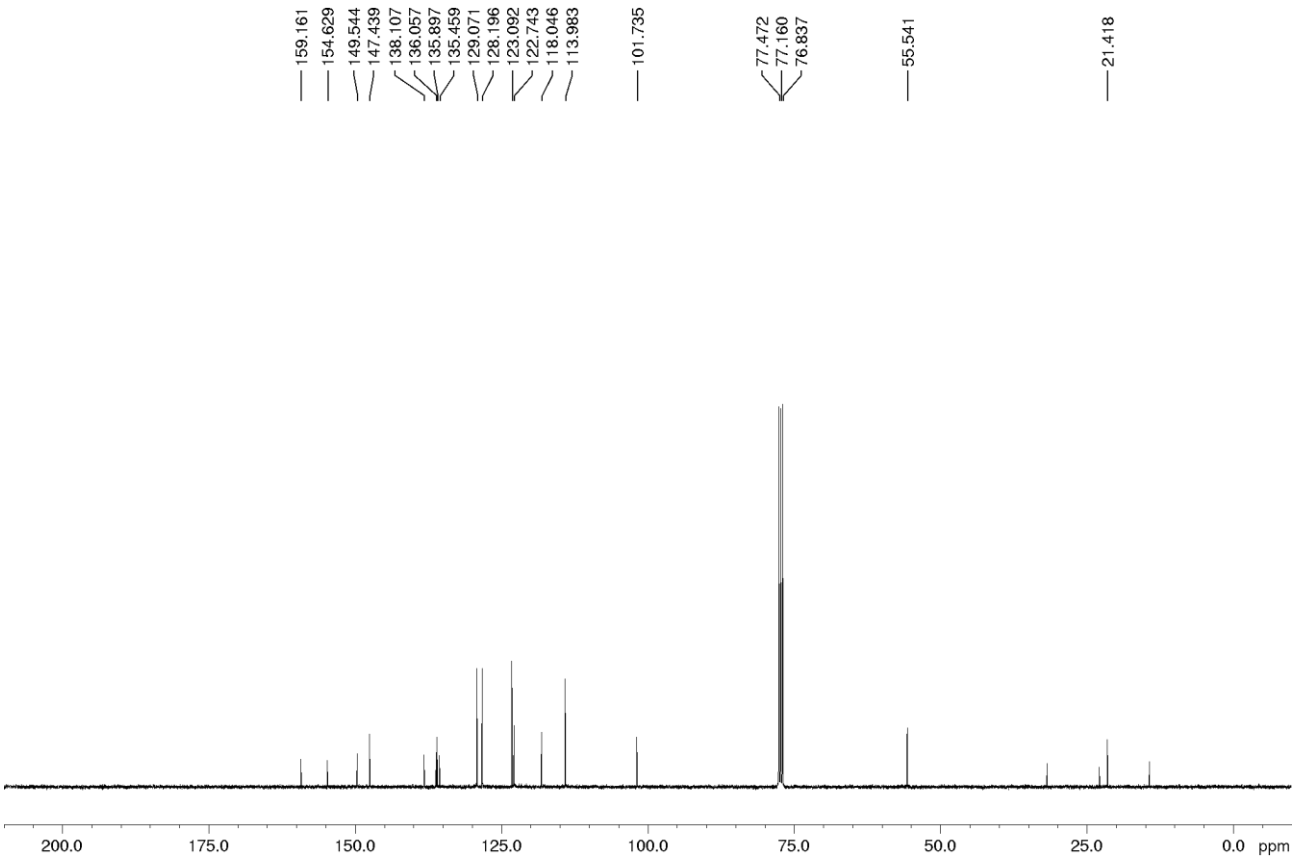

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



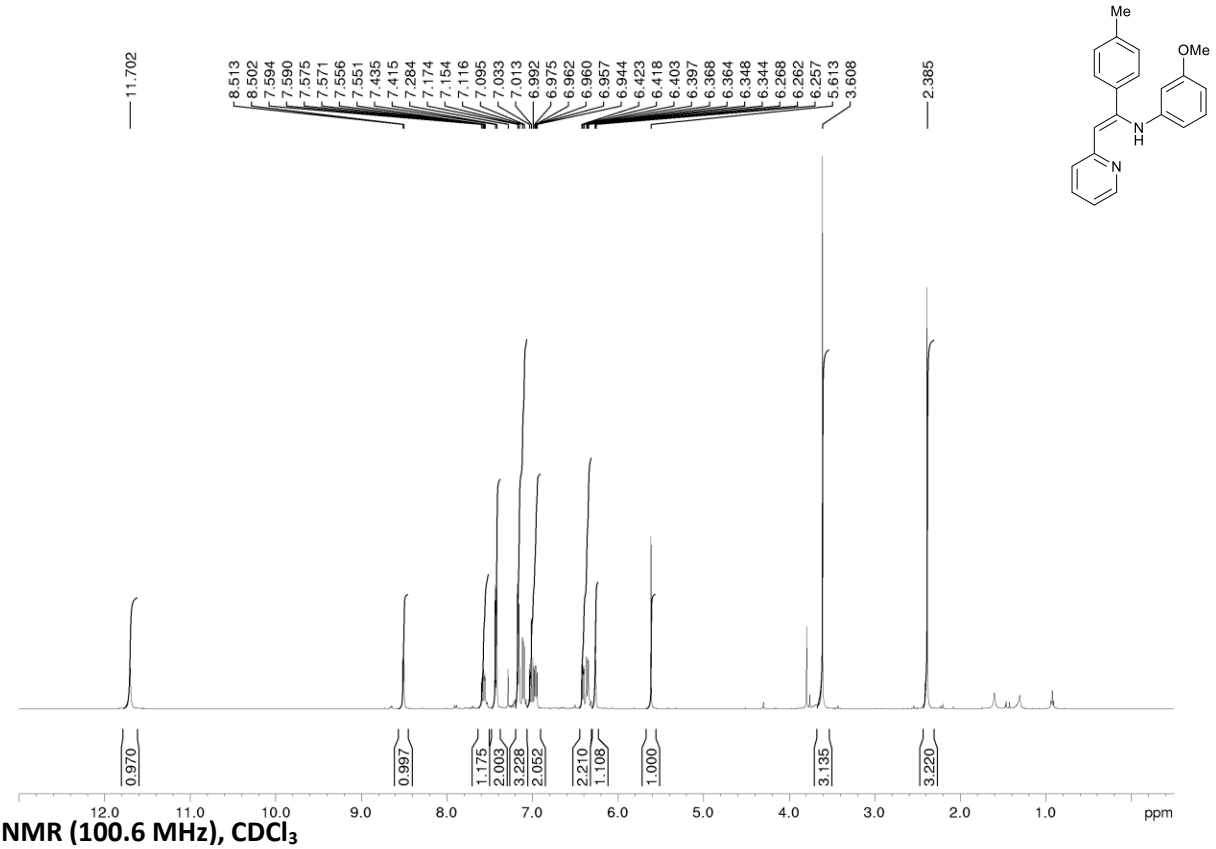
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-4-methoxy-*N*-(2-(pyridin-2-yl)-1-*p*-tolylvinyl)aniline (**3h**)




**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



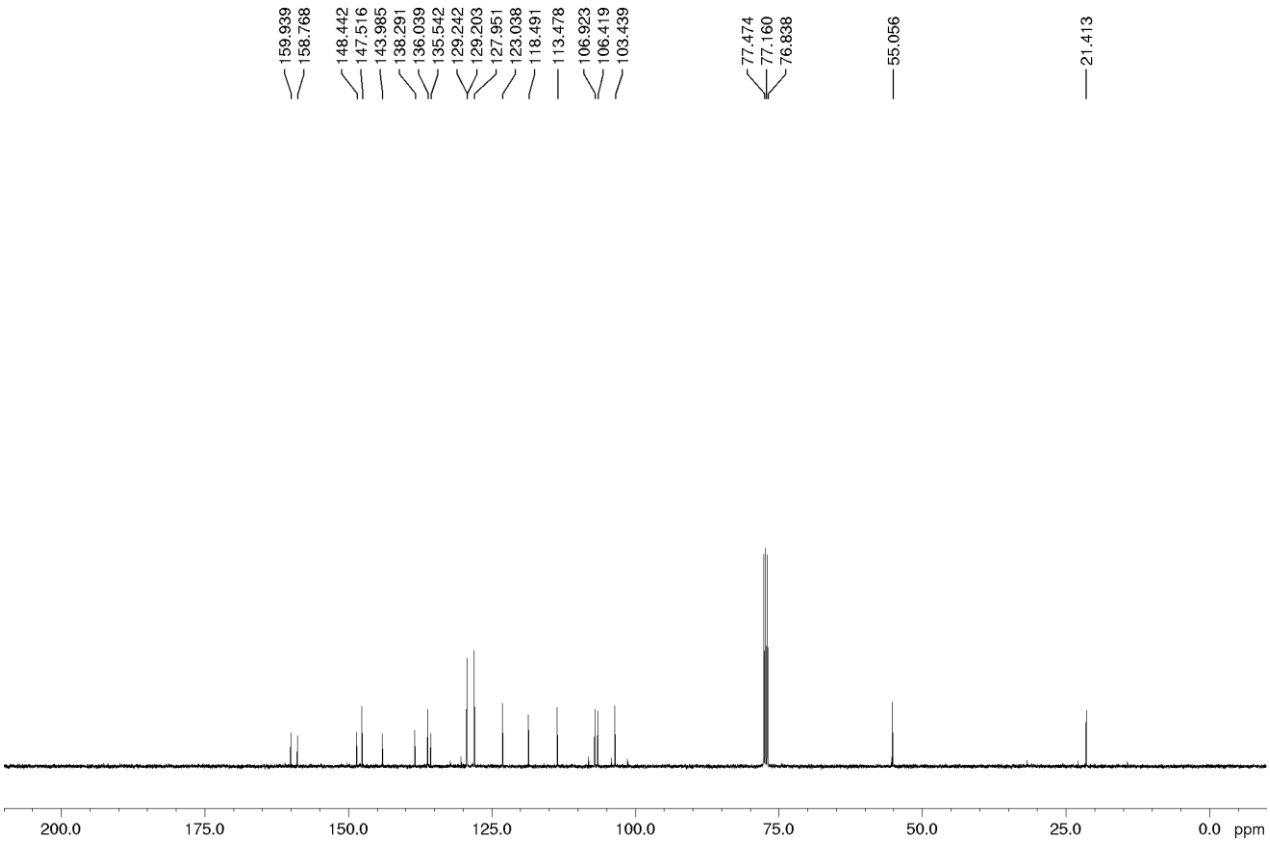
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-3-methoxy-*N*-(2-(pyridin-2-yl)-1-*p*-tolylvinyl)aniline (**3i**)



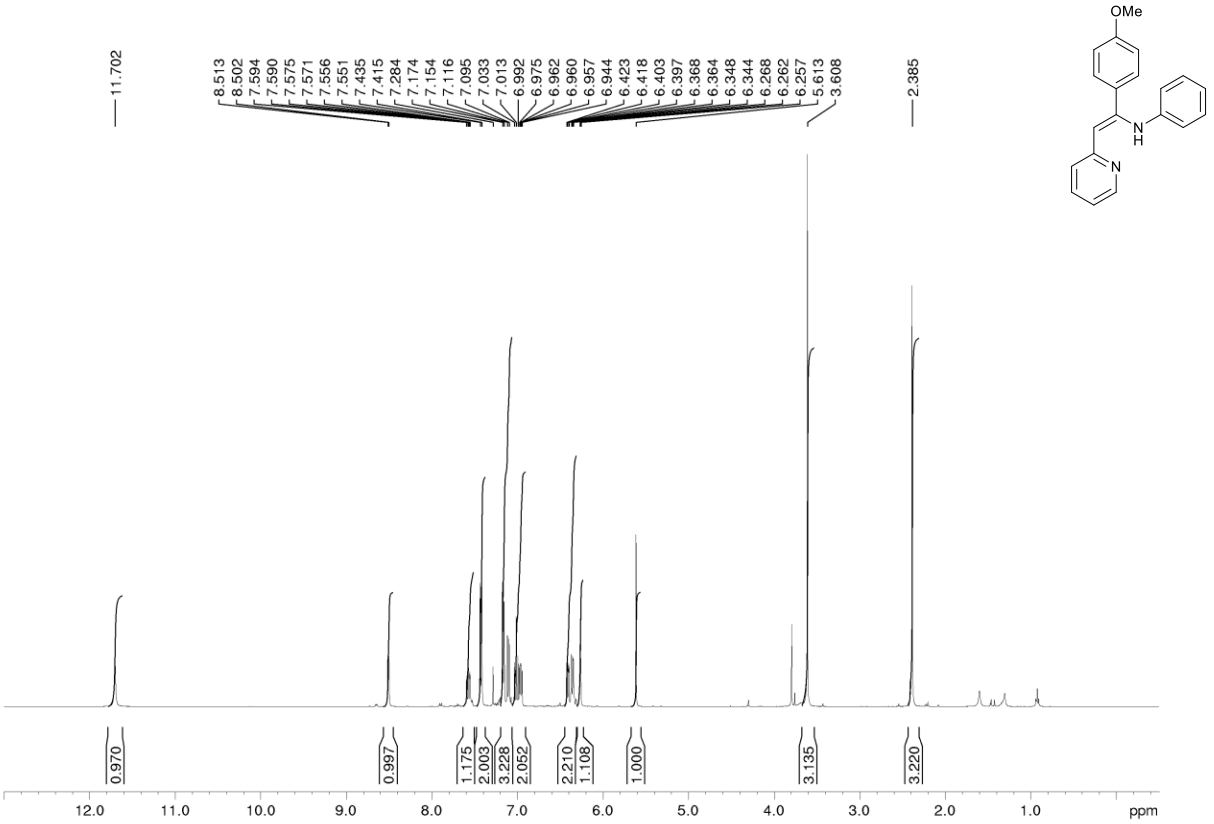




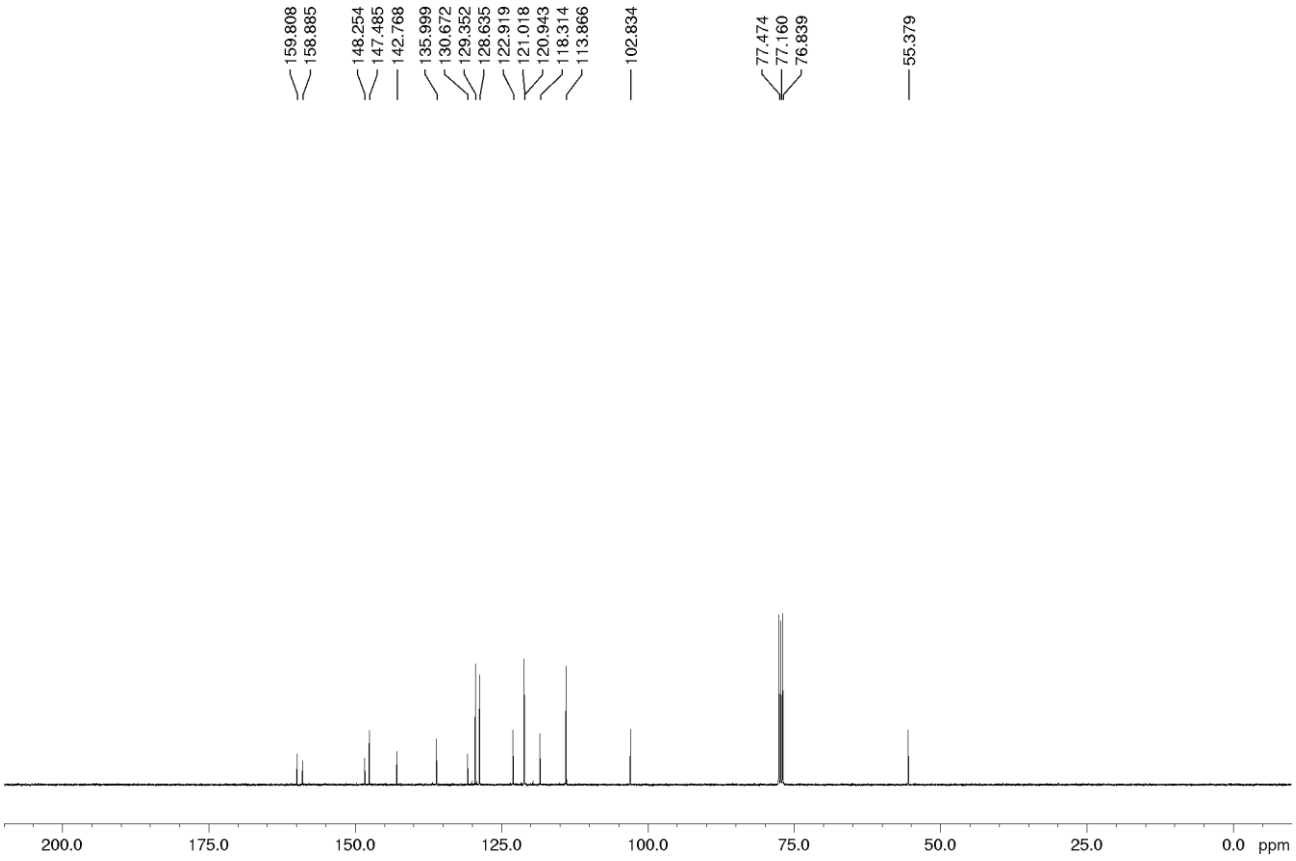
**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



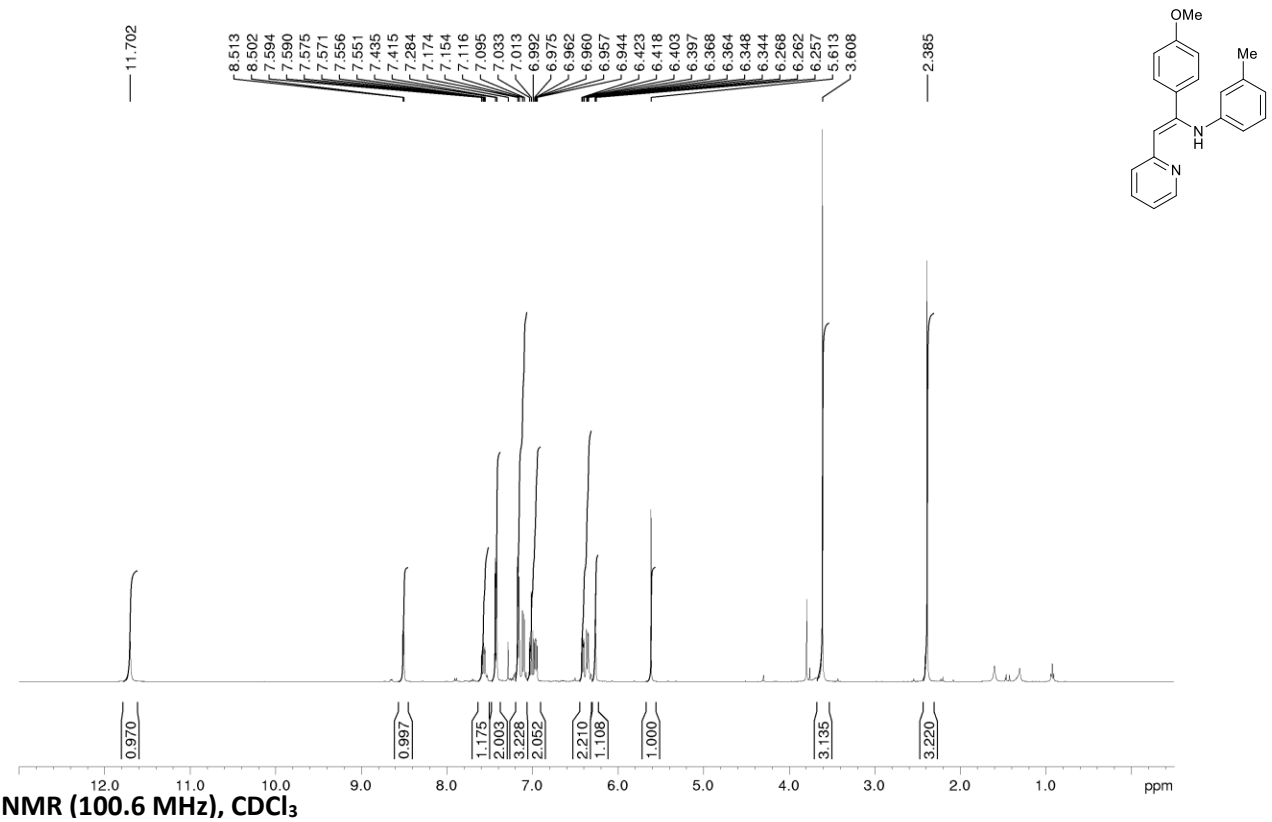
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-*N*-(1-(4-methoxyphenyl)-2-(pyridin-2-yl)vinyl)aniline (**3j**)



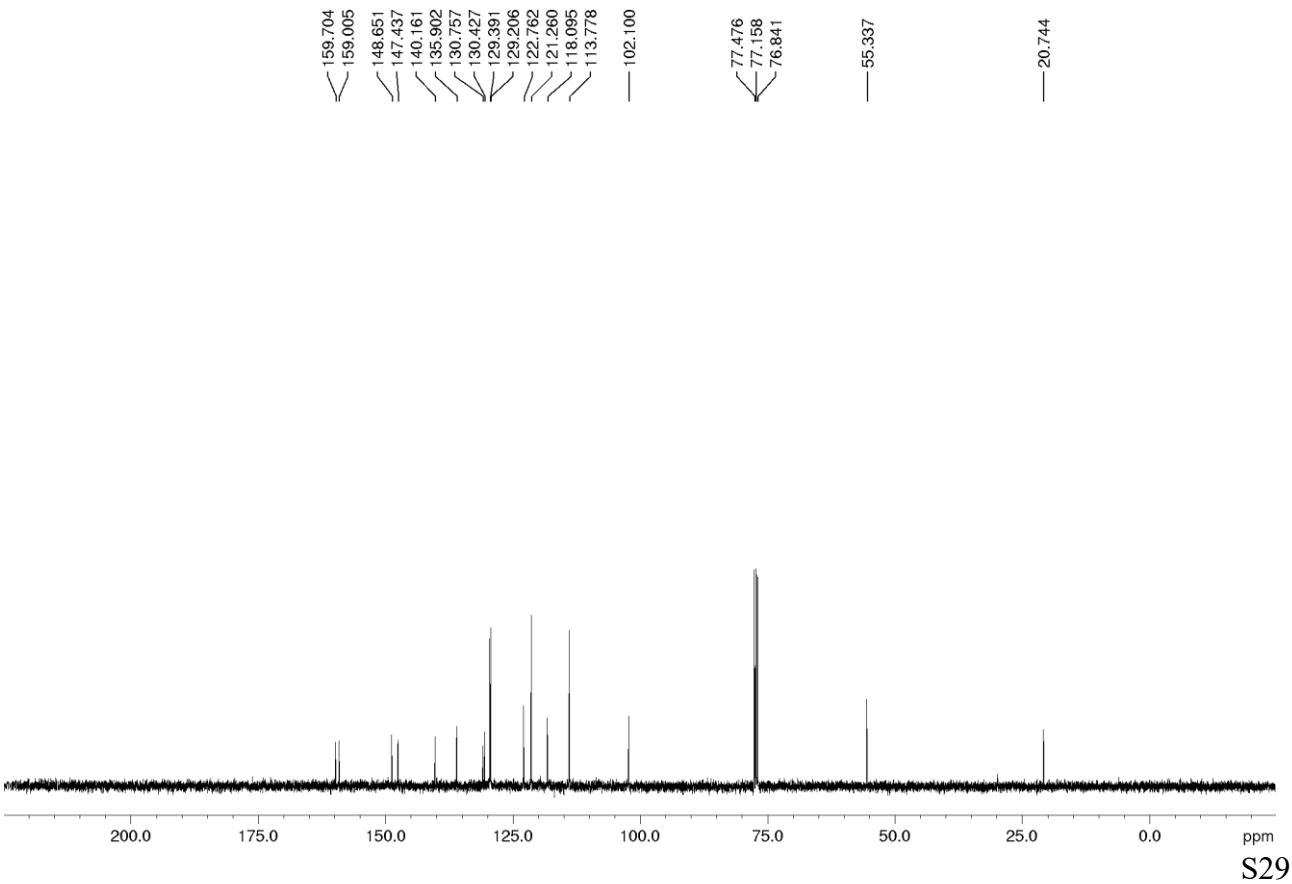

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



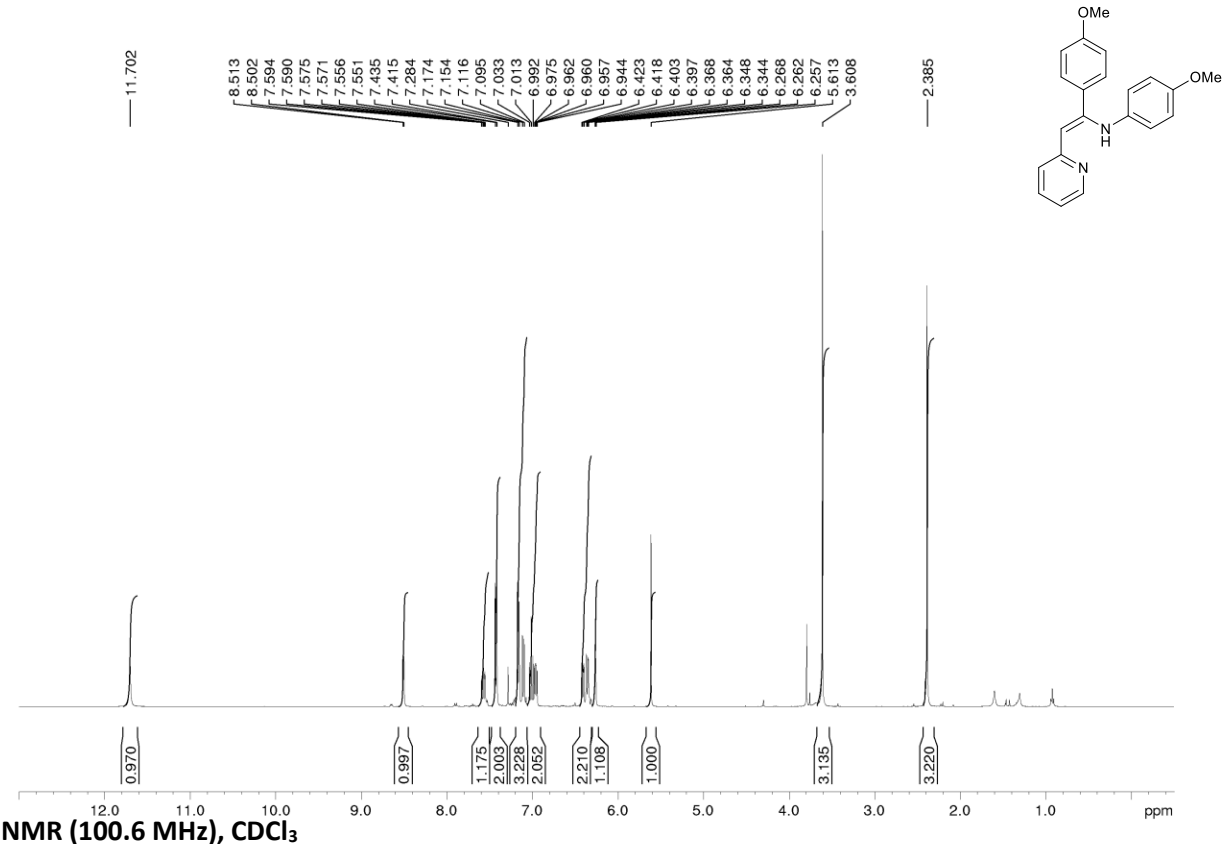
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-*N*-(1-(4-methoxyphenyl)-2-(pyridin-2-yl)vinyl)-3-methylaniline (**3k**)



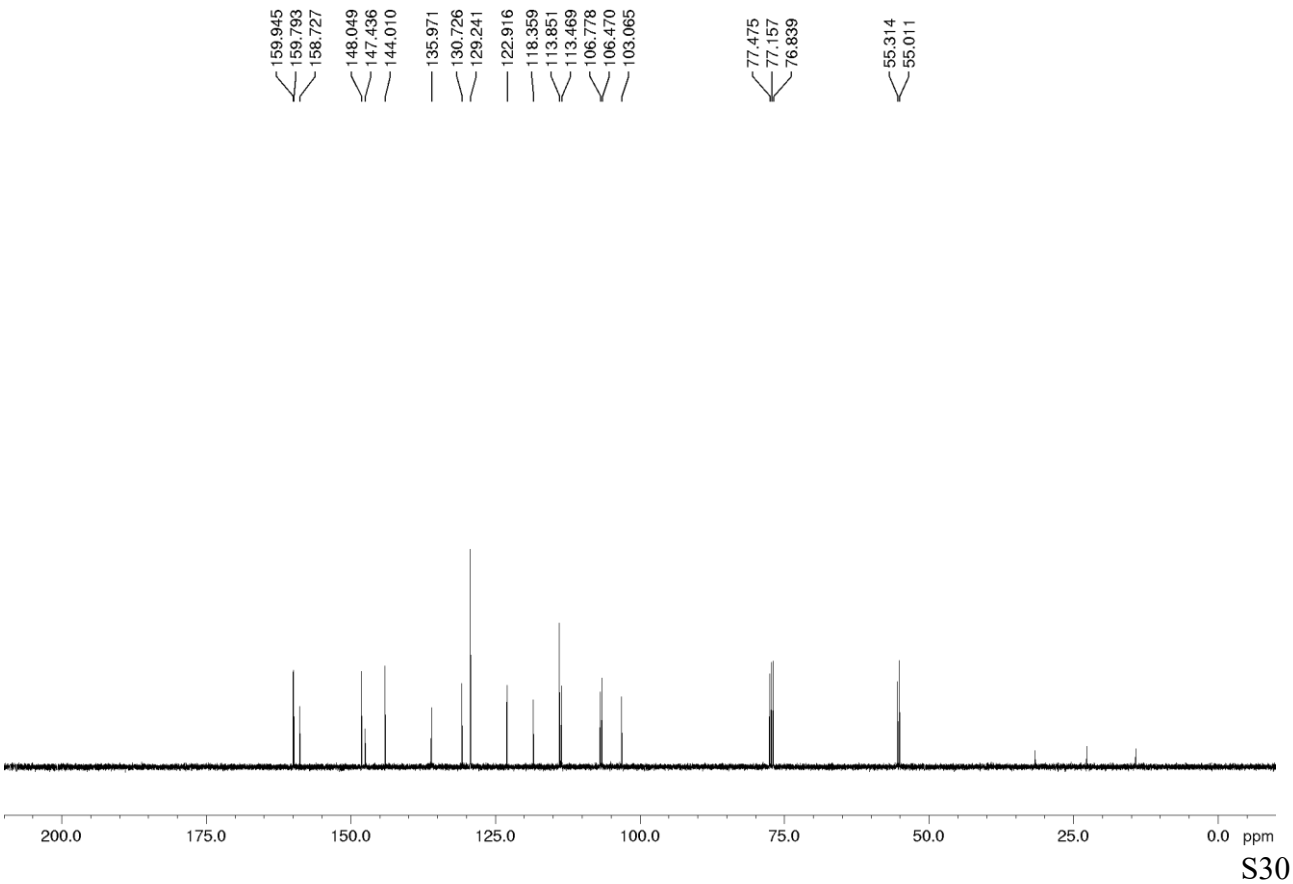

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



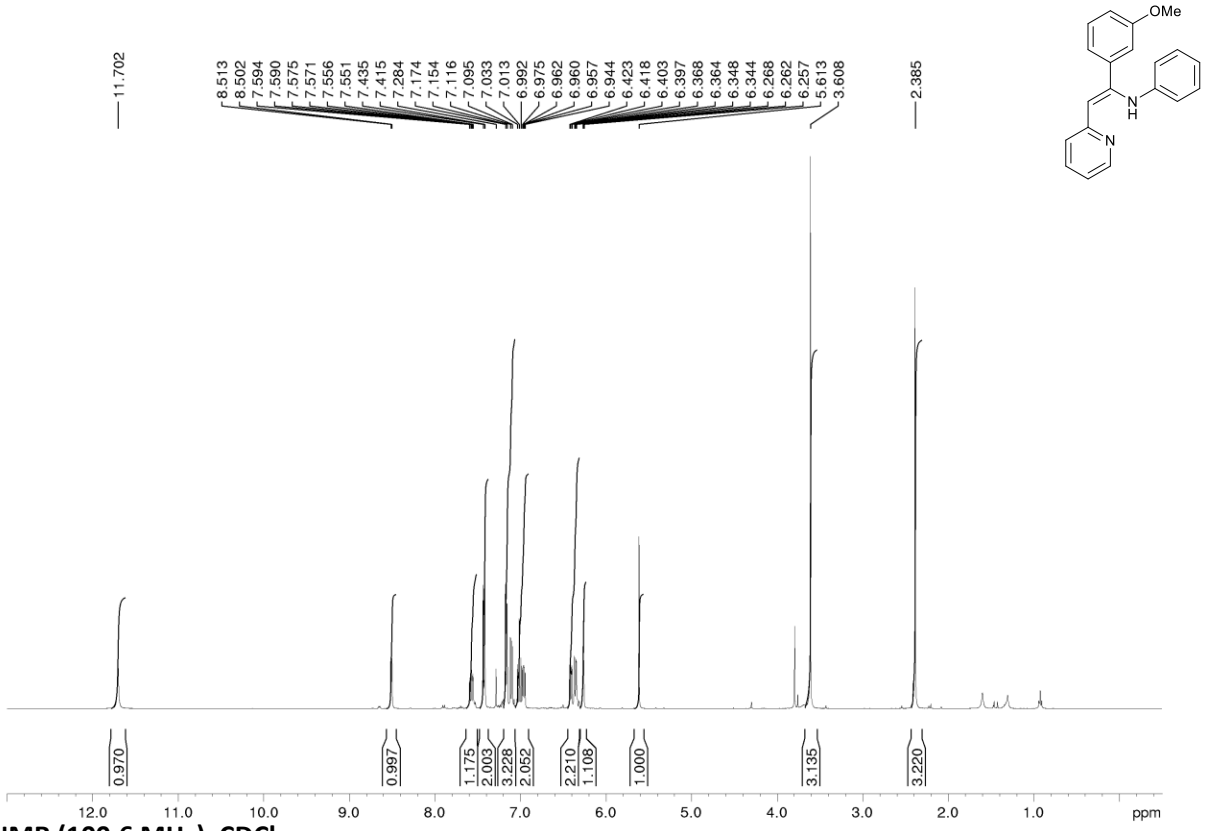
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-4-methoxy-N-(1-(4-methoxyphenyl)-2-(pyridin-2-yl)vinyl)aniline (**3l**)



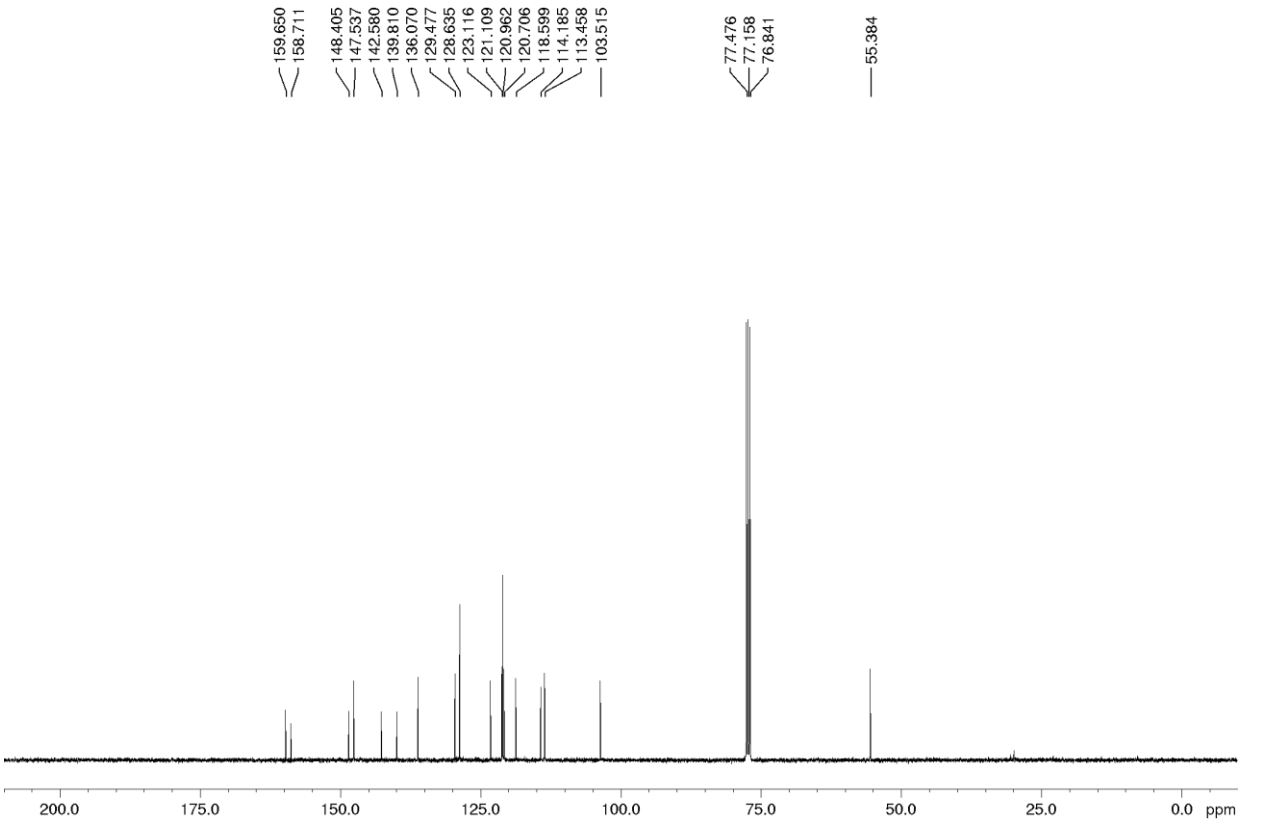

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



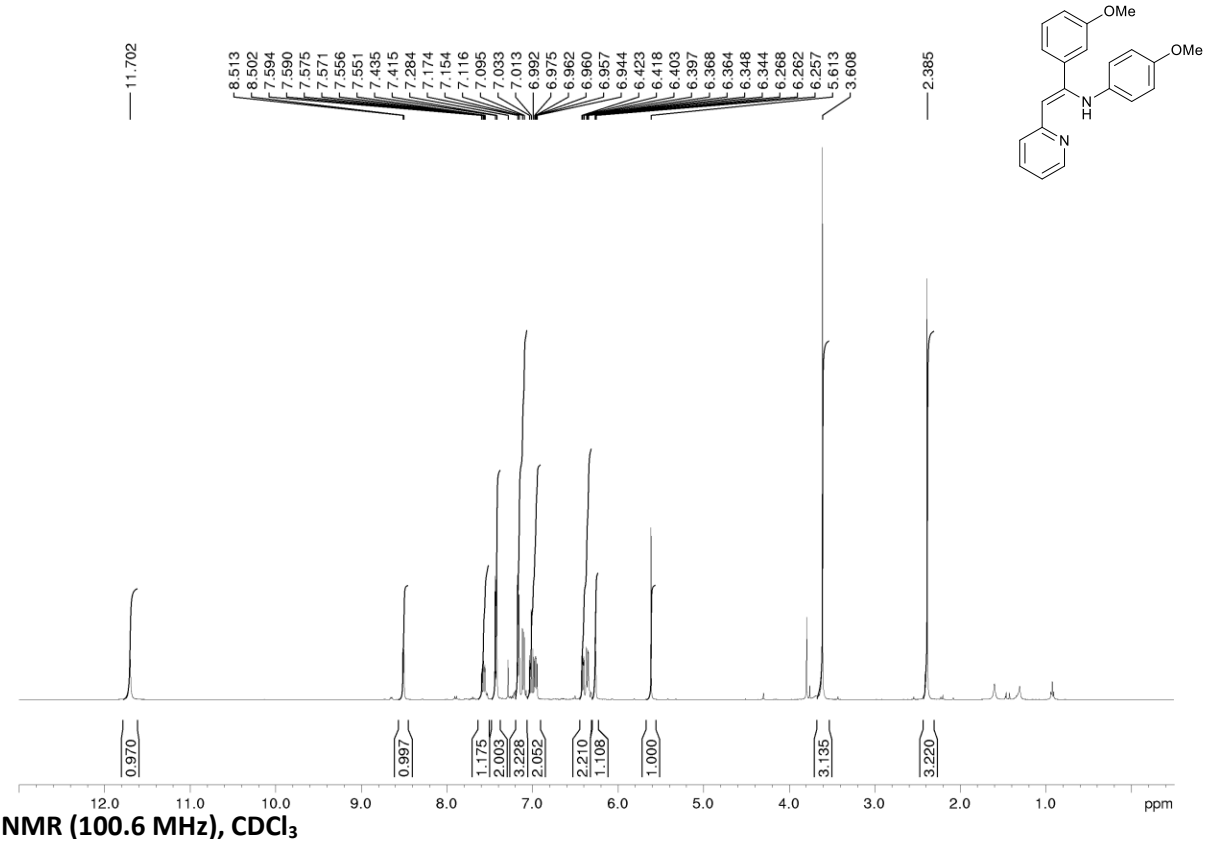
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-*N*-(1-(3-methoxyphenyl)-2-(pyridin-2-yl)vinyl)aniline (**3m**)



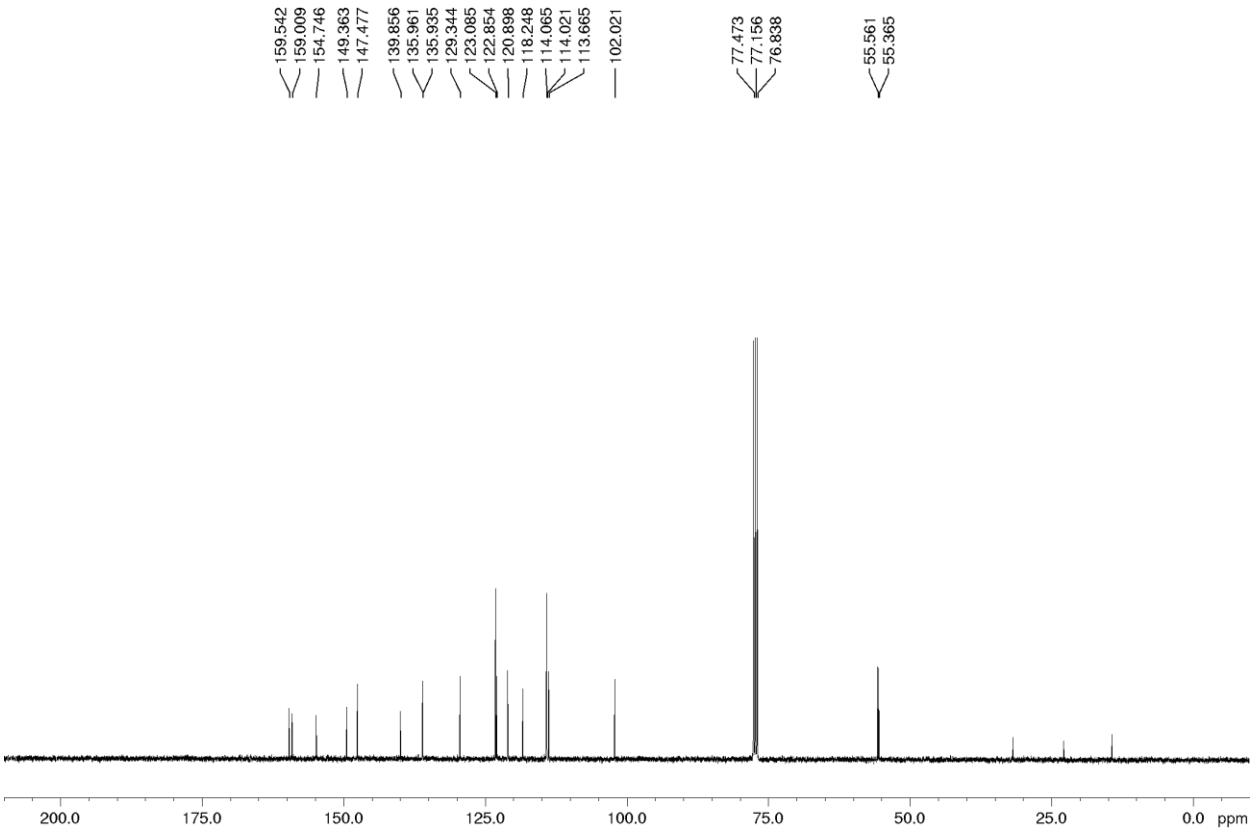

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



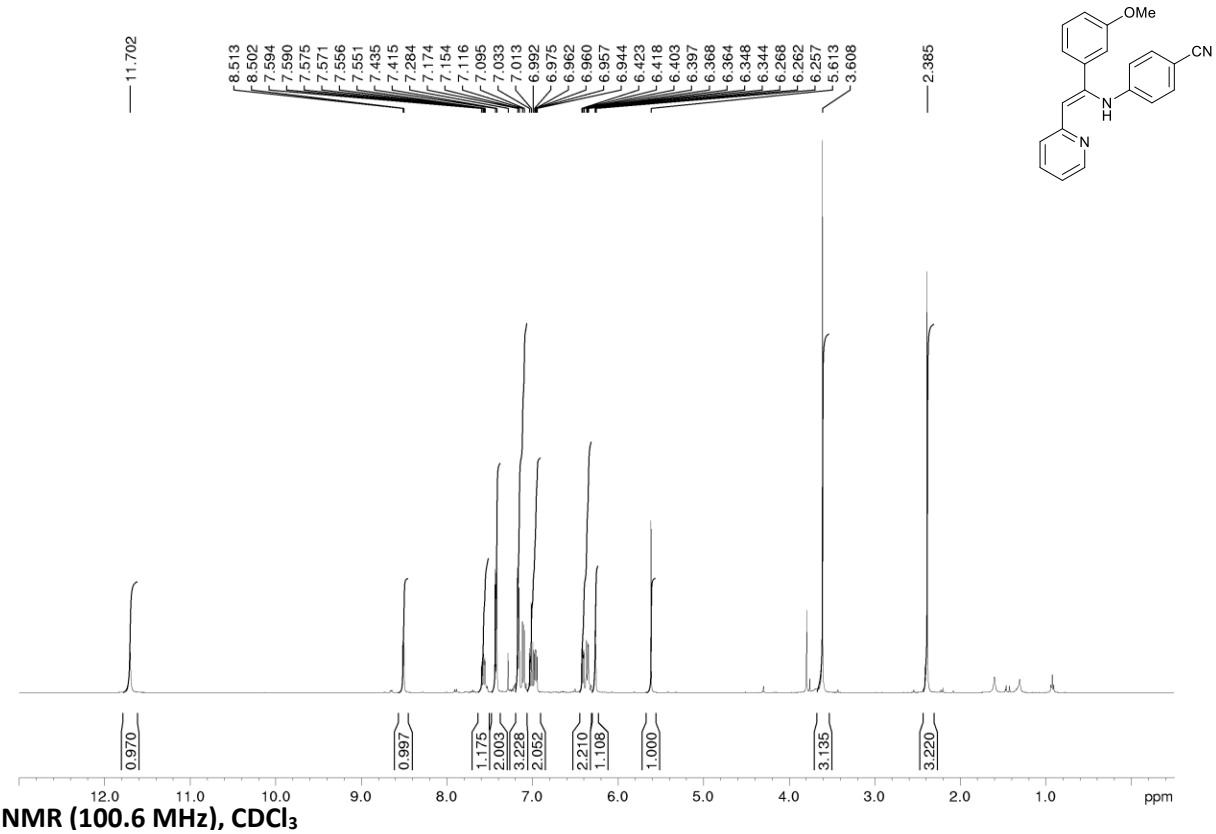
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-4-methoxy-*N*-(1-(3-methoxyphenyl)-2-(pyridin-2-yl)vinyl)aniline (**3n**)



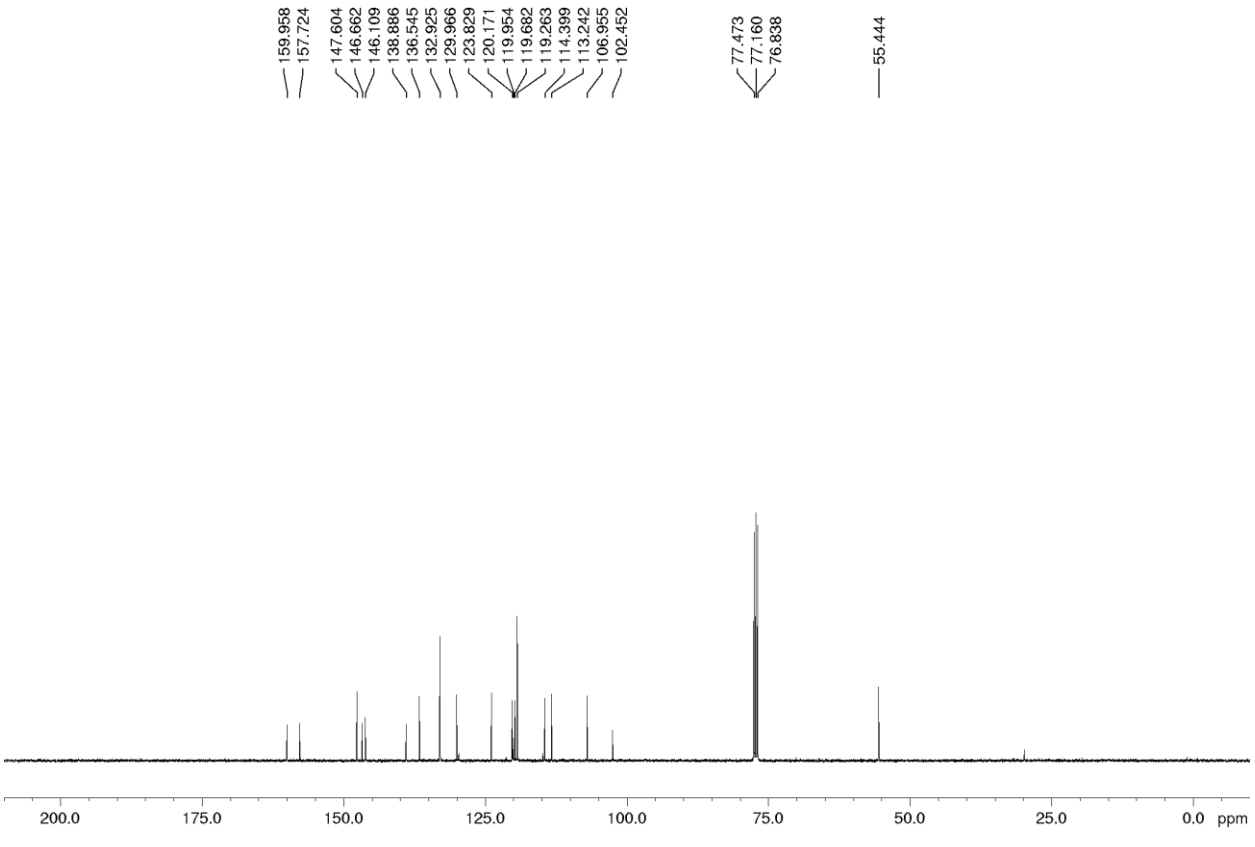

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



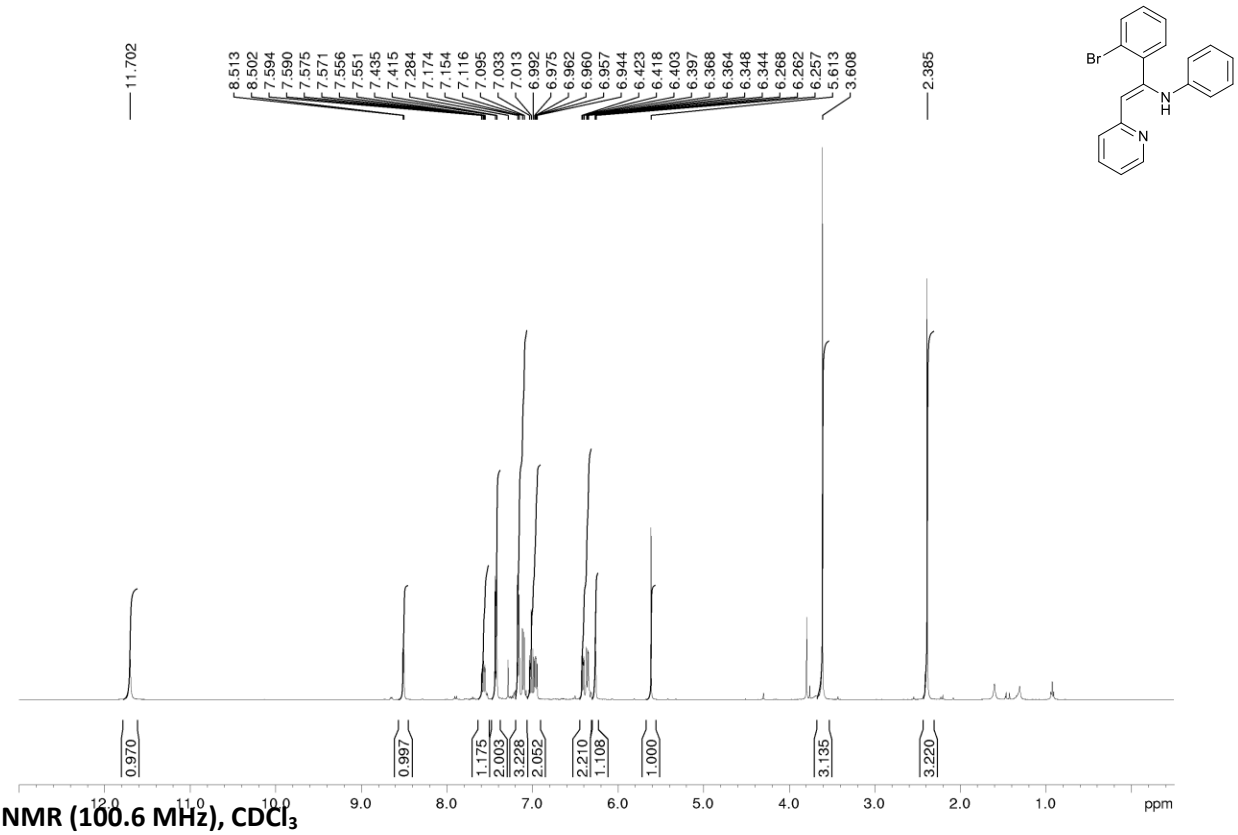
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-4-(1-(3-methoxyphenyl)-2-(pyridin-2-yl)vinylamino)benzonitrile (**3o**)



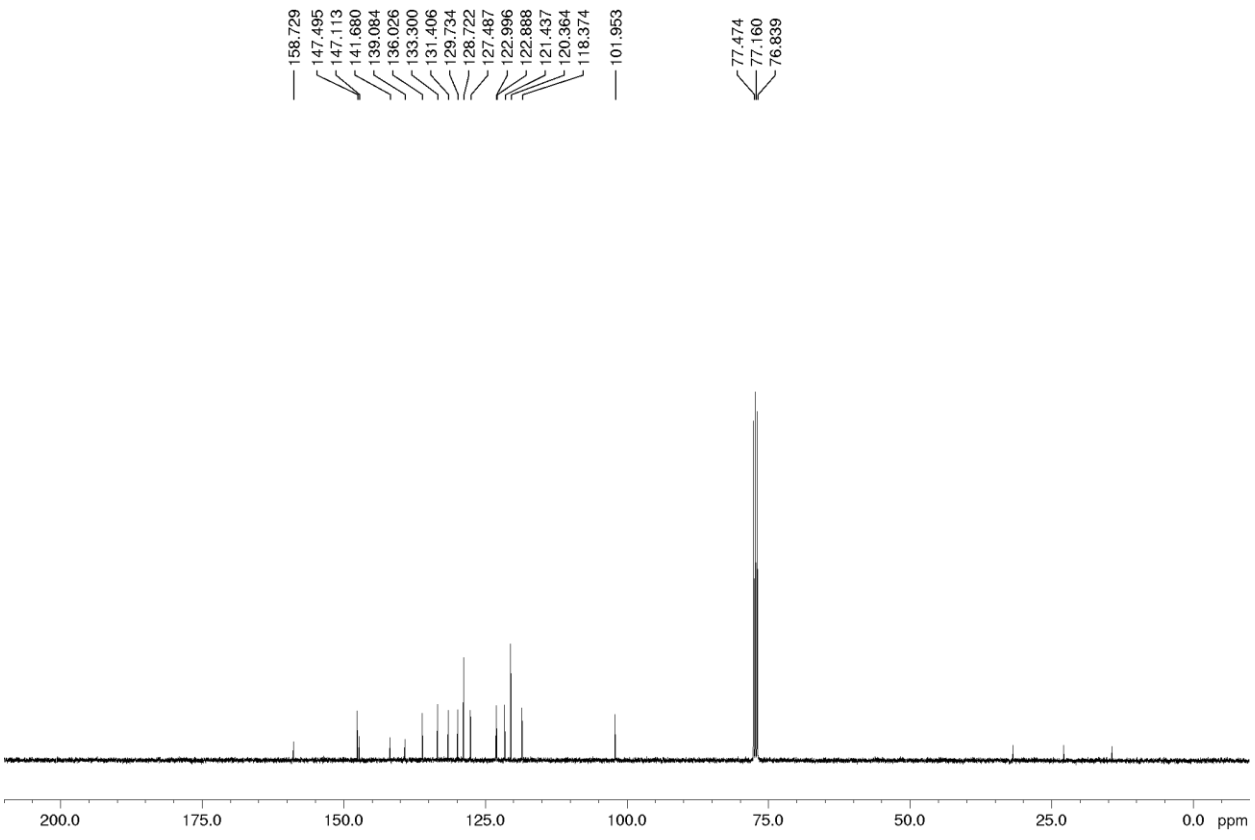

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



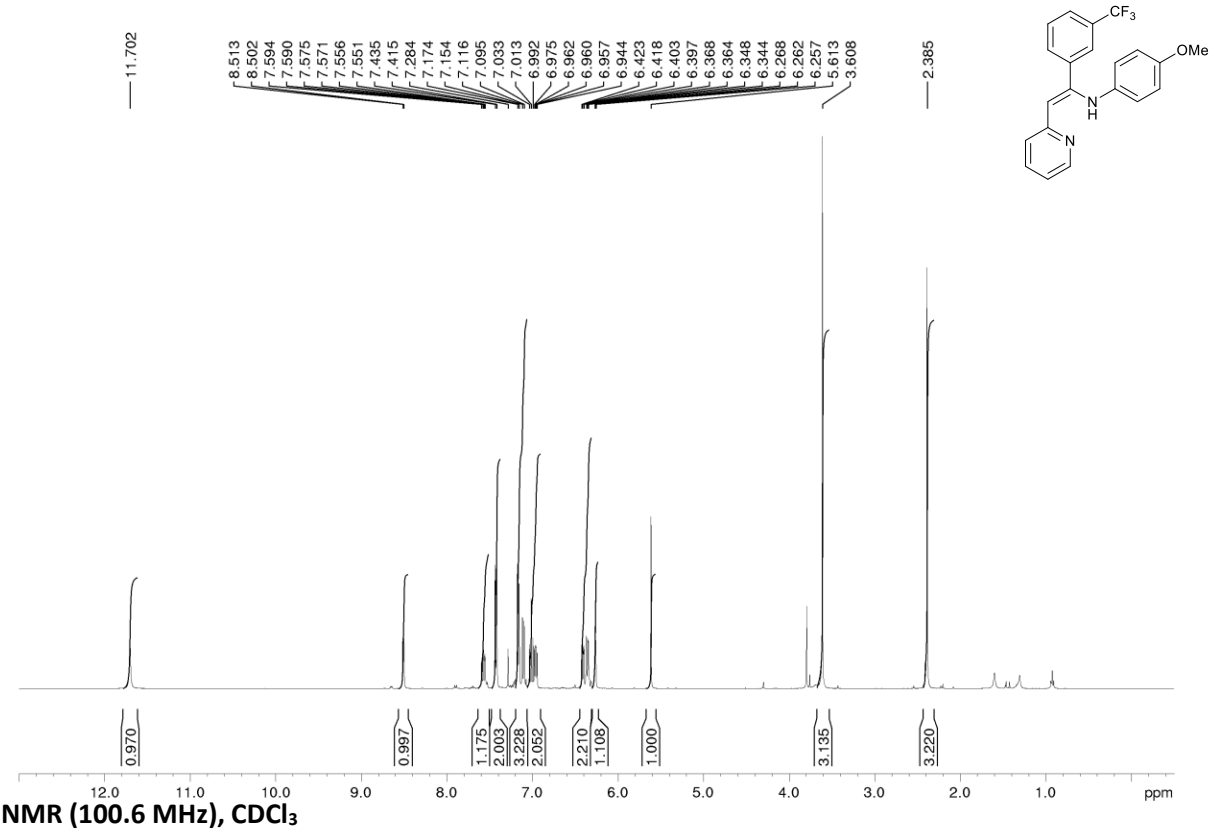
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-*N*-(1-(2-bromophenyl)-2-(pyridin-2-yl)vinyl)aniline (**3p**)



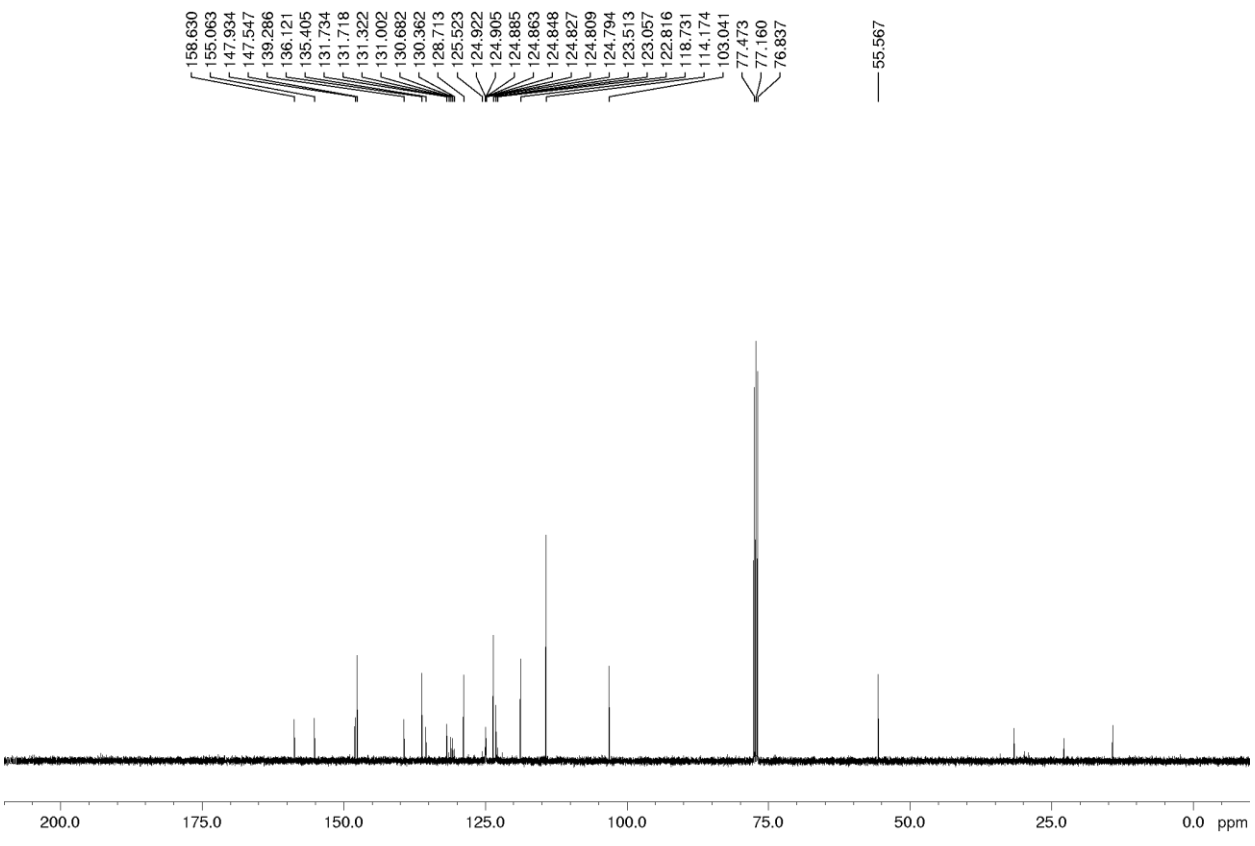

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



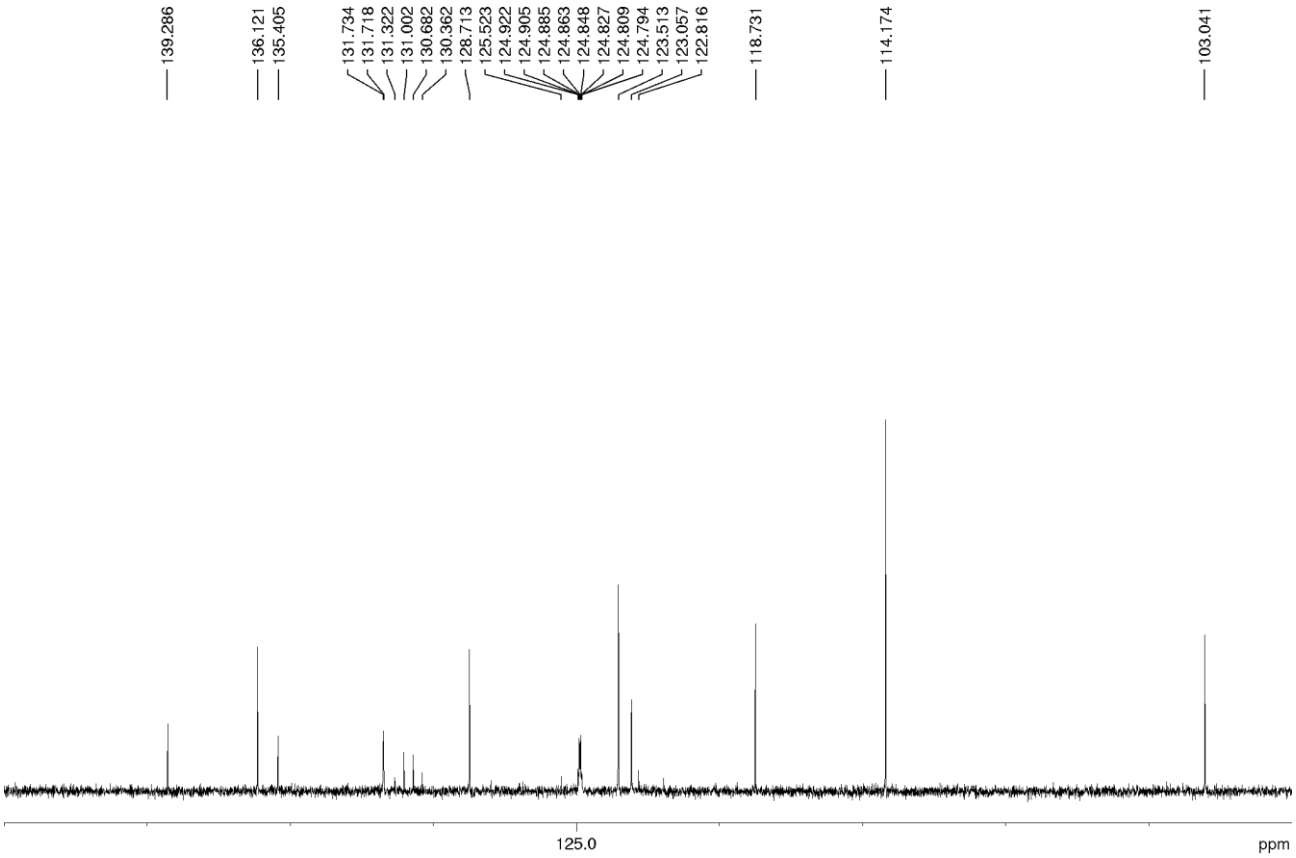
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-4-methoxy-*N*-(2-(pyridin-2-yl)-1-(3-(trifluoromethyl)phenyl)vinyl)aniline (**3q**)



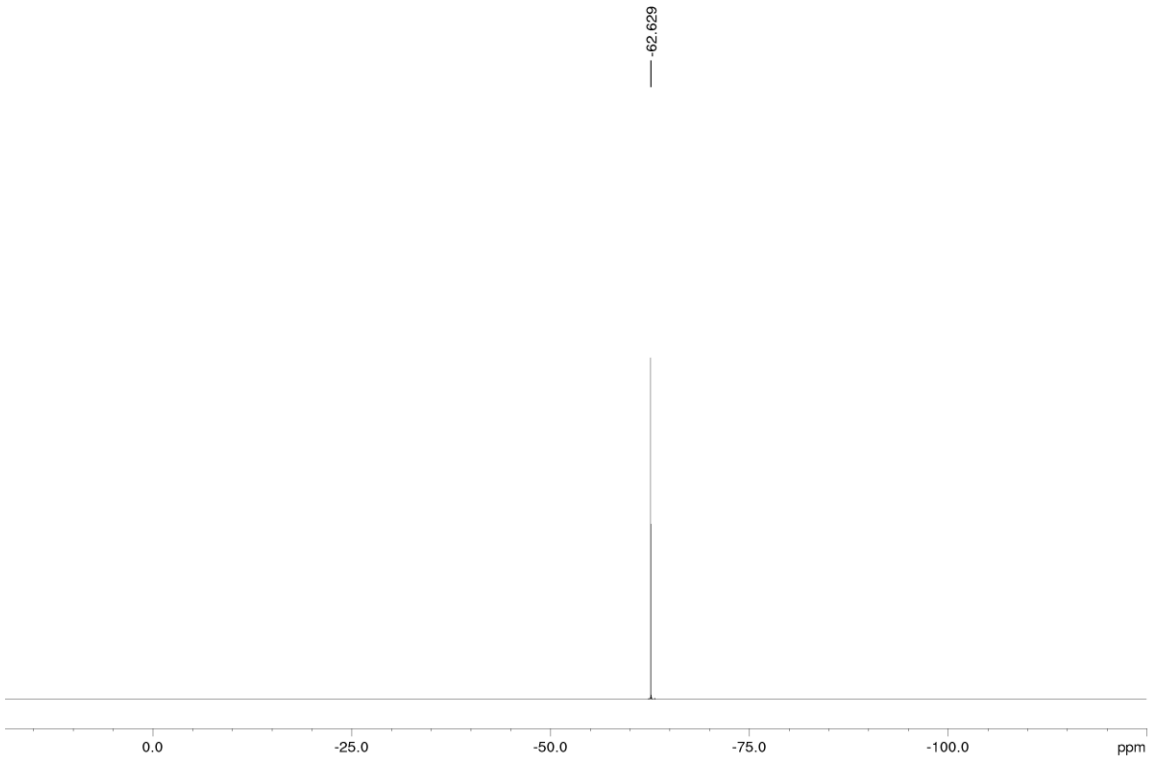

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



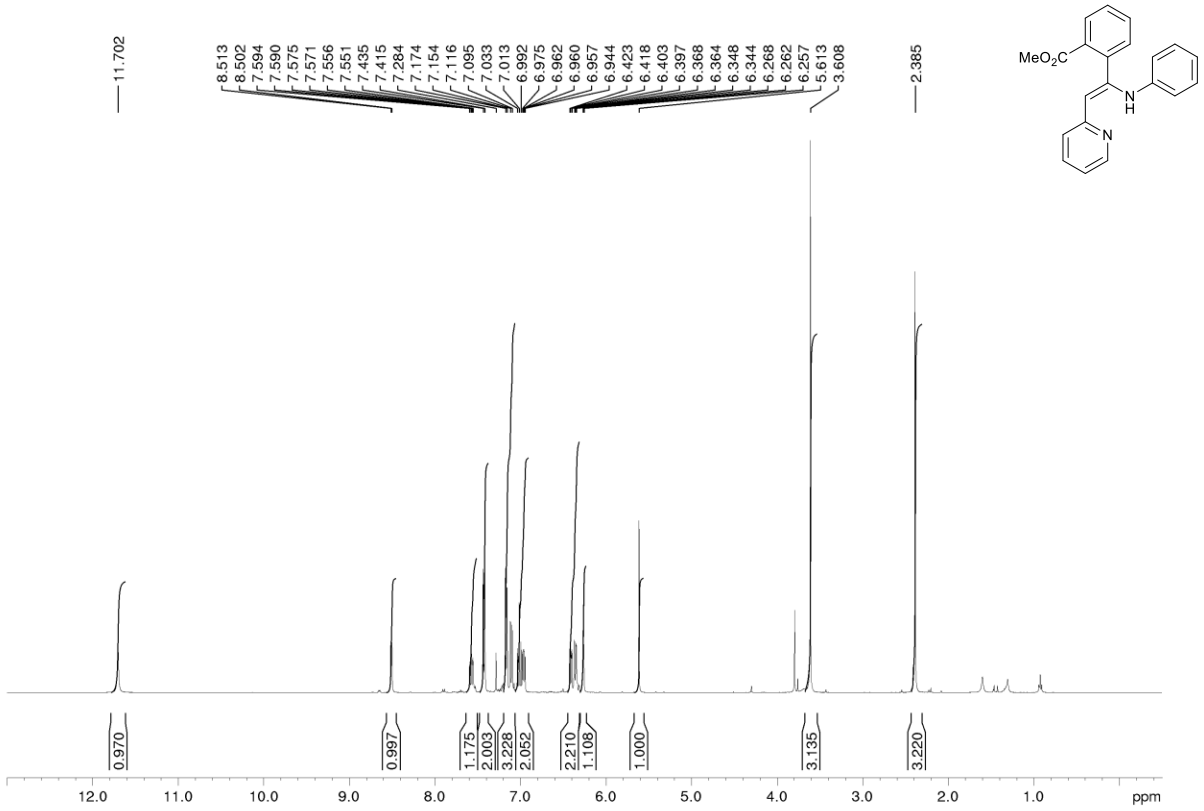
**$^{13}$C NMR (100.6 MHz), $CDCl_3$ (expansion)**



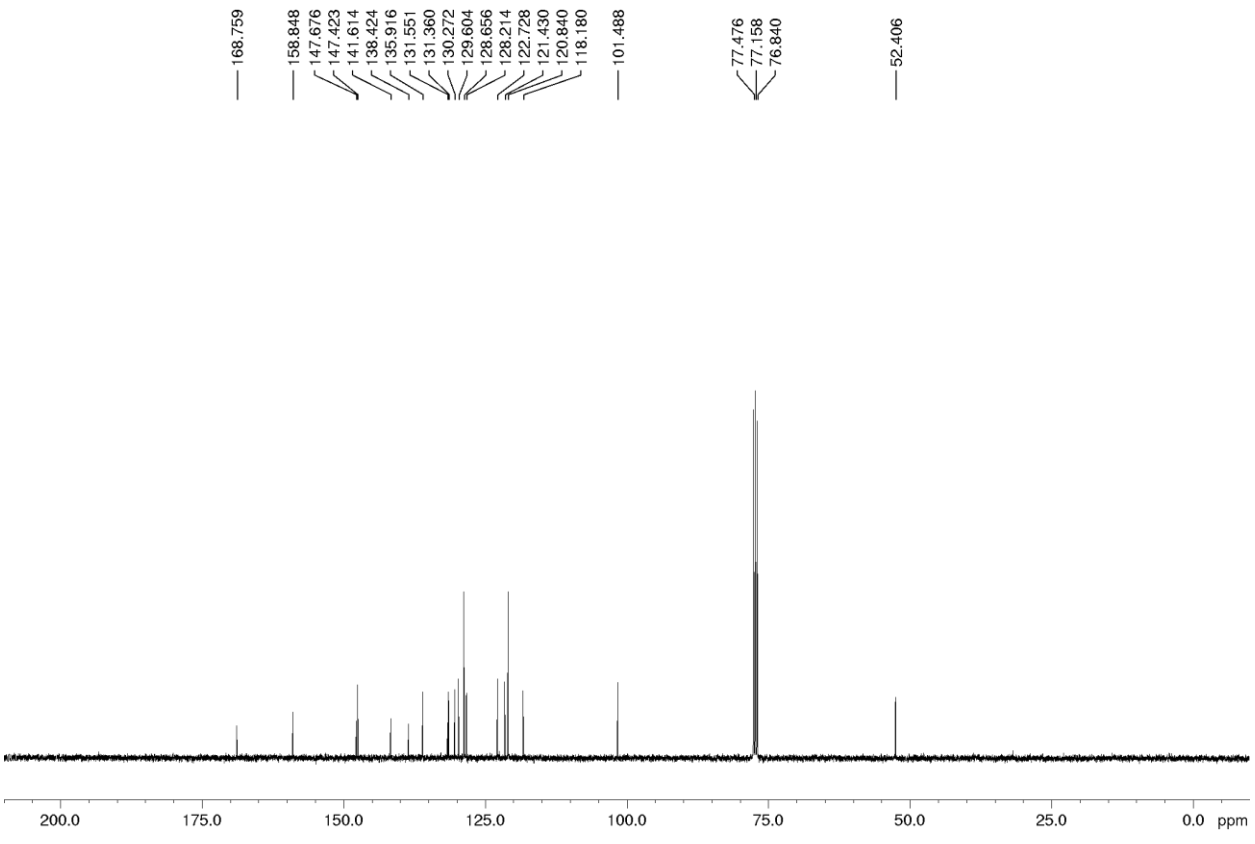

**$^{19}$F NMR (376.5 MHz), $CDCl_3$**



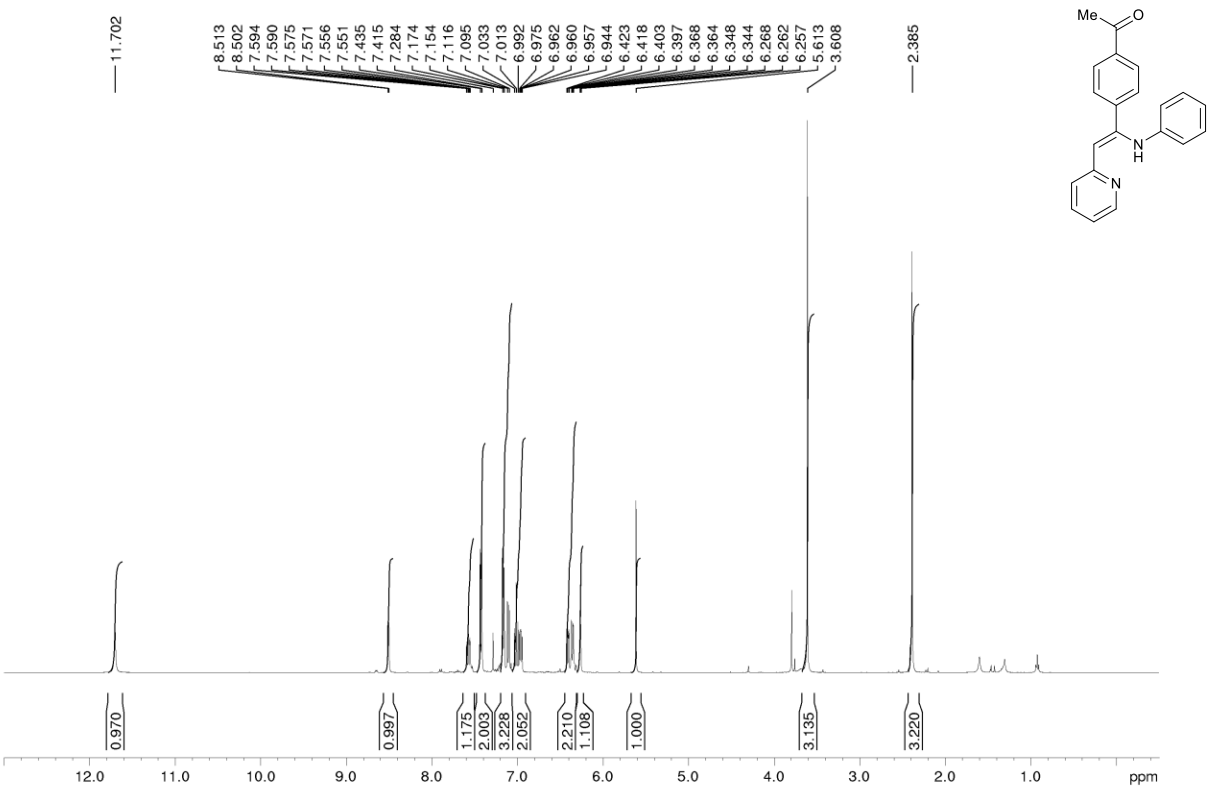
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-methyl 2-(1-(phenylamino)-2-(pyridin-2-yl)vinyl)benzoate (**3r**)



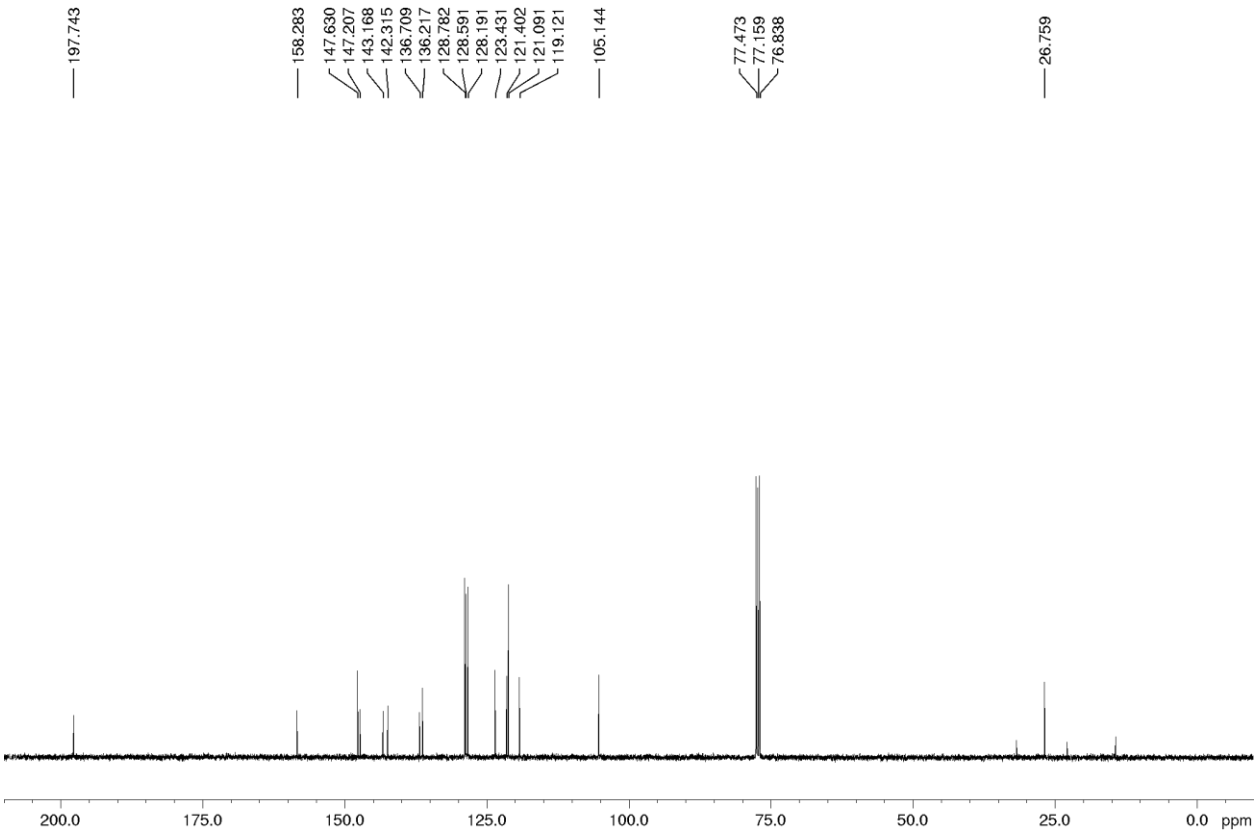

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



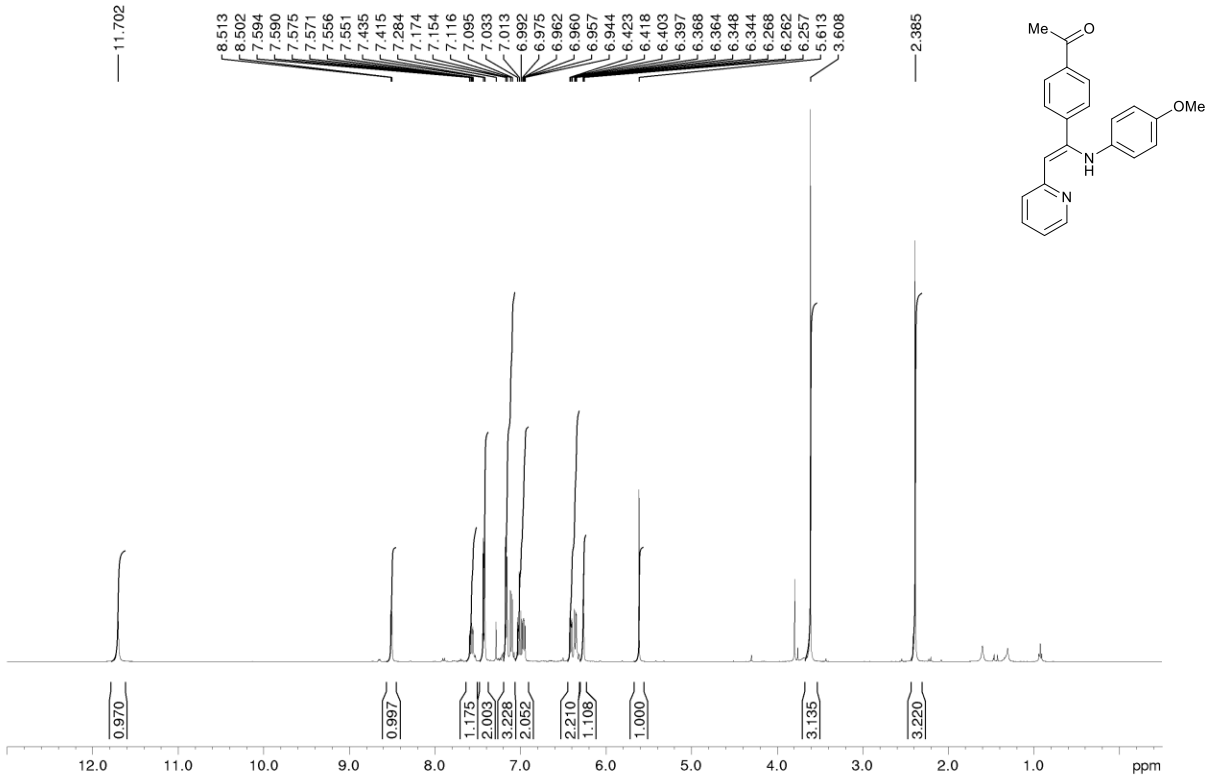
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-1-(4-(1-(phenylamino)-2-(pyridin-2-yl)vinyl)phenyl)ethanone (**3s**)



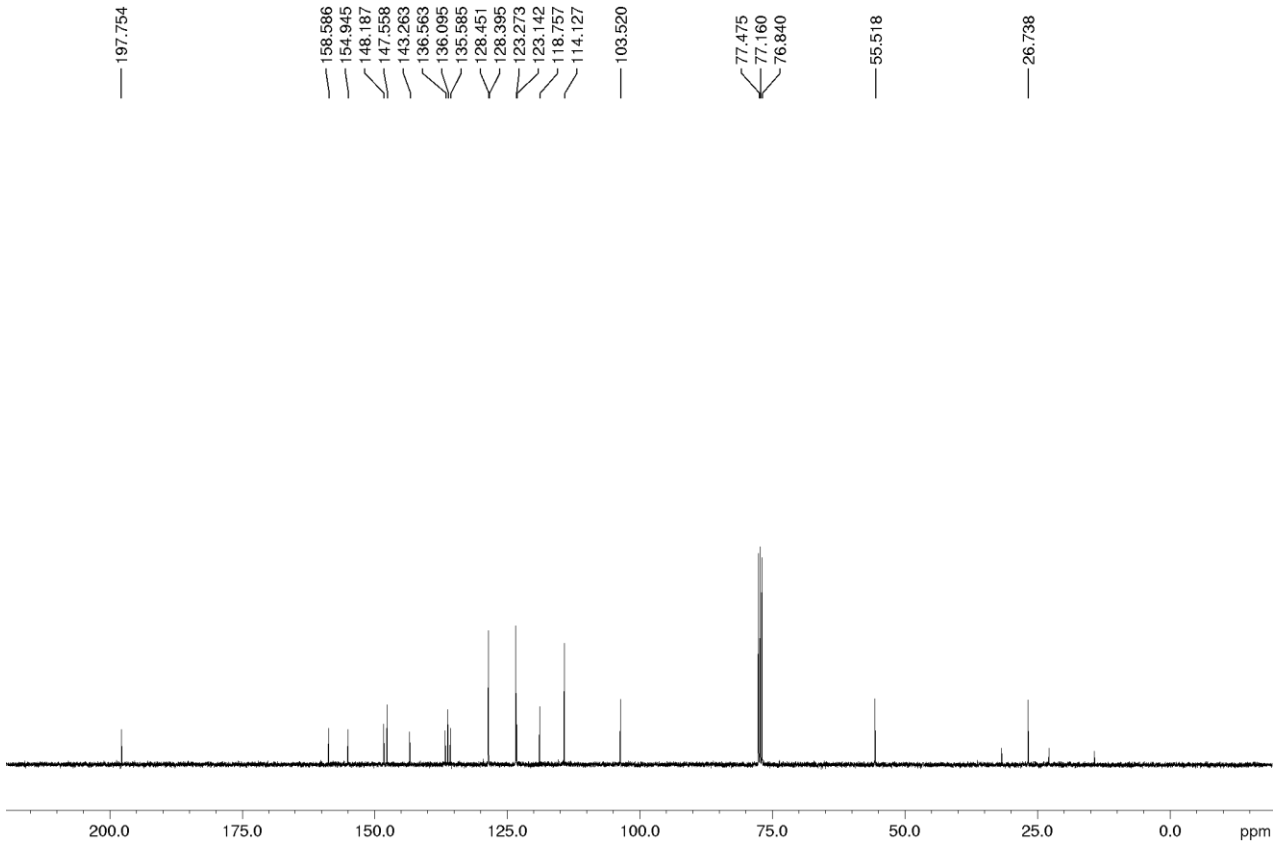

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



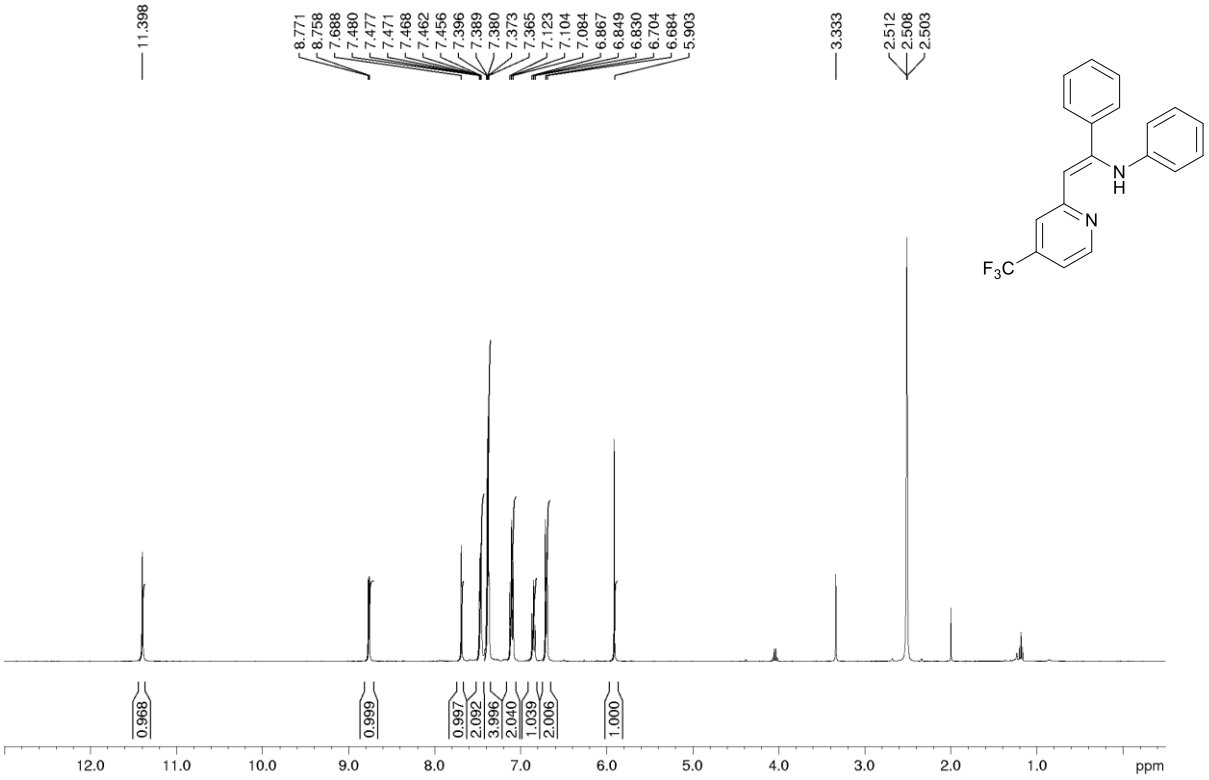
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** (*Z*)-1-(4-(1-(4-methoxyphenylamino)-2-(pyridin-2-yl)vinyl)phenyl)ethanone (**3t**)



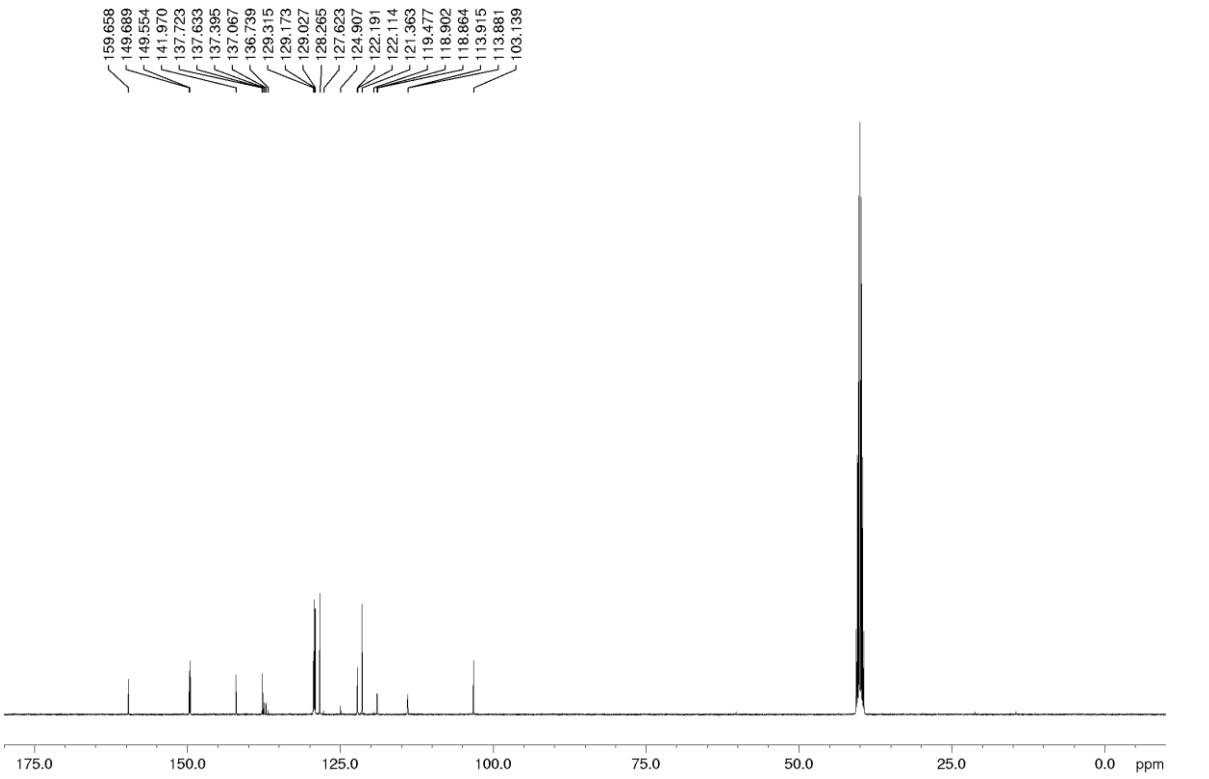

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



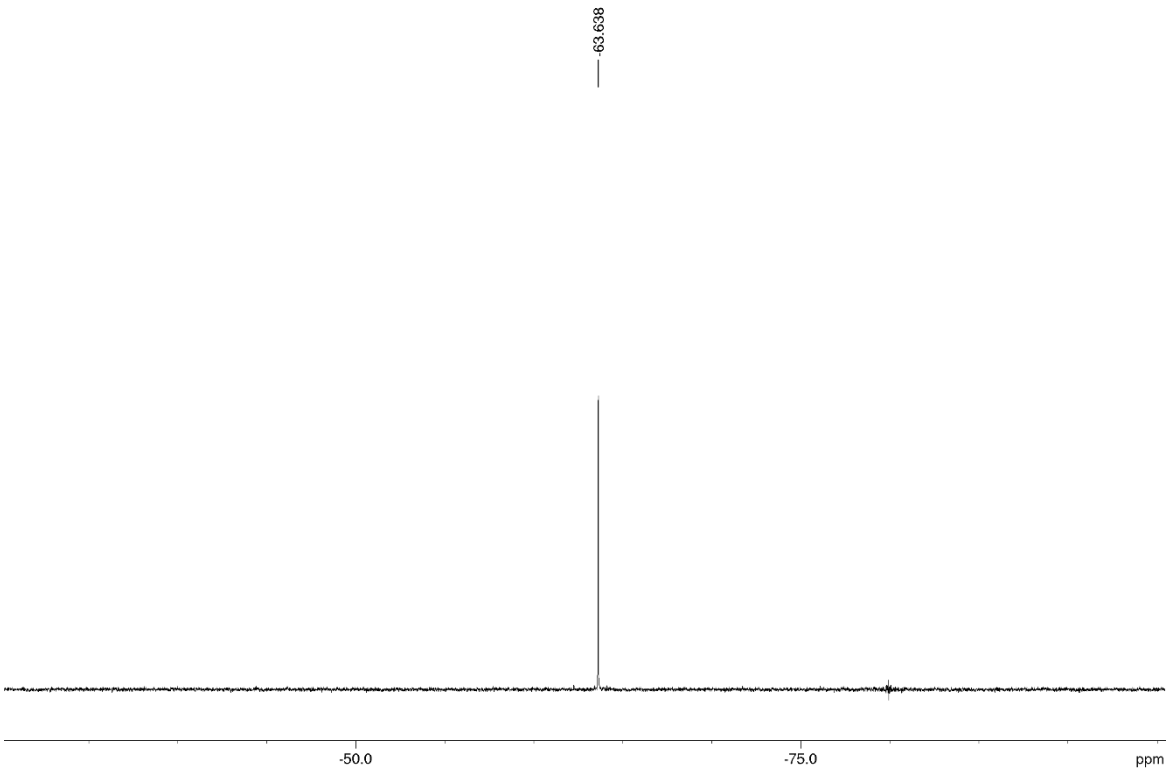
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: (*Z*)-*N*-(1-phenyl-2-(4-(trifluoromethyl)pyridin-2-yl)vinyl)aniline (**7a**)



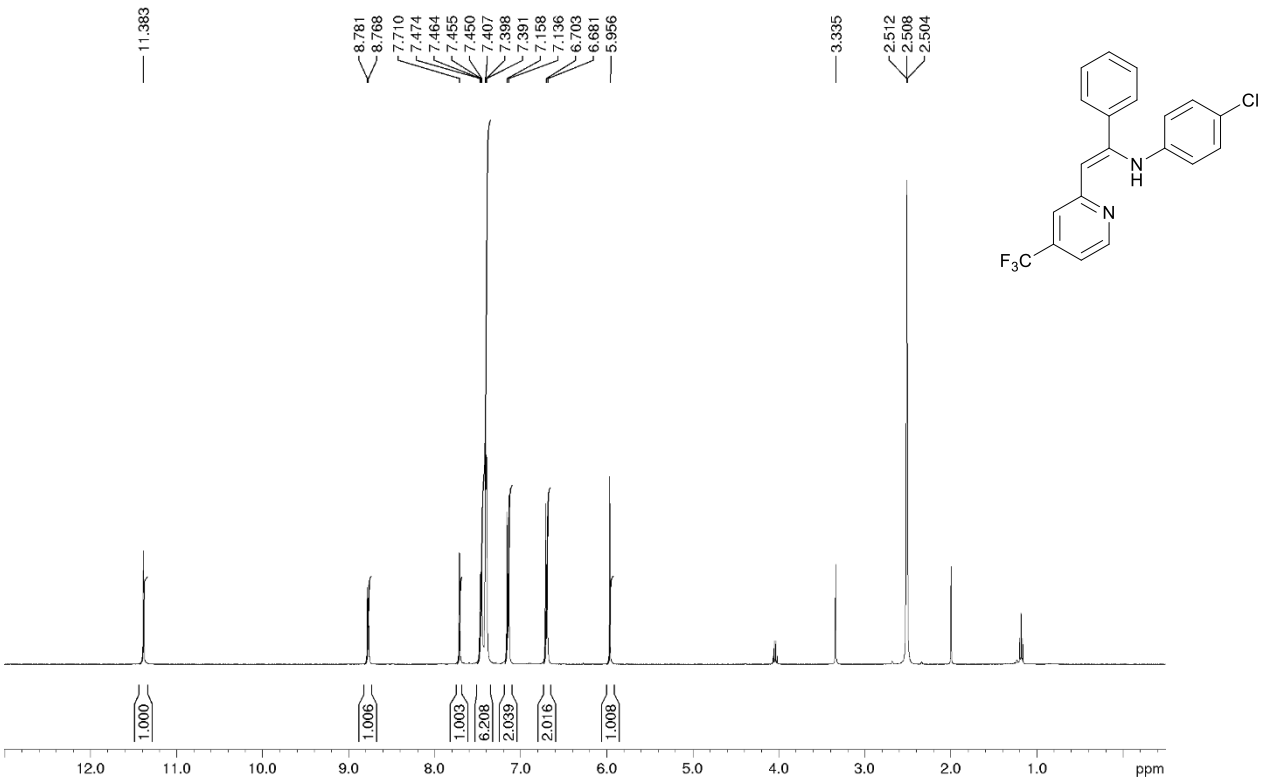

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



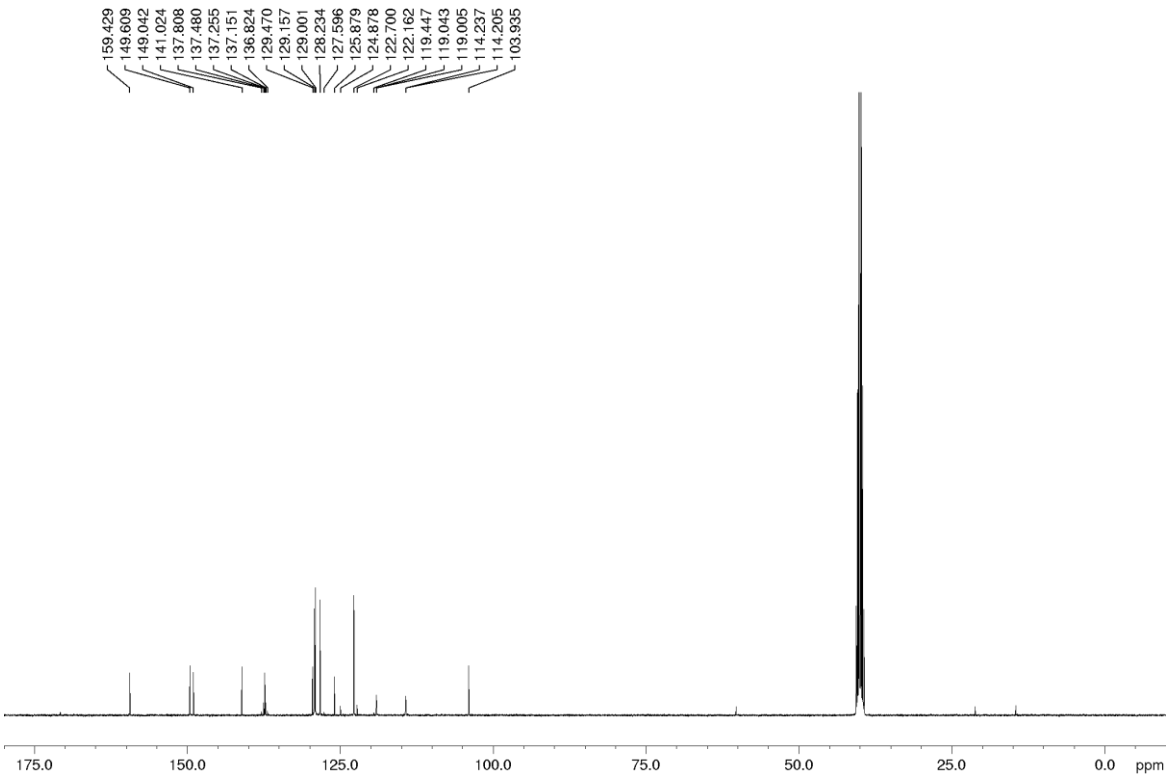
**$^{19}$F NMR (376.5 MHz MHz), DMSO$d_6$**



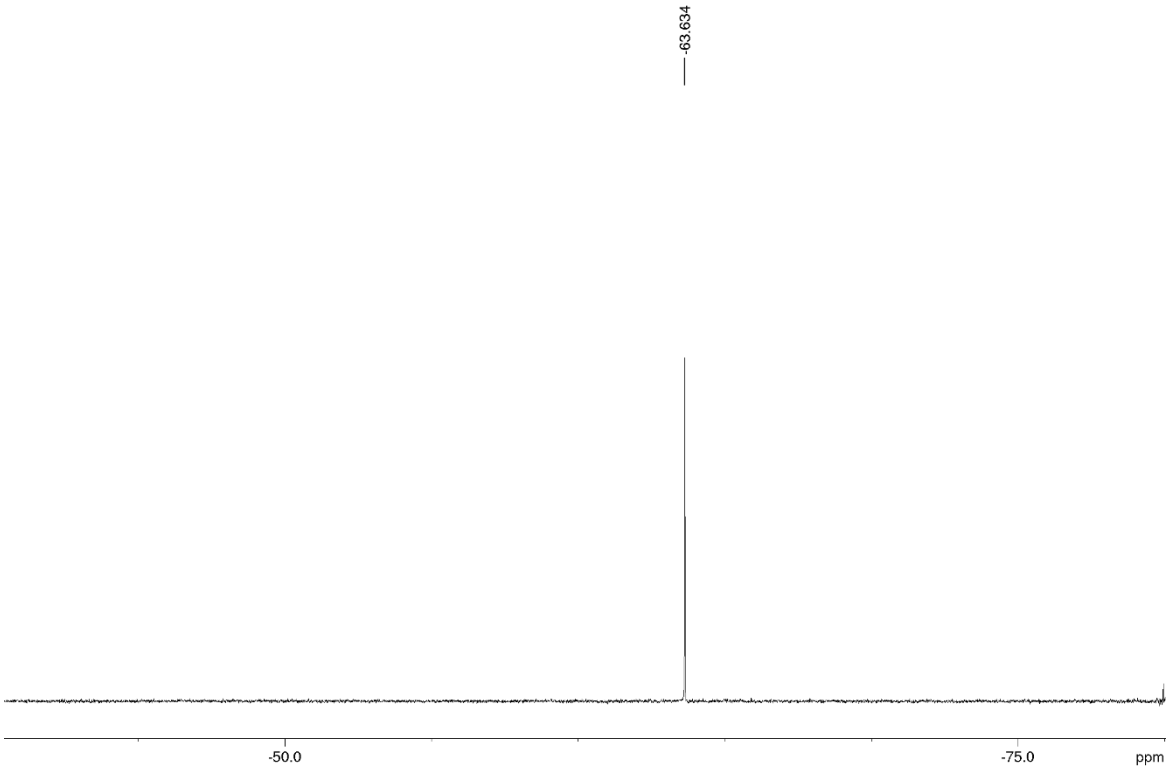
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: (*Z*)-4-chloro-*N*-(1-phenyl-2-(4-(trifluoromethyl)pyridin-2-yl)vinyl)aniline (**7b**)



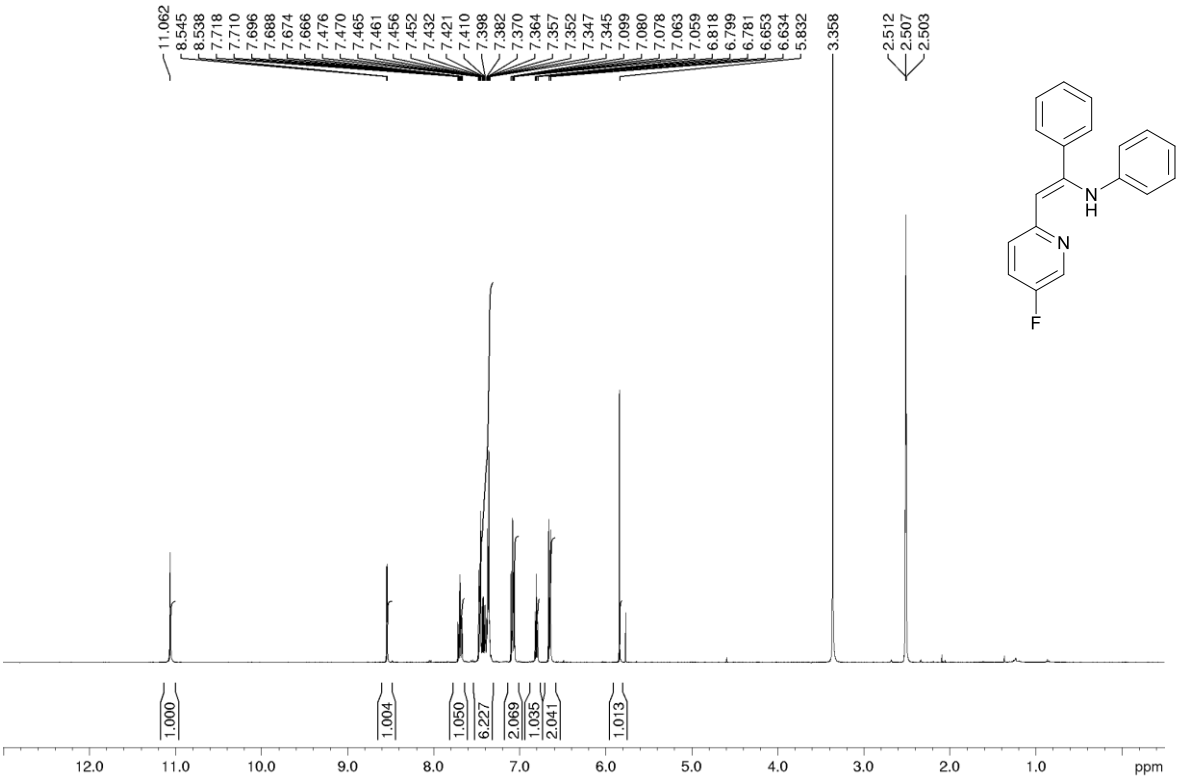

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



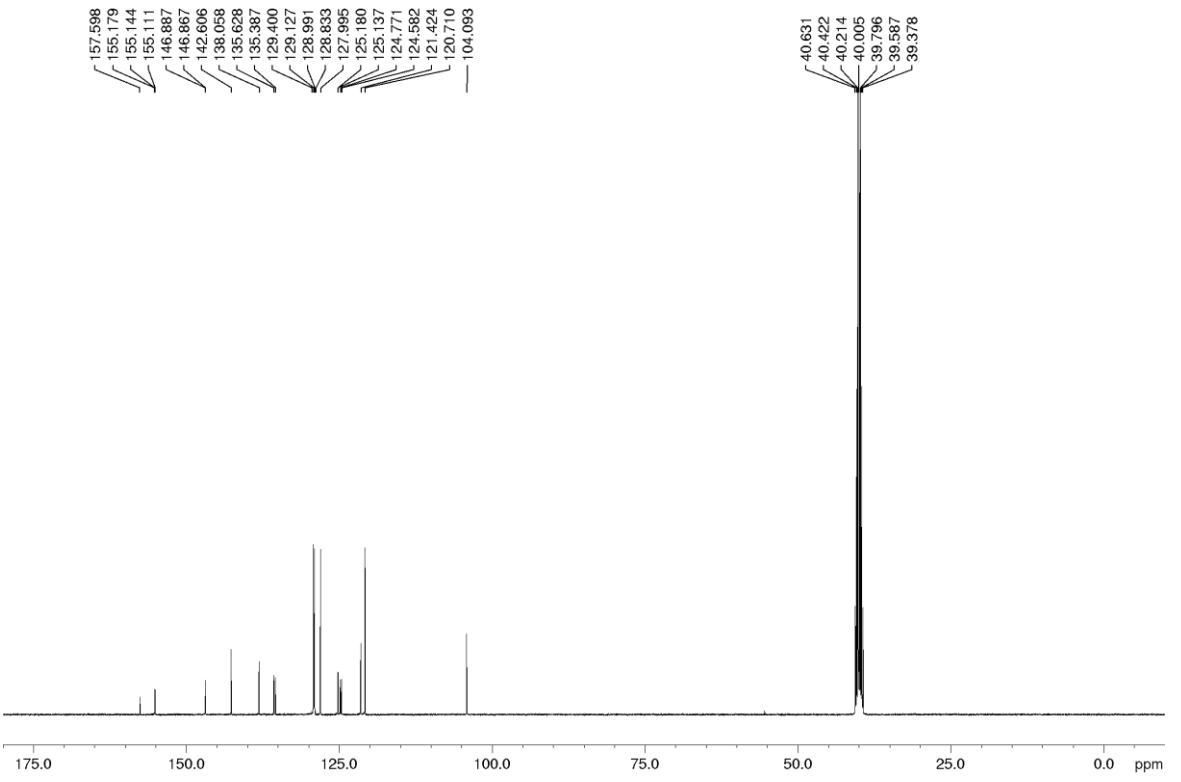
**$^{19}$F NMR (376.5 MHz MHz), DMSO$d_6$**



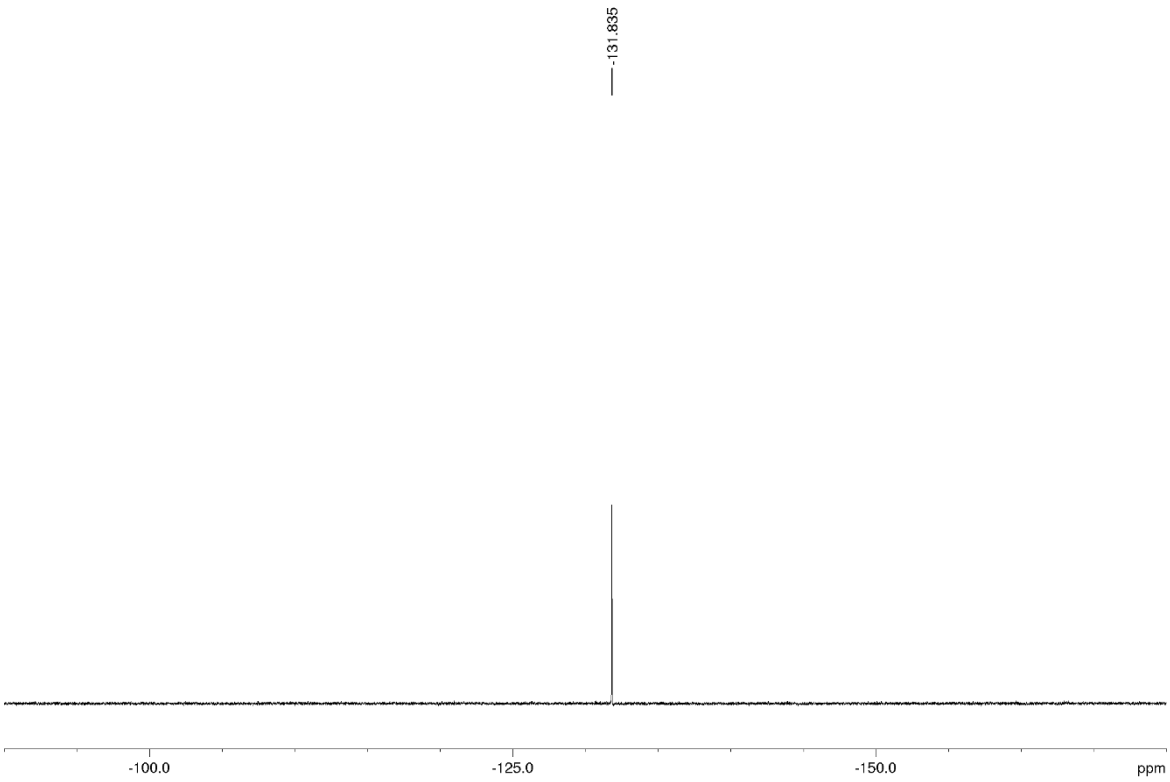
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: (*Z*)-*N*-(2-(5-fluoropyridin-2-yl)-1-phenylvinyl)aniline (**7c**)



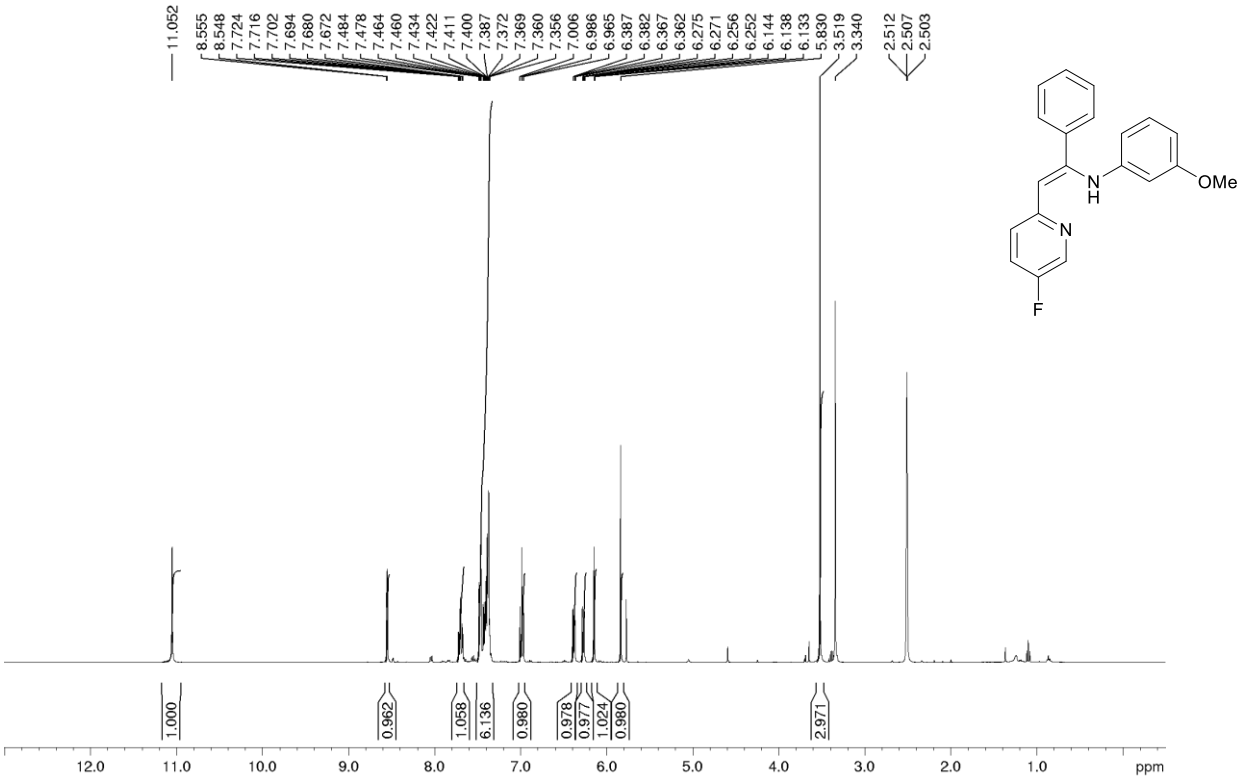

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



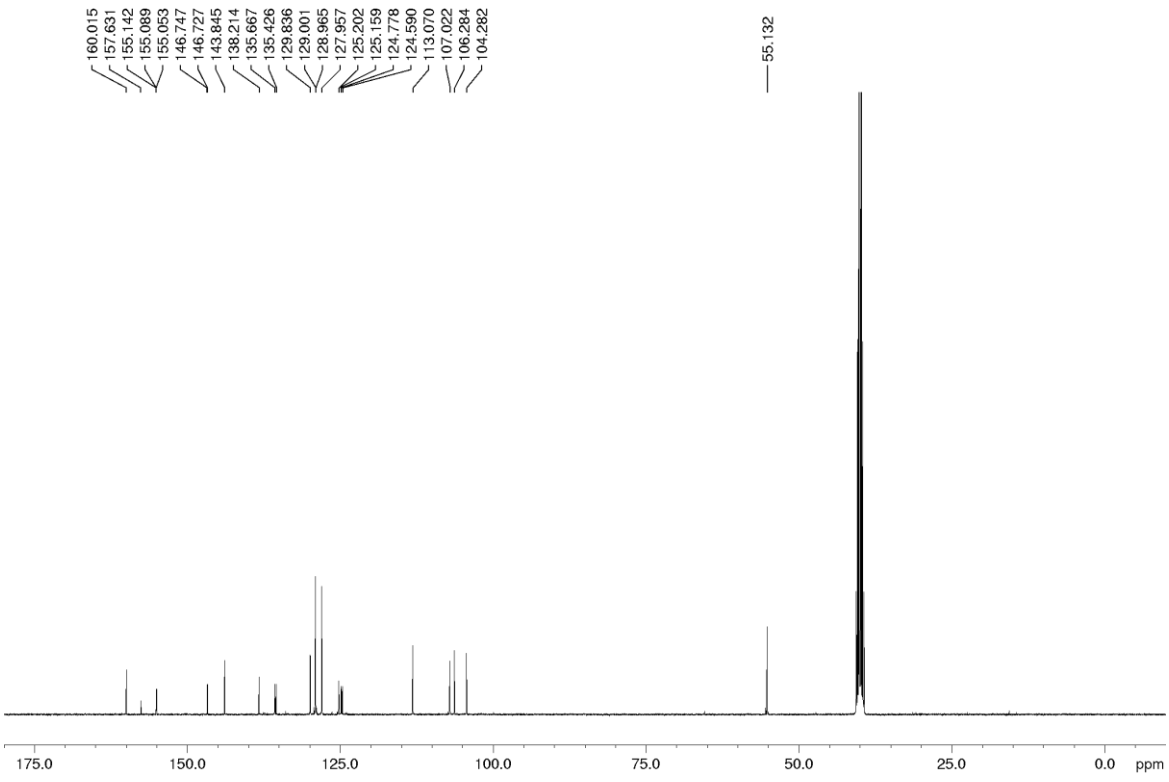
**$^{19}$F NMR (376.5 MHz MHz), DMSO$d_6$**



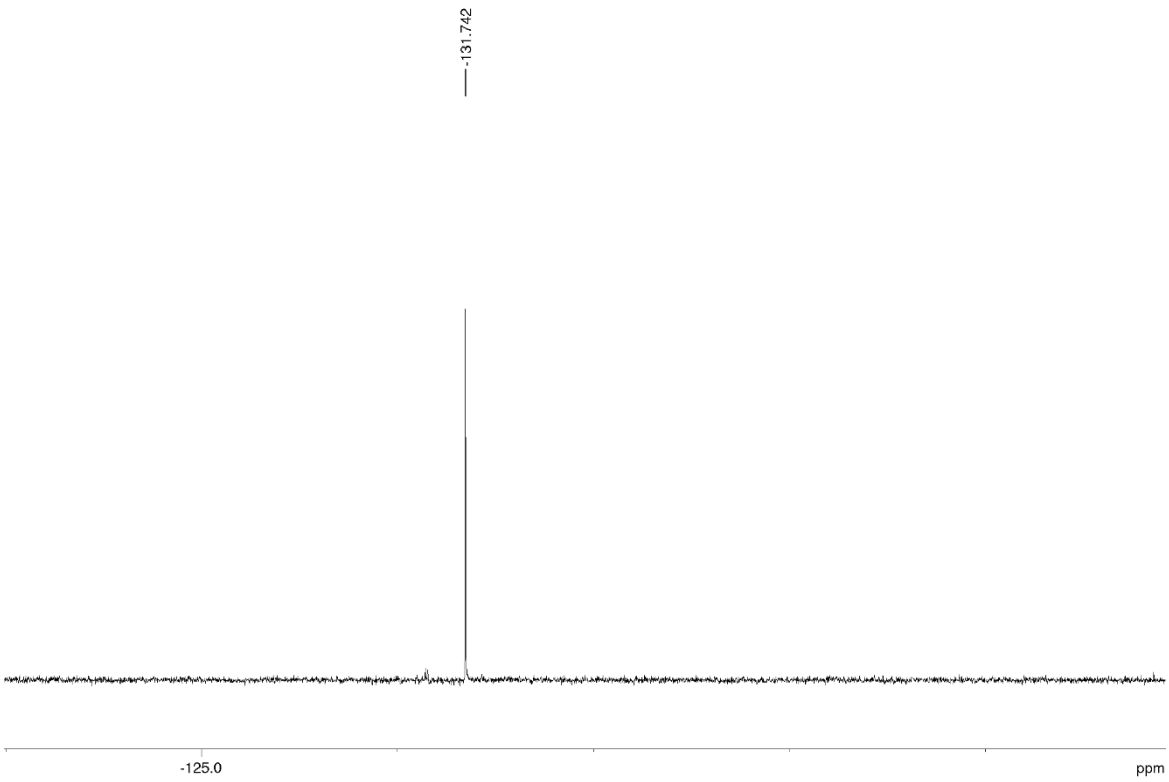
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: (*Z*)-*N*-(2-(5-fluoropyridin-2-yl)-1-phenylvinyl)-3-methoxyaniline (**7d**)



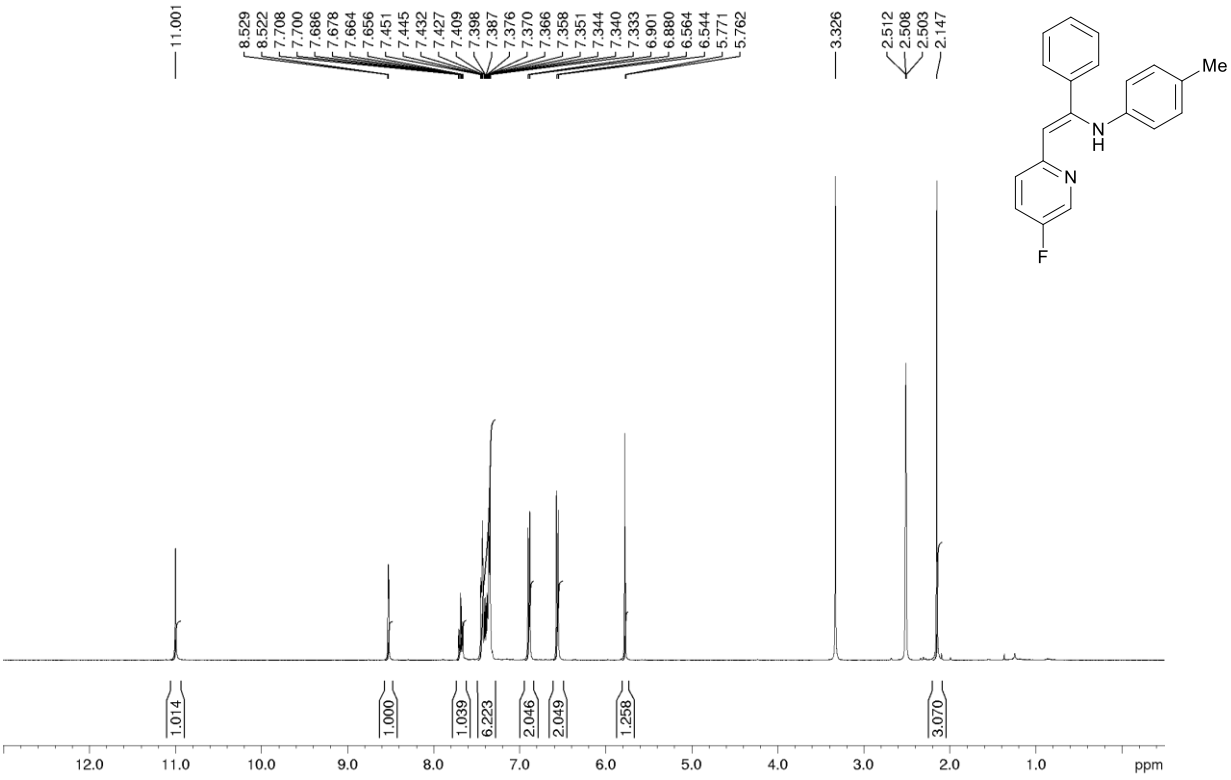

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



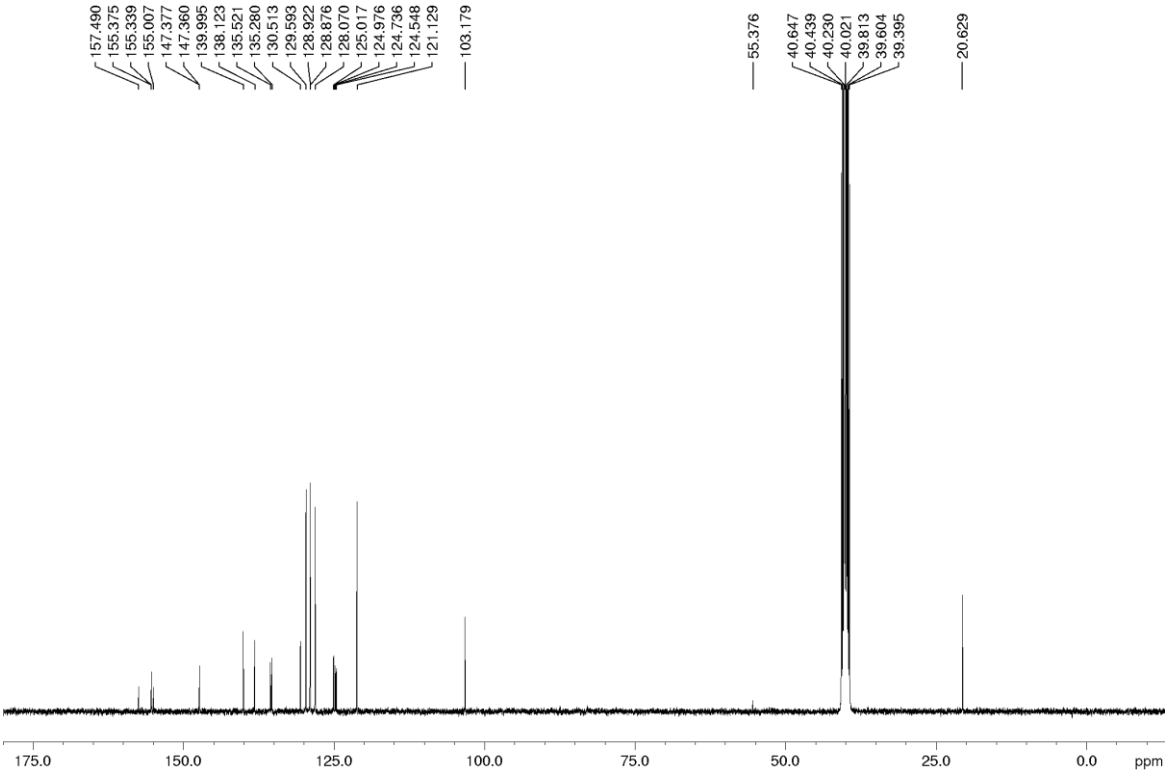
**$^{19}$F NMR (376.5 MHz MHz), DMSO$d_6$**



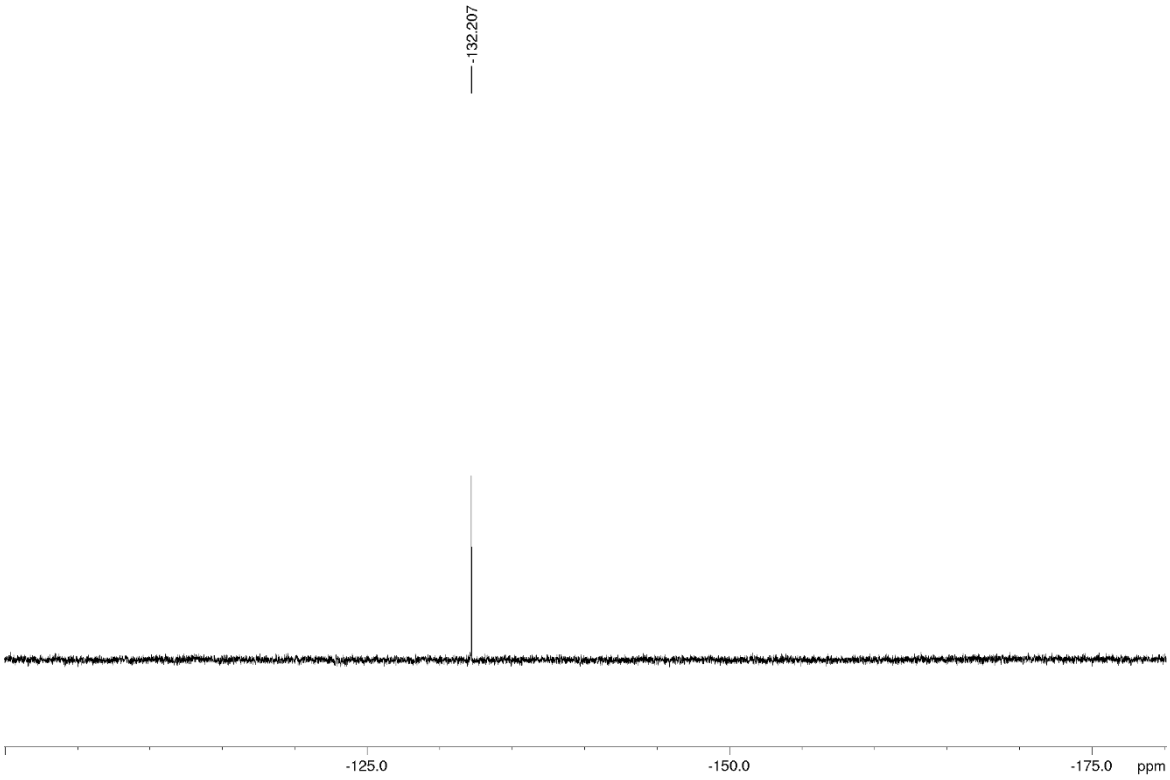
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: (*Z*)-*N*-(2-(5-fluoropyridin-2-yl)-1-phenylvinyl)-4-methylaniline (**7e**)



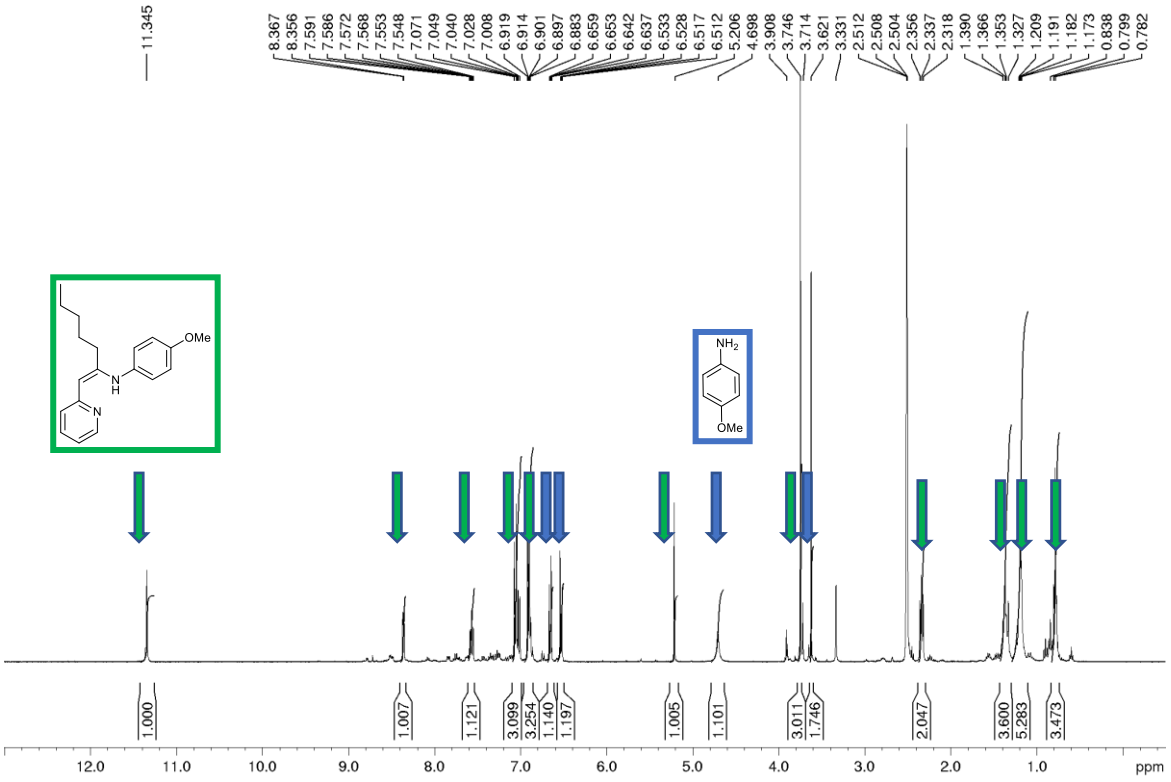

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



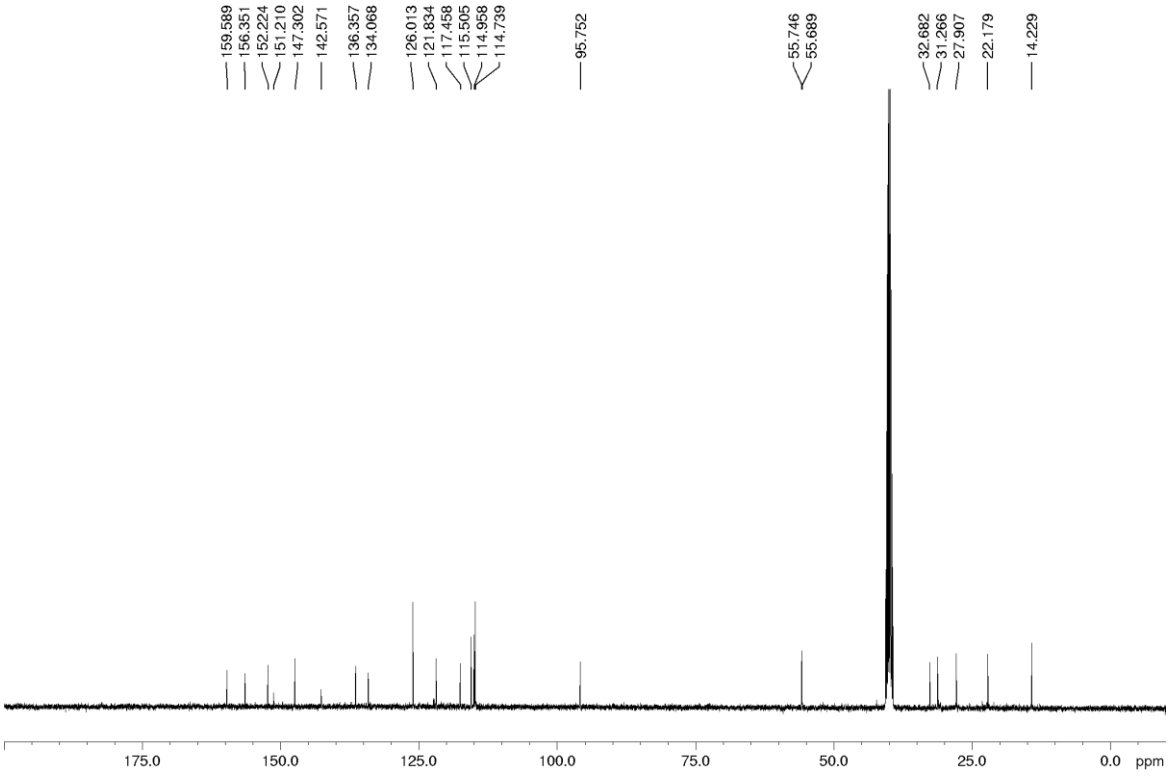
**$^{19}$F NMR (376.5 MHz MHz), DMSO$d_6$**



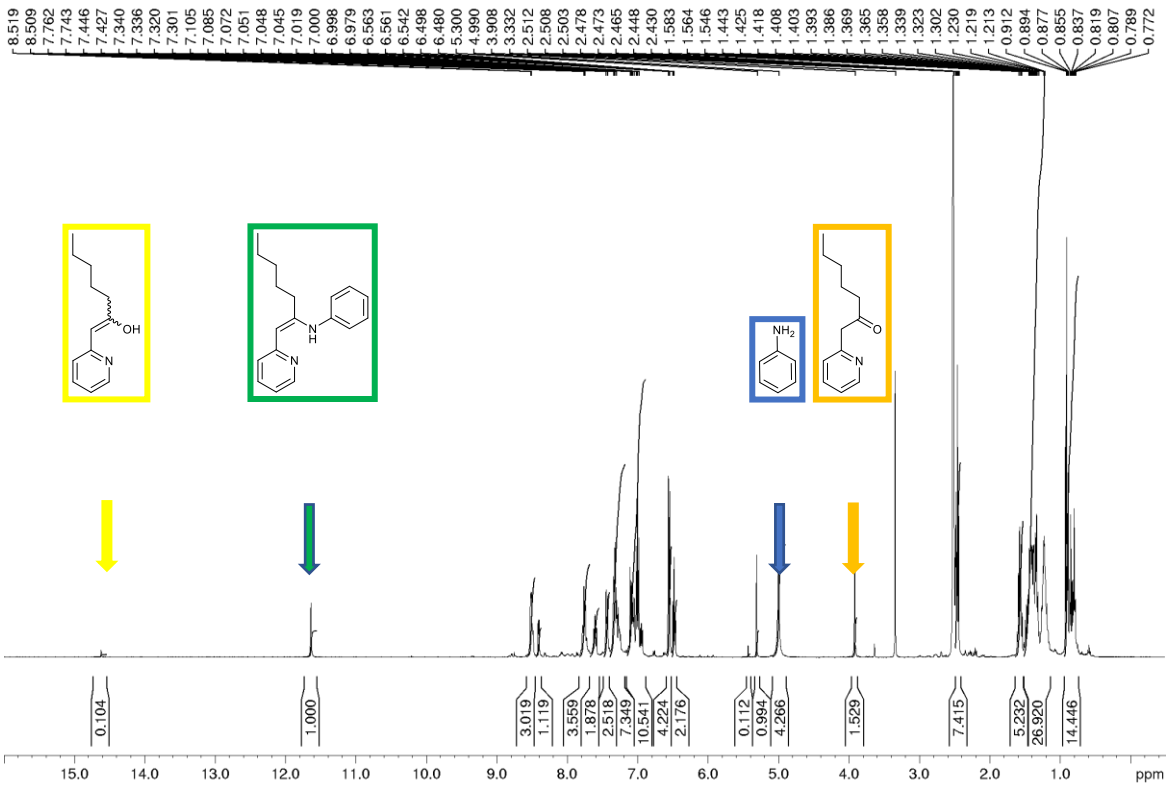
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: (*Z*)-4-methoxy-*N*-(1-(pyridin-2-yl)hept-1-en-2-yl)aniline (**7f**)




**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**

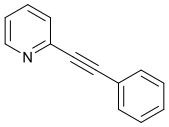


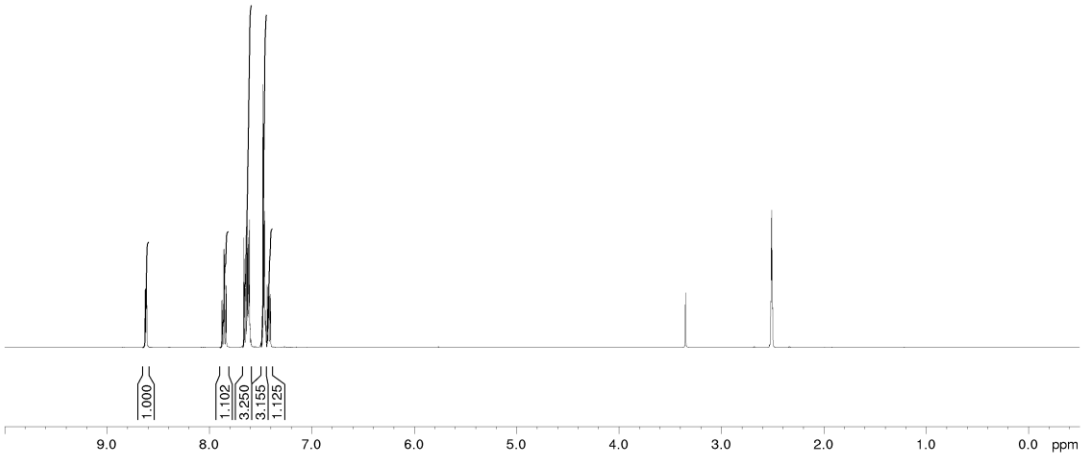
**$^1$H NMR (400.13 MHz), DMSO$d_6$: (*Z*)-*N*-(1-(pyridin-2-yl)hept-1-en-2-yl)aniline (7g)**



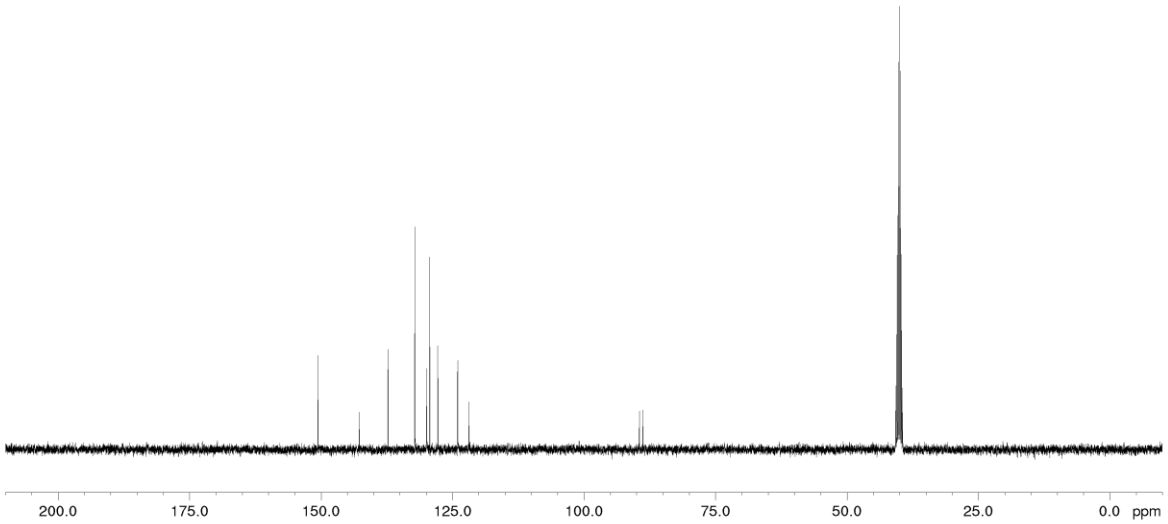
**$^{1}$H, $^{13}$C, $^{19}$F NMR SPECTRA Compounds 1a – h, 6a – c, 8, 9**

**$^{1}$H NMR (400.13 MHz), DMSO$d_6$:** 2-(phenylethynyl)pyridine (**1a**)

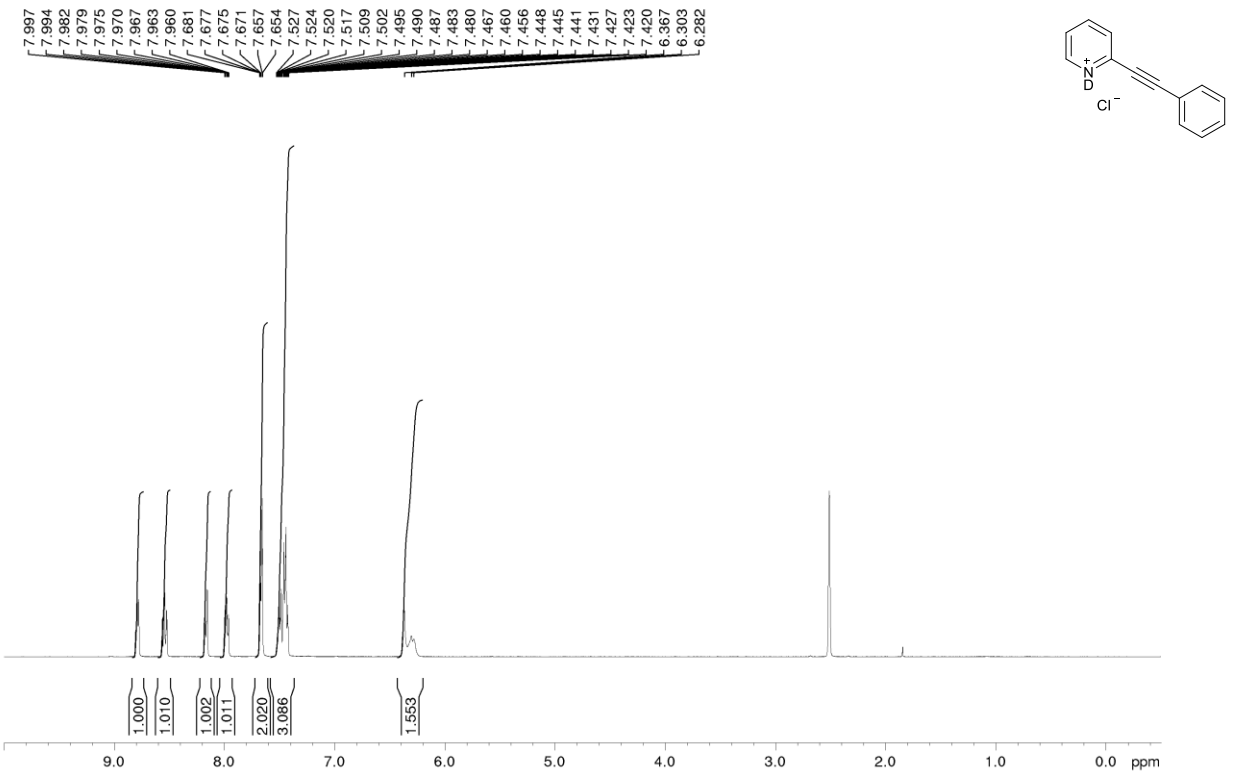



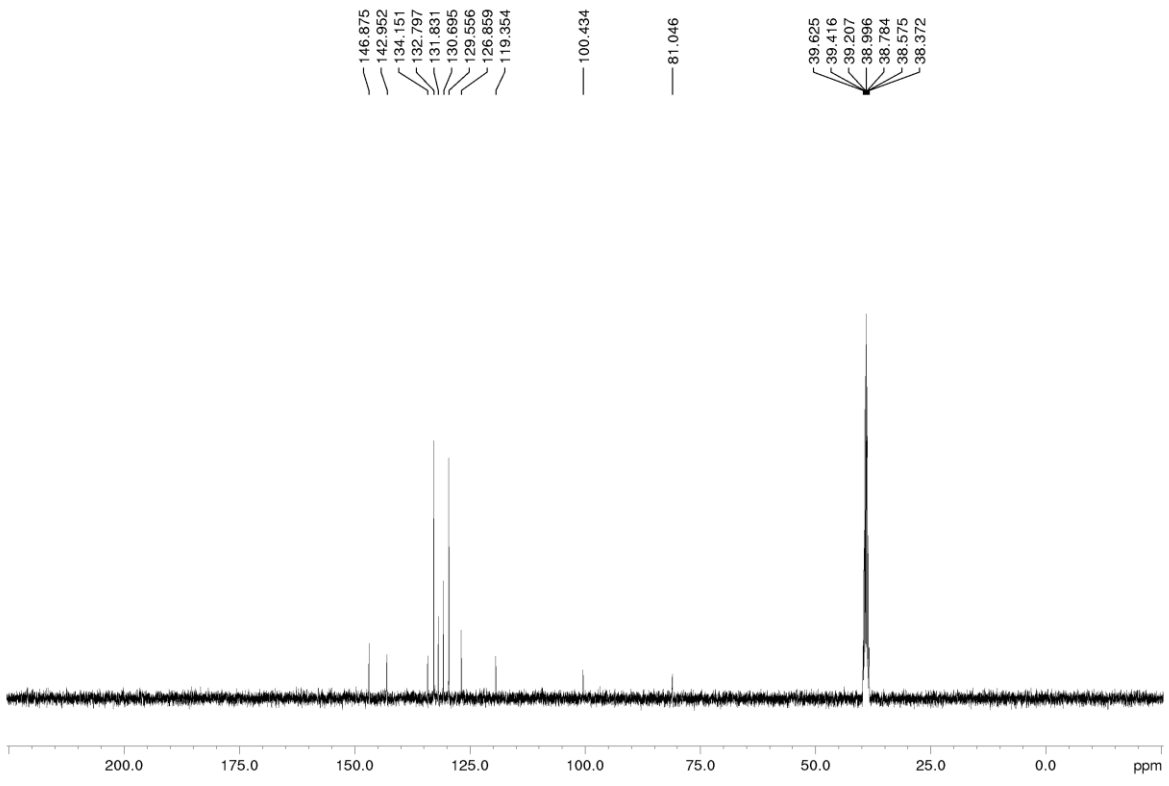

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**

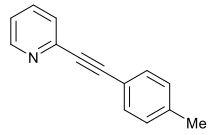
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$/DCl/$D_2O$:** 2-(phenylethynyl)pyridinium chloride (**1a'**)

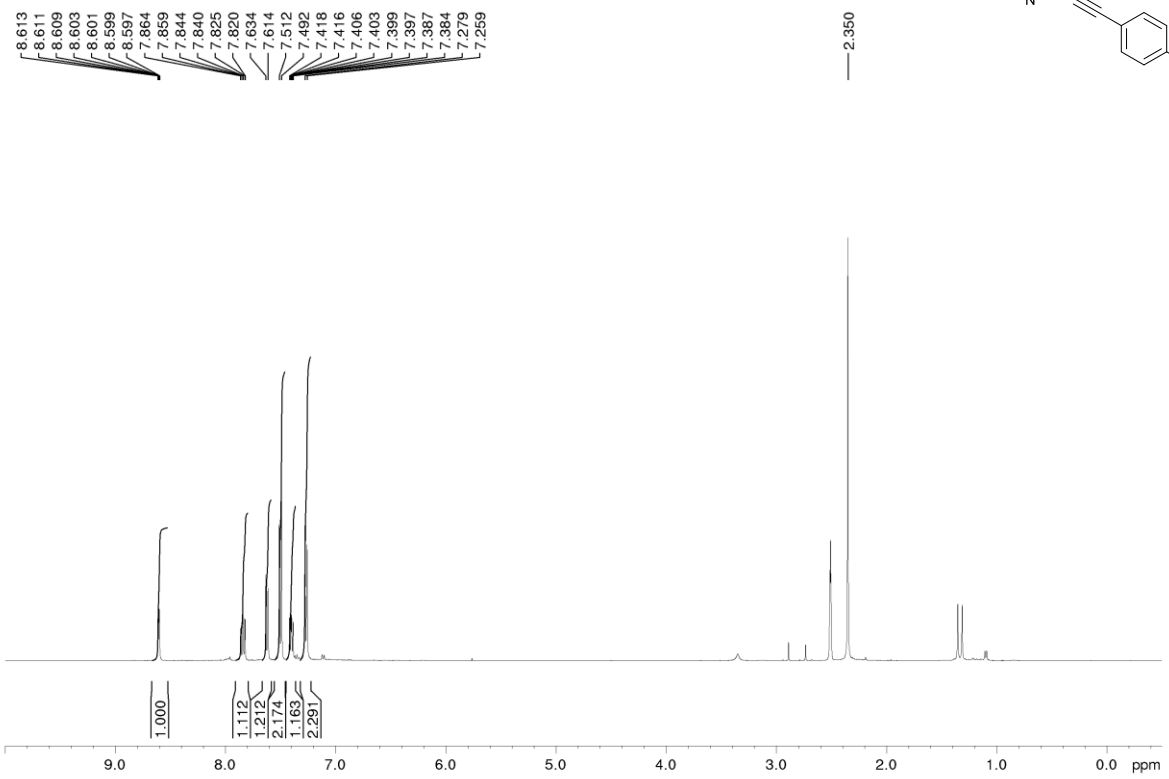



**$^{13}$C NMR (100.6 MHz), DMSO$d_6$/DCl/$D_2O$**

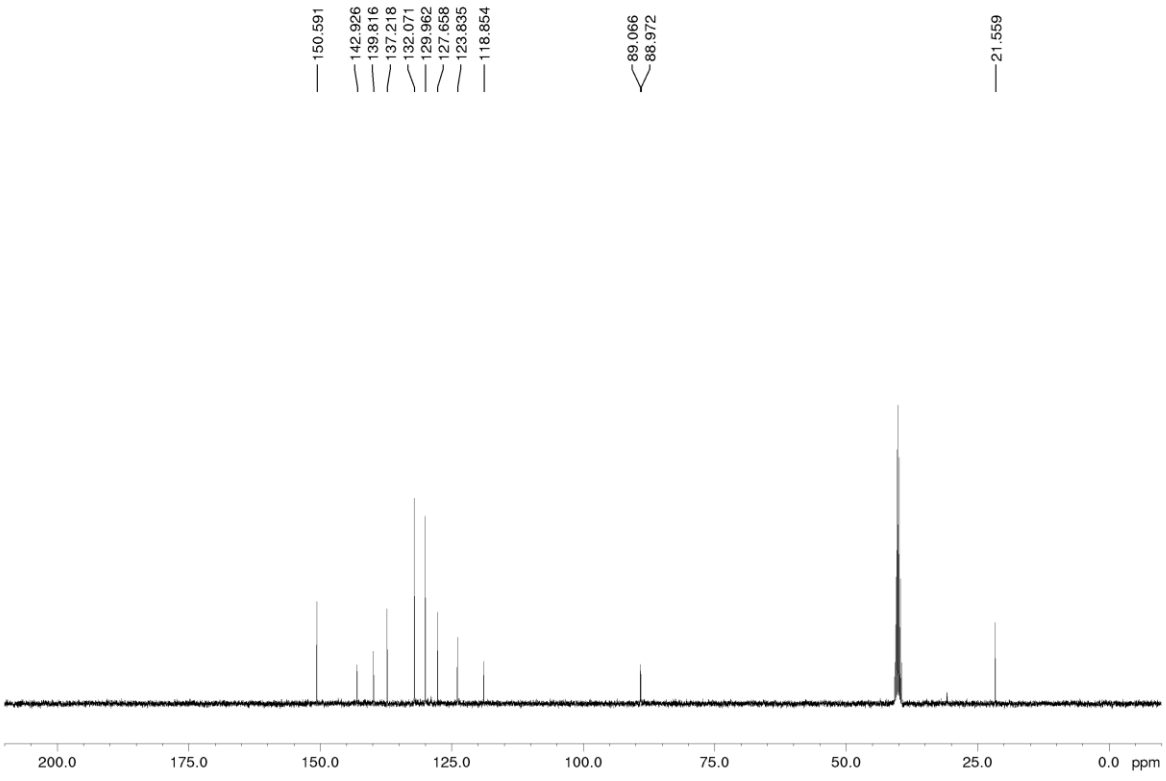


**$^{1}$H NMR (400.13 MHz), DMSO$d_6$:** 2-(*p*-tolylethynyl)pyridine (**1b**)

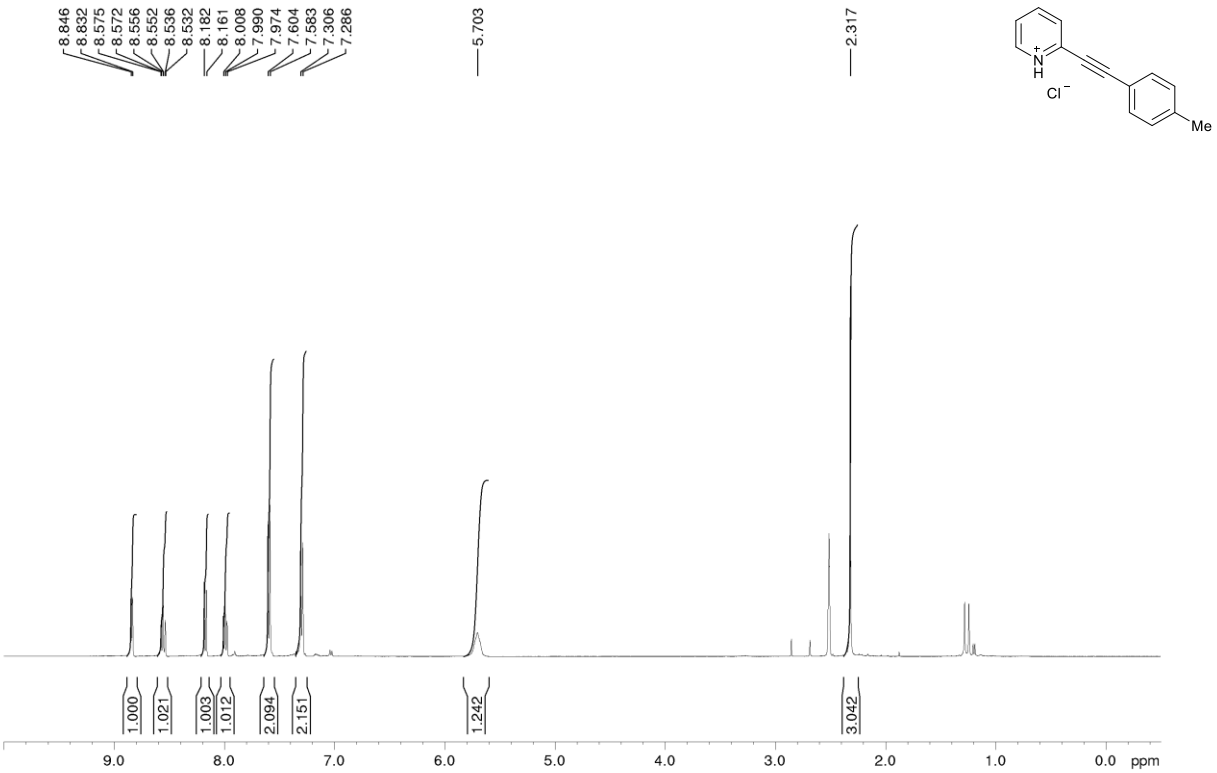


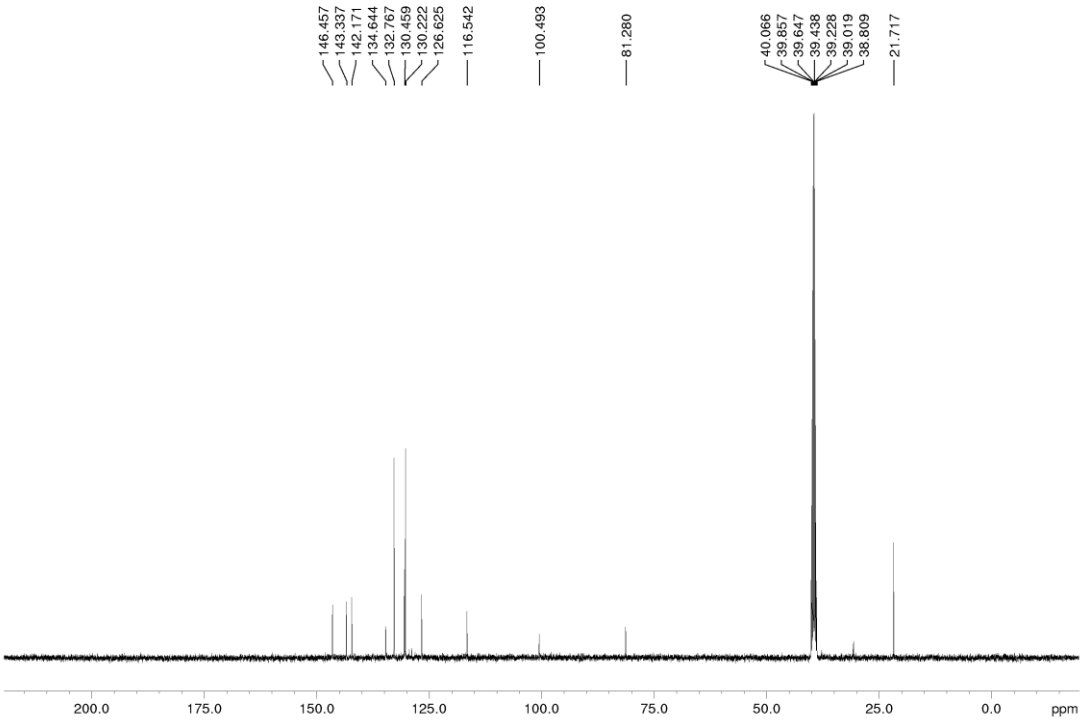

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



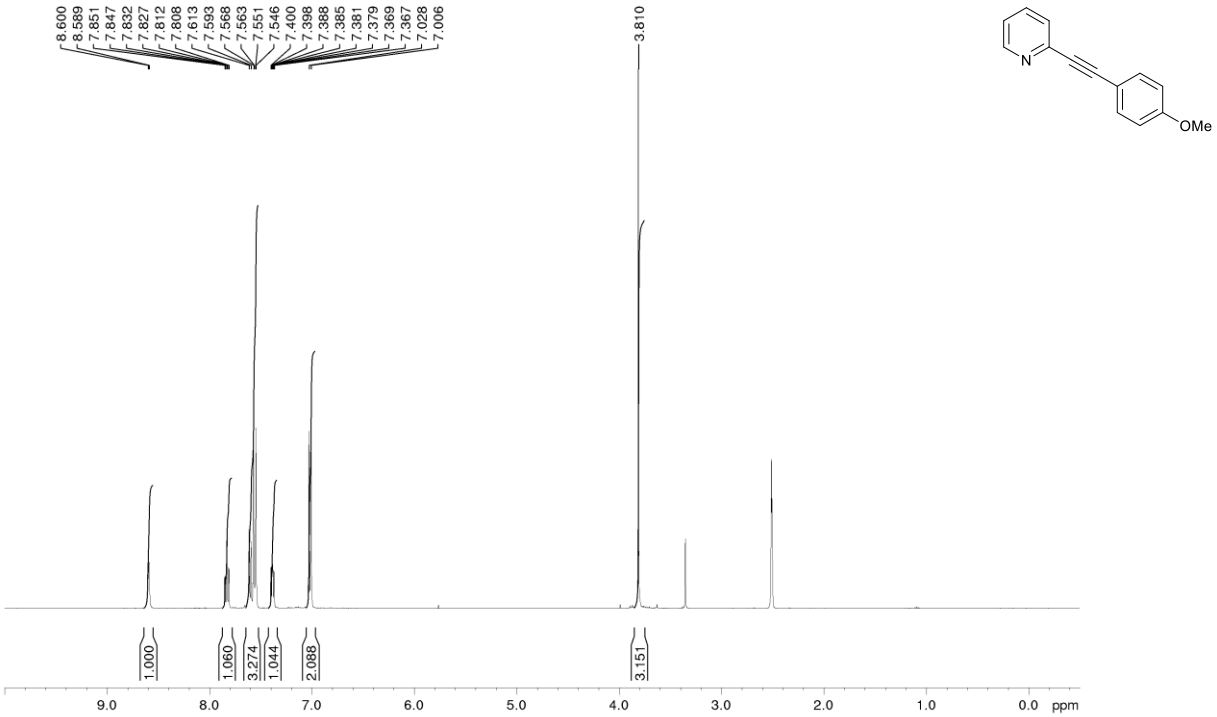
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$/DCl/$D_2O$:** 2-(*p*-tolylethynyl)pyridinium chloride (**1b'**)



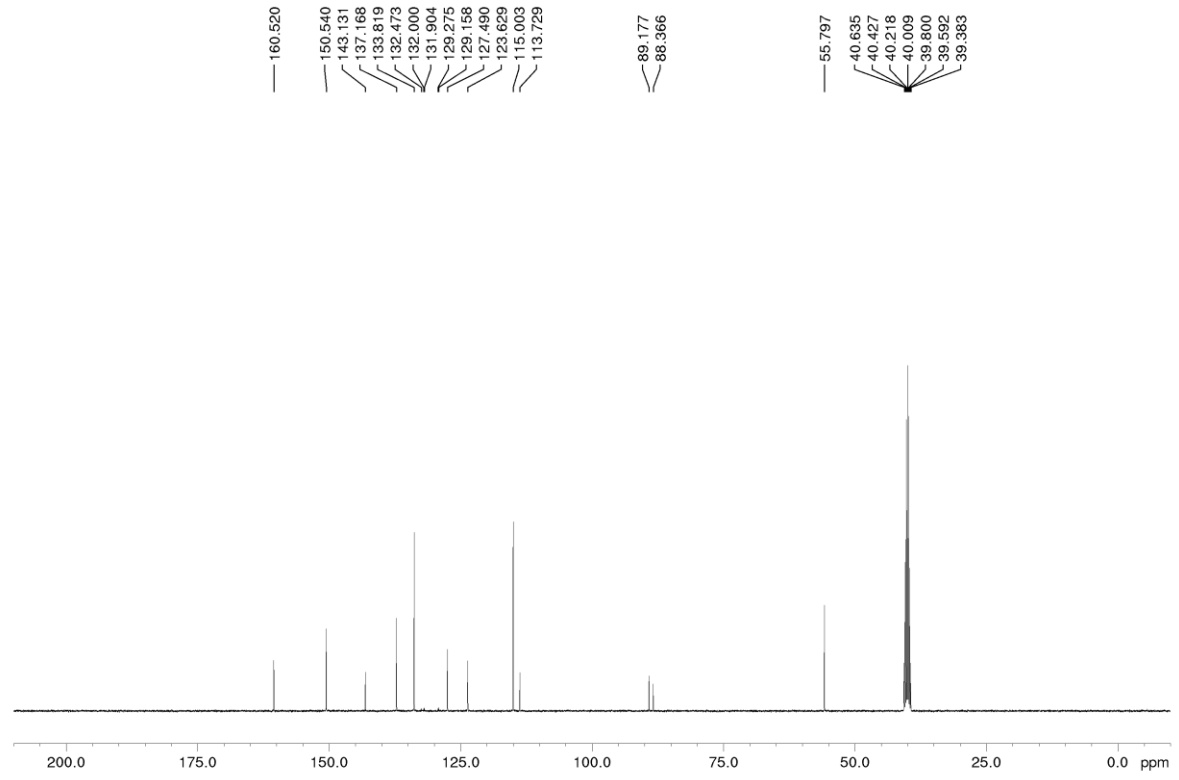

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$/DCl/$D_2O$**



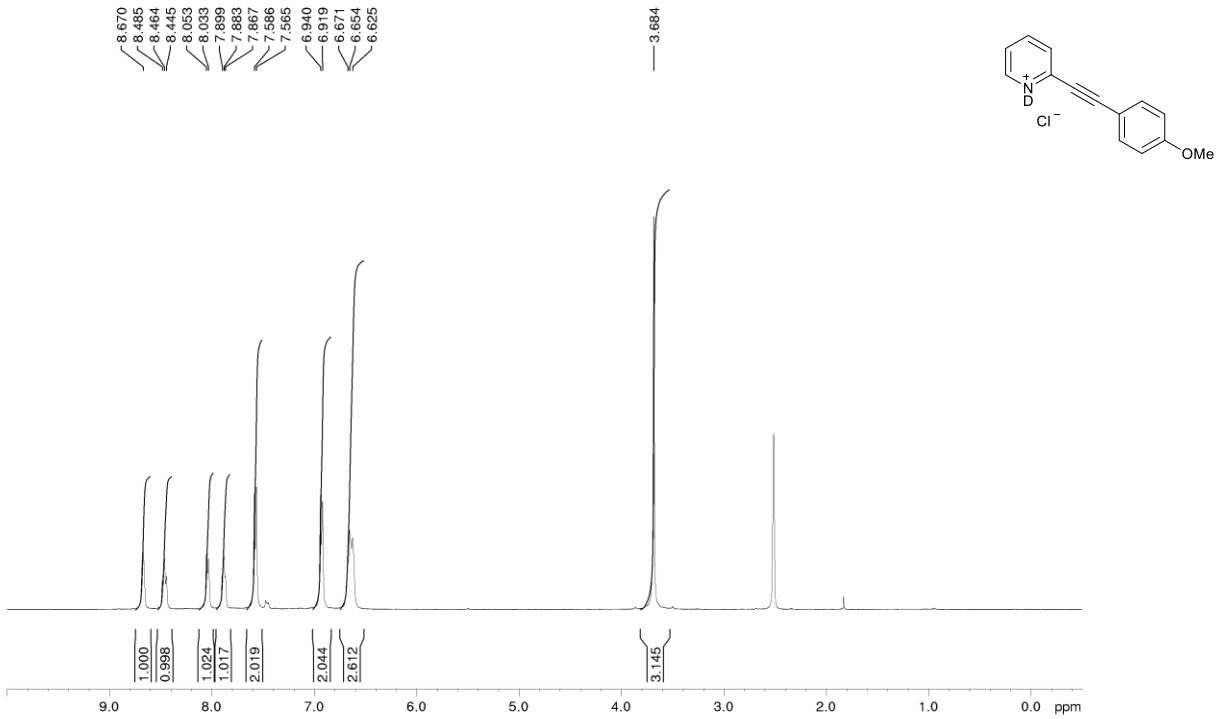
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$:** 2-((4-methoxyphenyl)ethynyl)pyridine (**1c**)



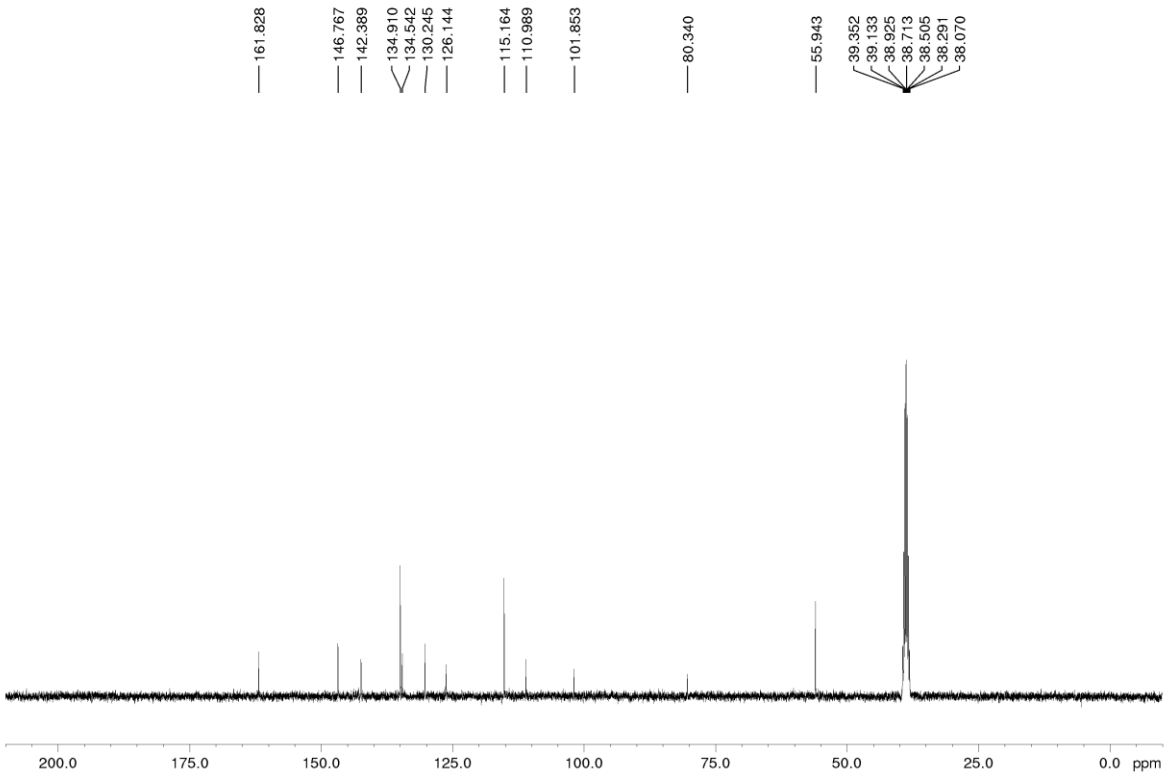

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



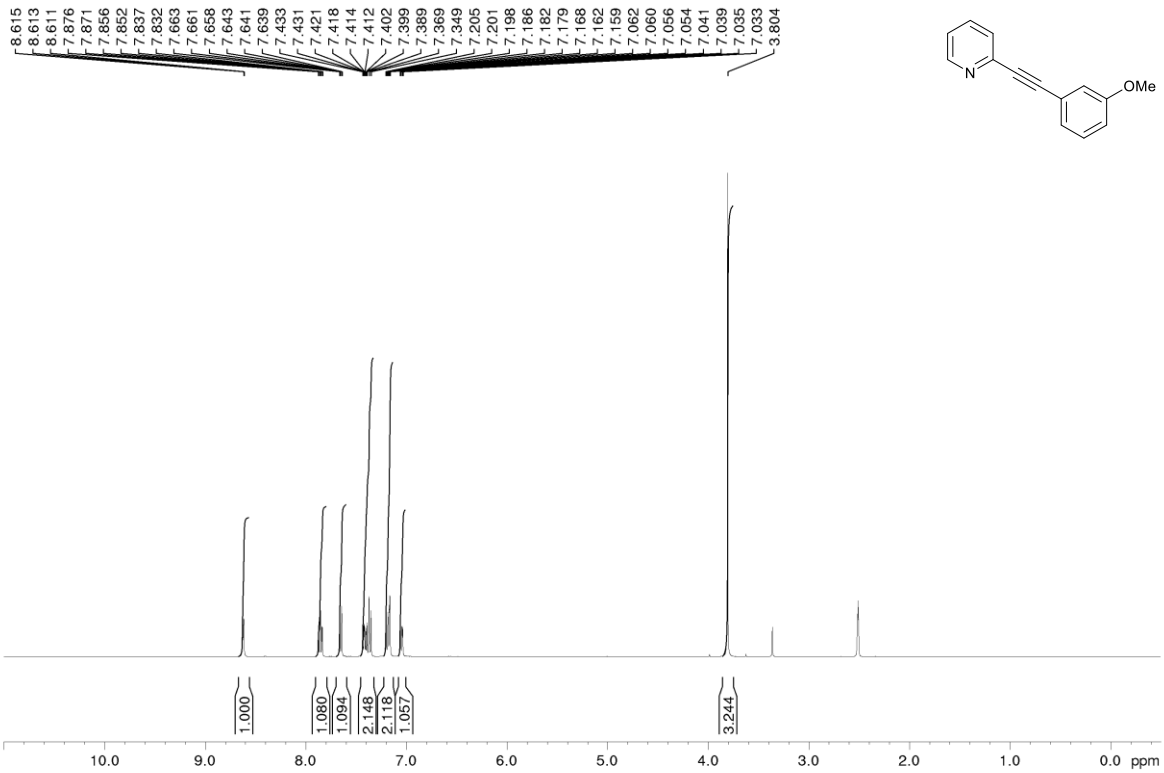
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$/DCl/$D_2O$:** 2-((4-methoxyphenyl)ethynyl)pyridinium chloride (**1c'**)



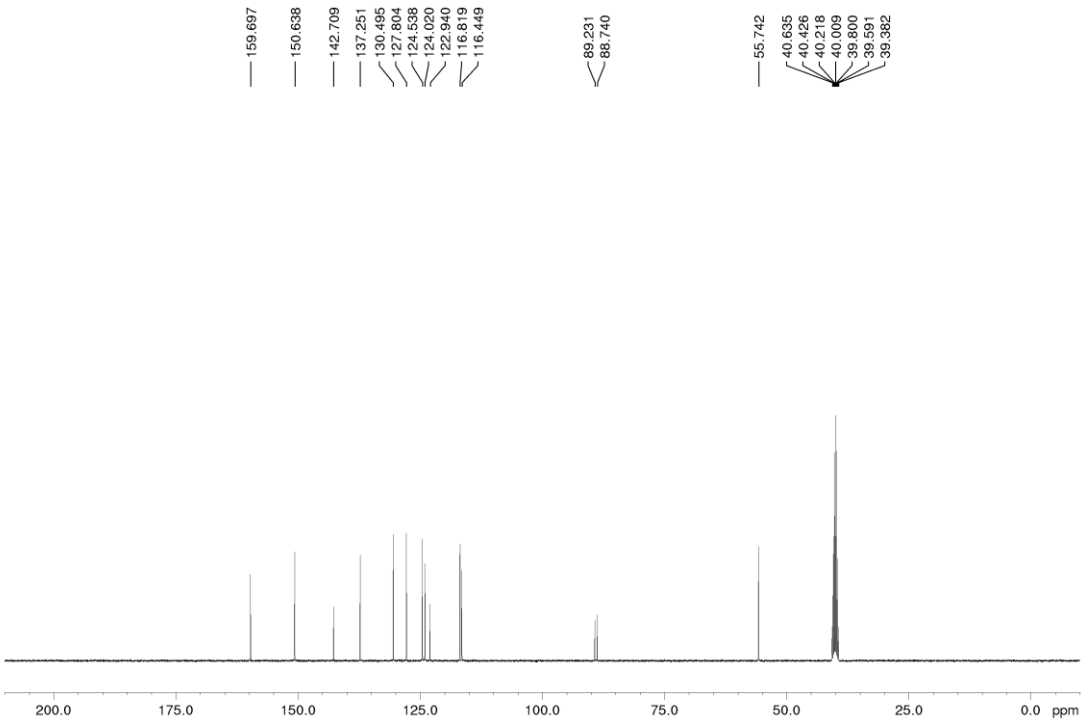

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$/DCl/$D_2O$**



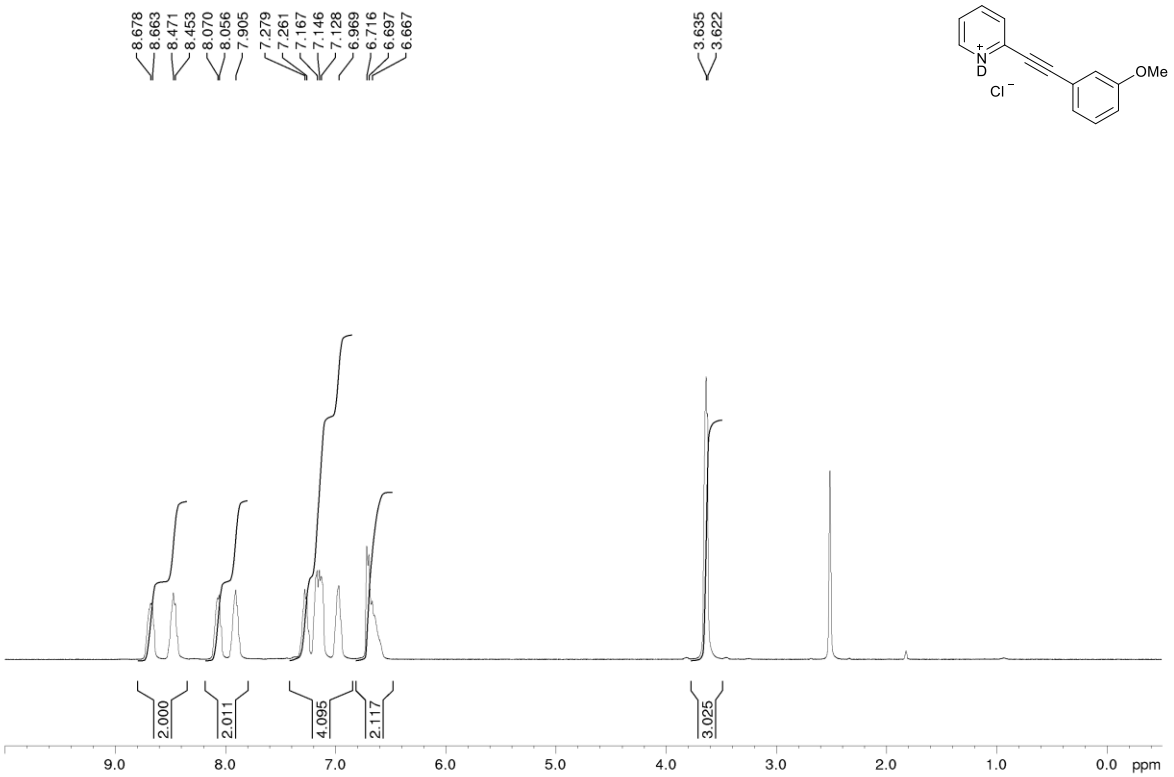
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: 2-((3-methoxyphenyl)ethynyl)pyridine (**1d**)



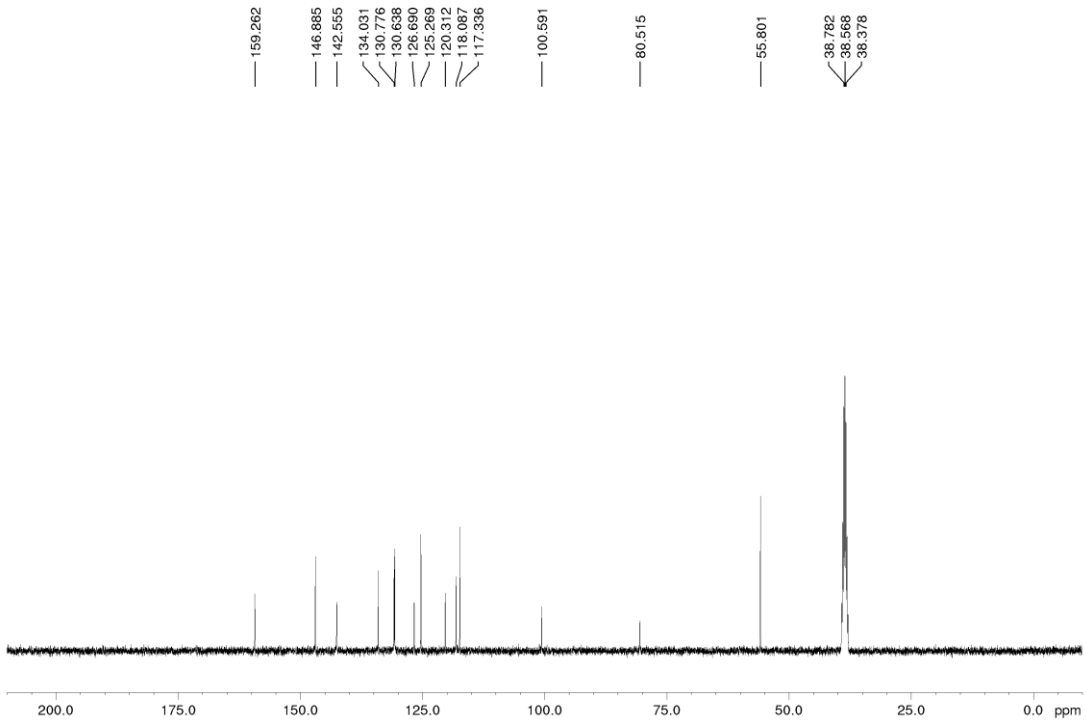

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



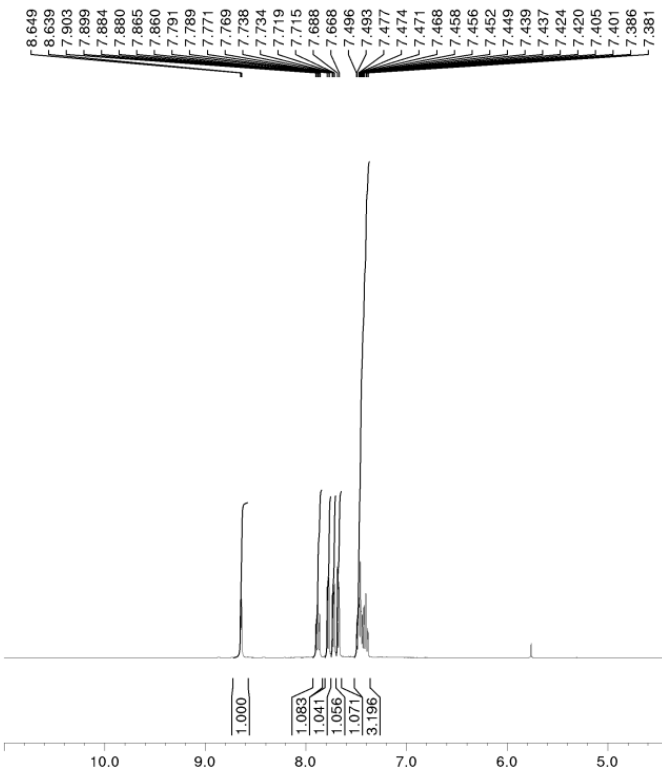
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: 2-((3-methoxyphenyl)ethynyl)pyridinium chloride (**1d'**)

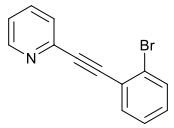



**$^{13}$C NMR (100.6 MHz), DMSO$d_6$/DCl/$D_2O$**

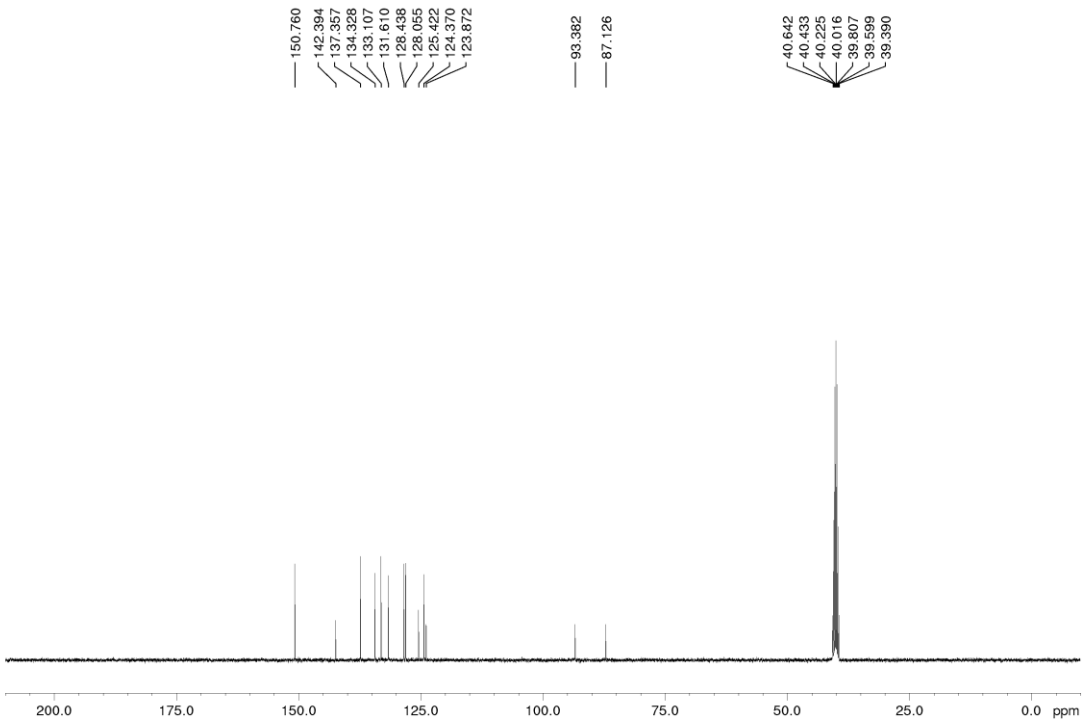


**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: 2-((2-bromophenyl)ethynyl)pyridine (**1e**)

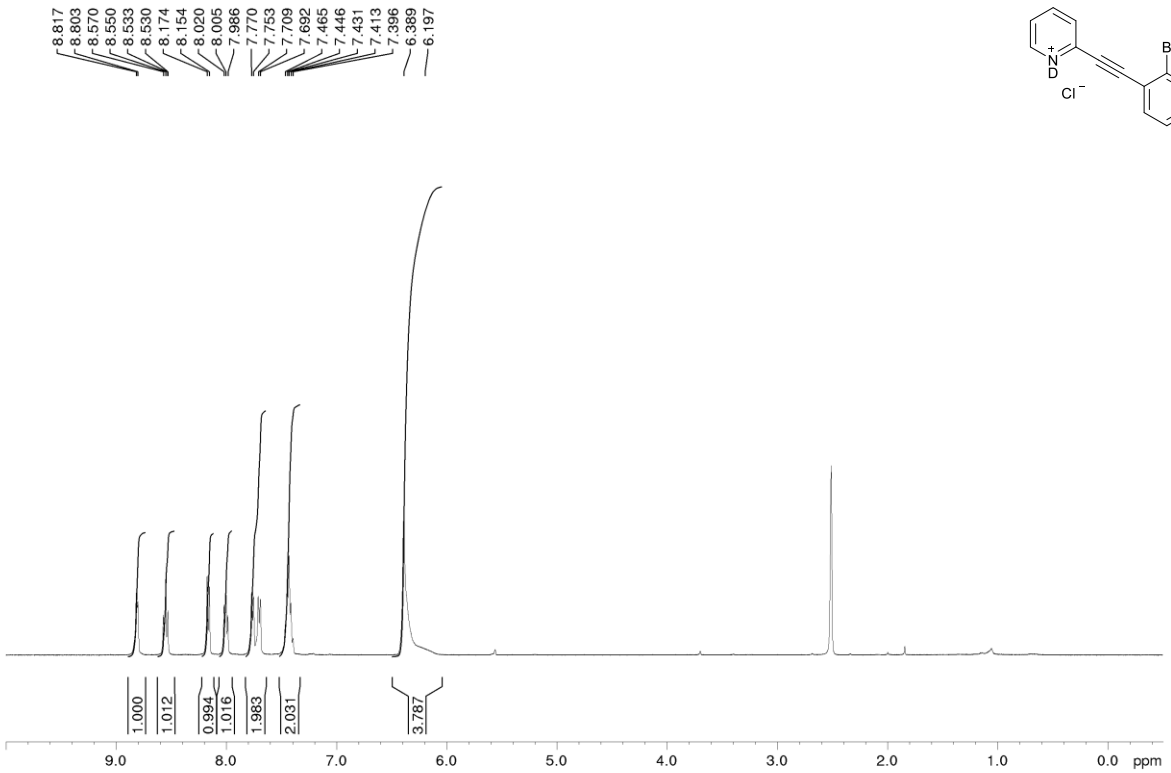


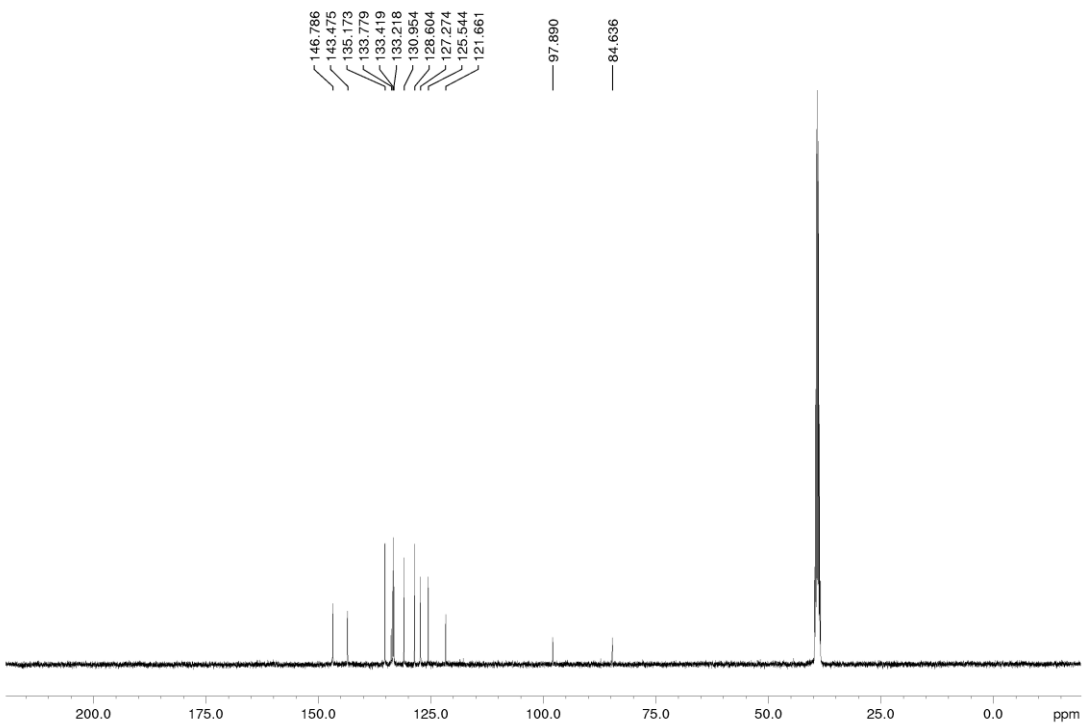

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



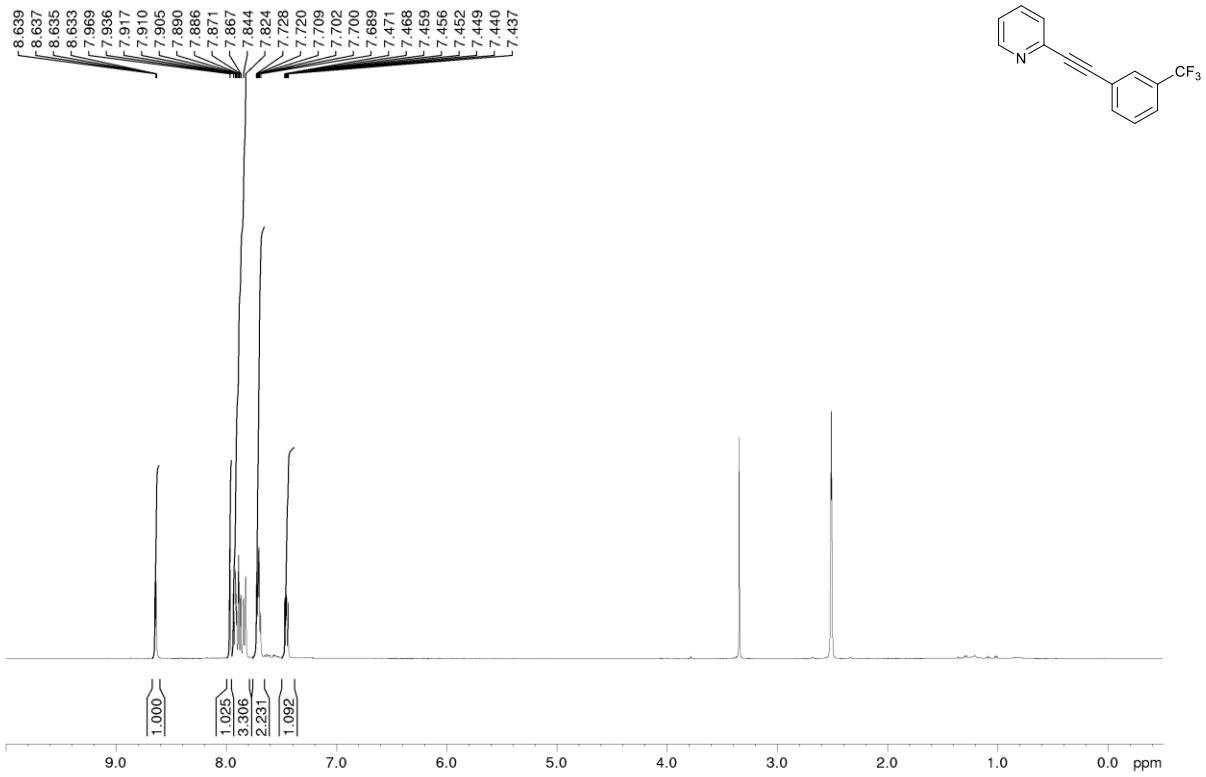
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$/DCl/$D_2O$**: 2-((2-bromophenyl)ethynyl)pyridinium chloride (**1e'**)



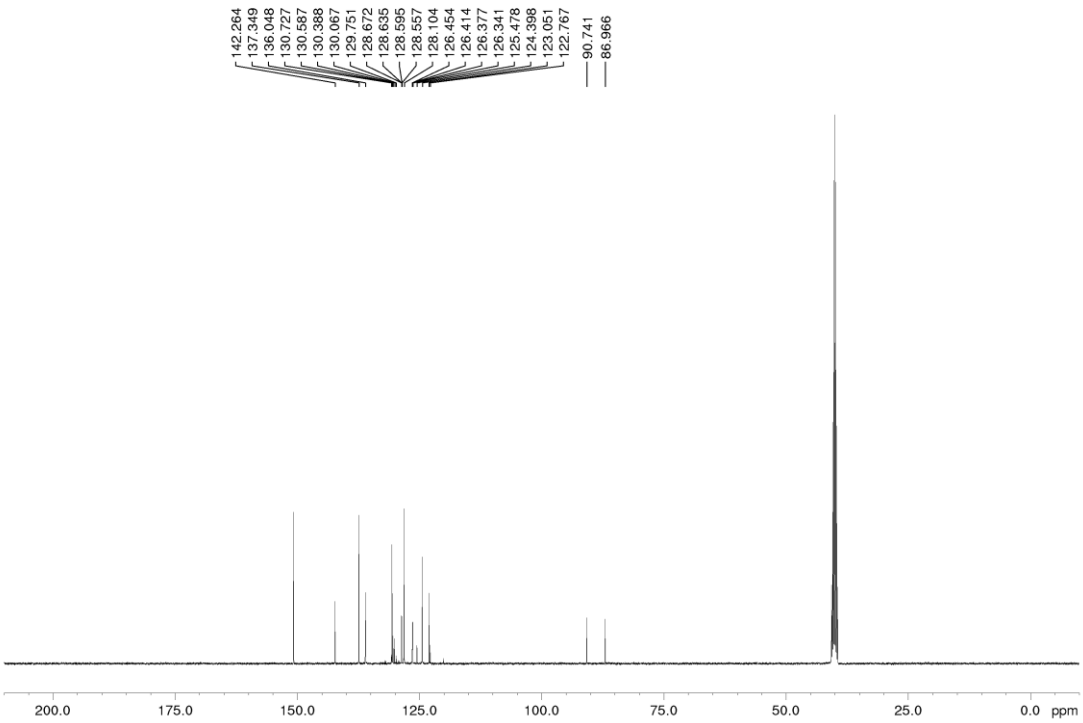

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$/DCl/$D_2O$**



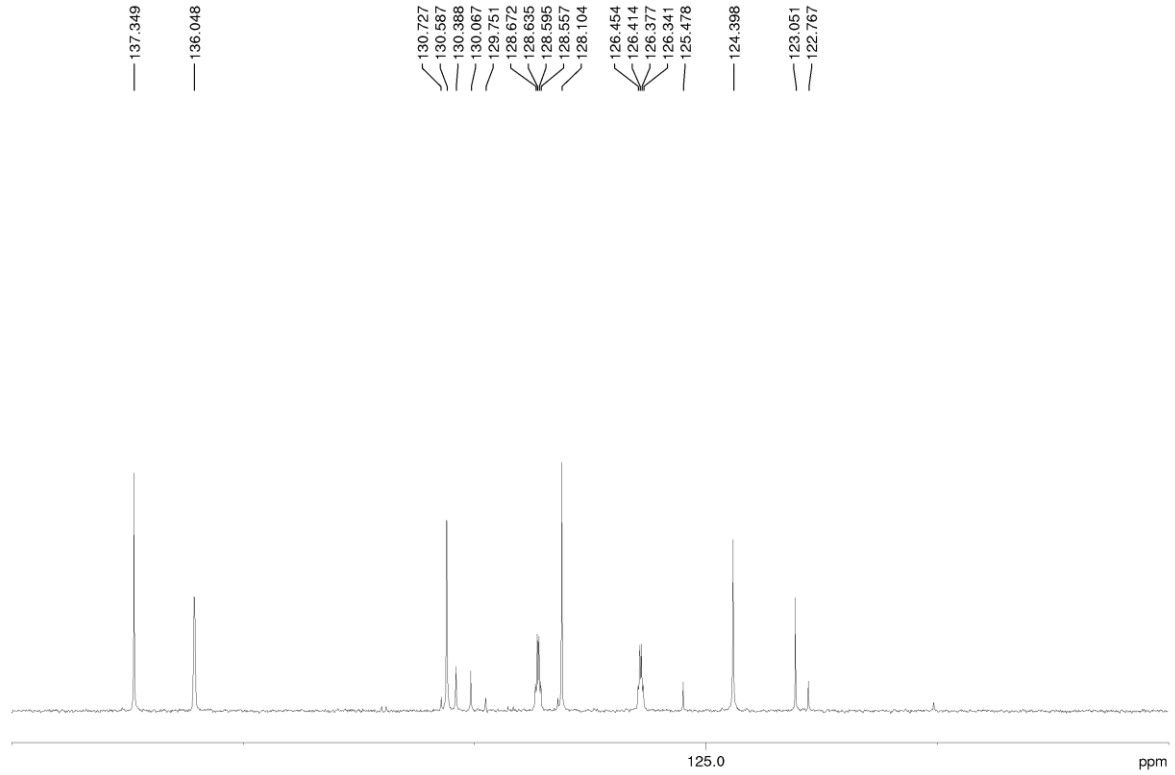
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: 2-((3-(trifluoromethyl)phenyl)ethynyl)pyridine (**1f**)



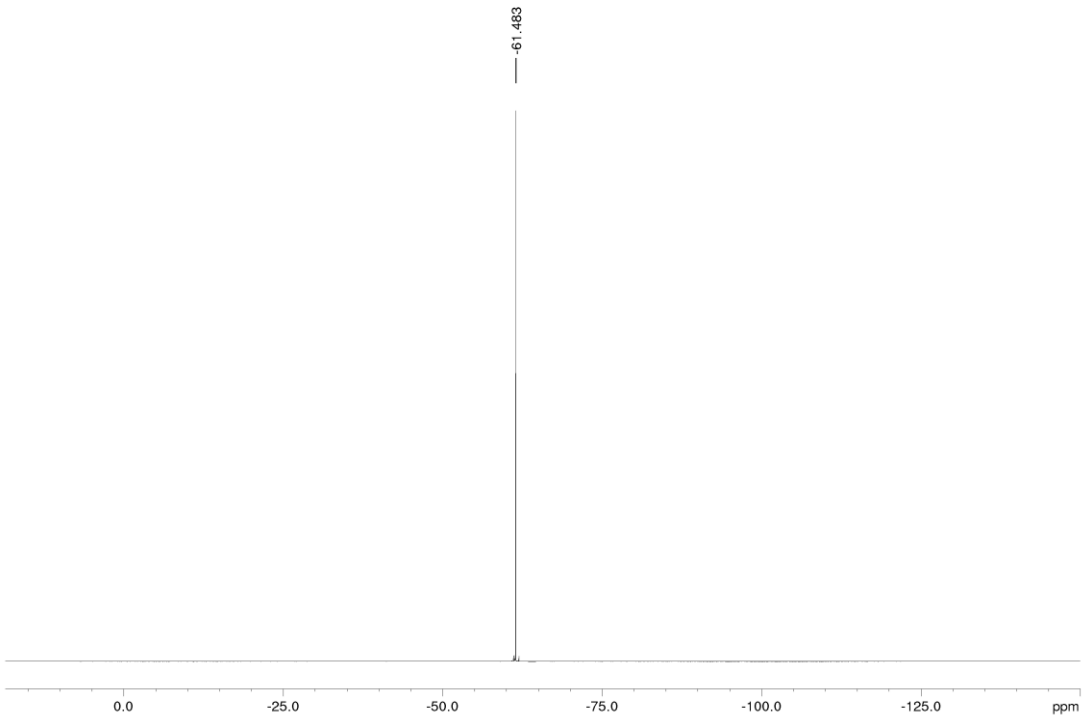

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



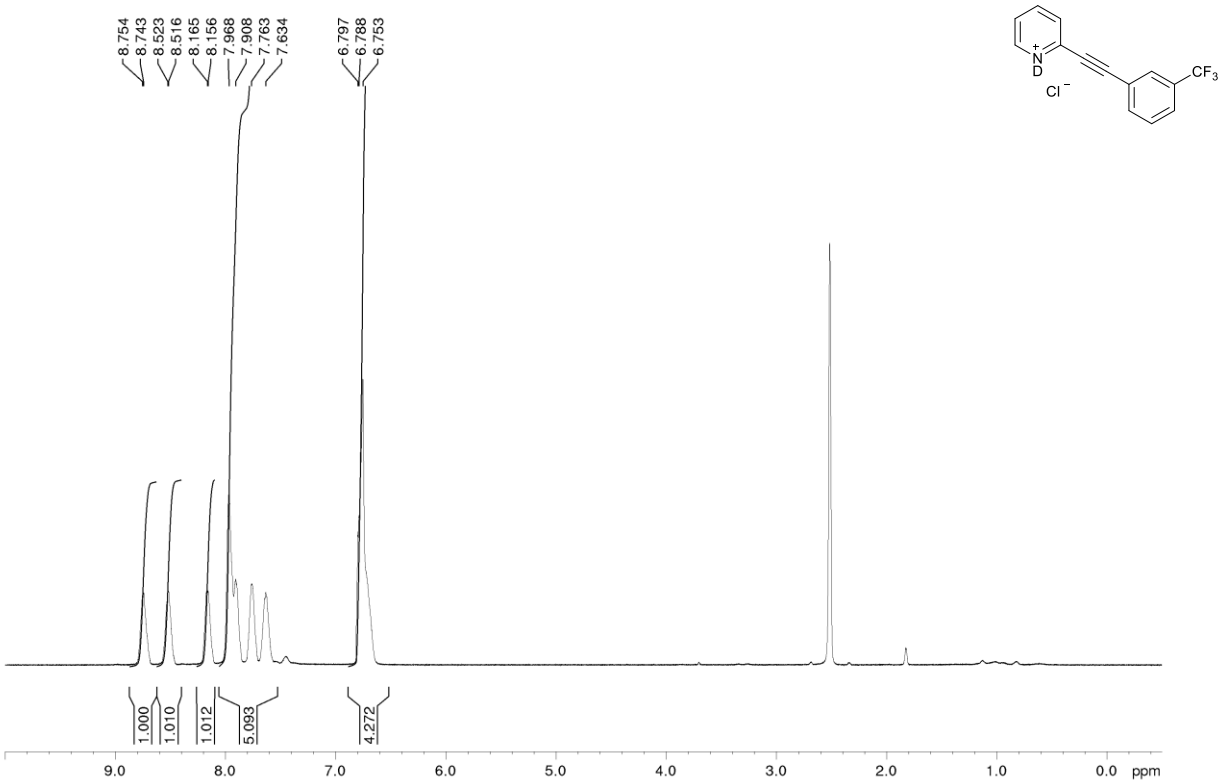
**$^{13}$C NMR (100.6 MHz), DMSO$d_6$ (expansion)**



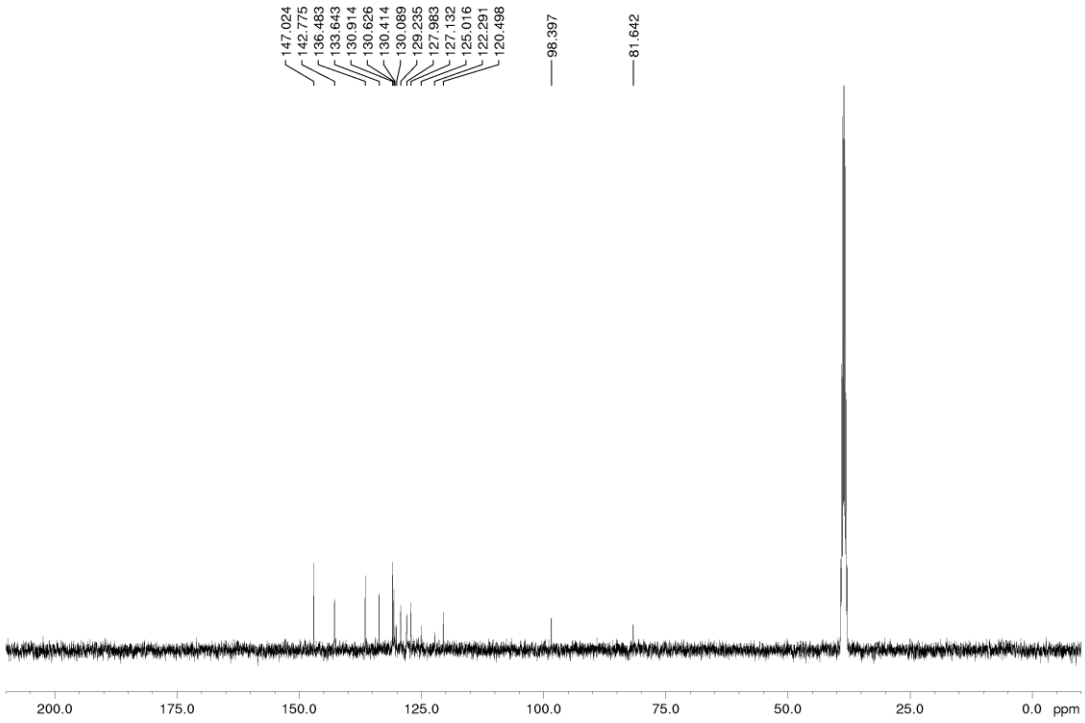

**$^{19}$F NMR (376.5 MHz), DMSO$d_6$**



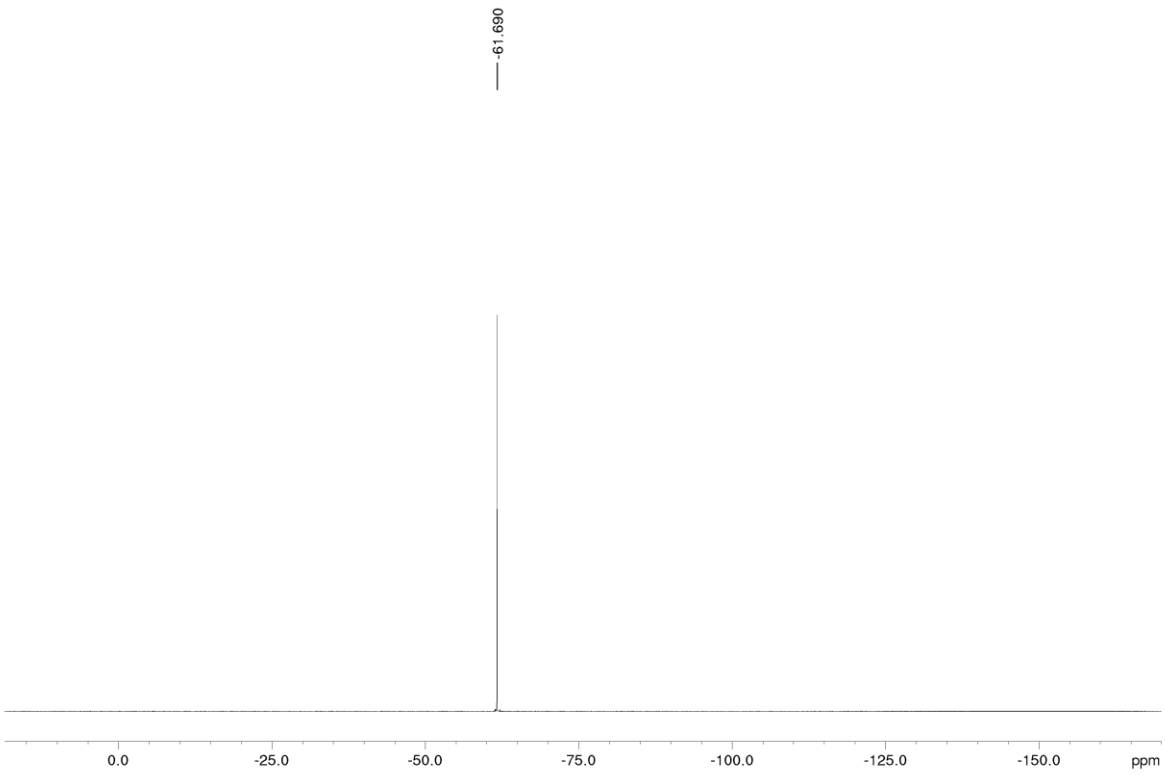
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$/DCl/$D_2O$**: 2-((3-(trifluoromethyl)phenyl)ethynyl)pyridinium chloride (**1f'**)



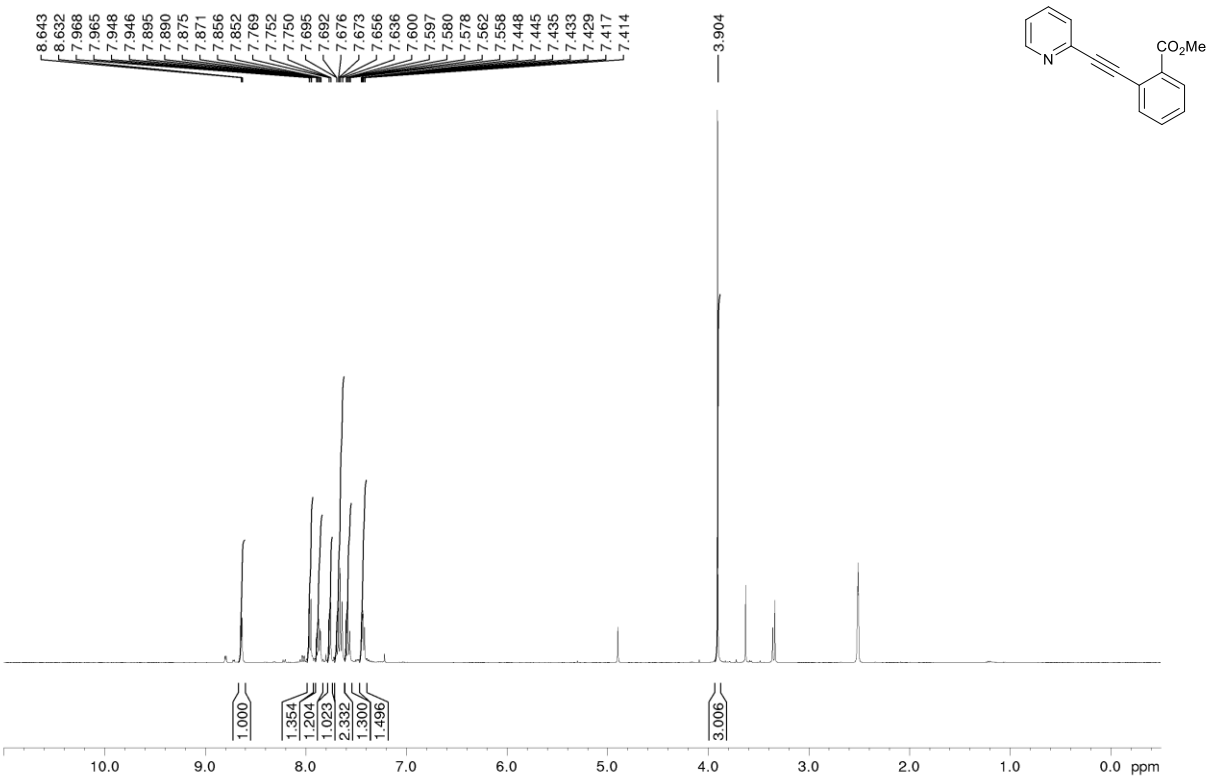

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$/DCl/$D_2O$**



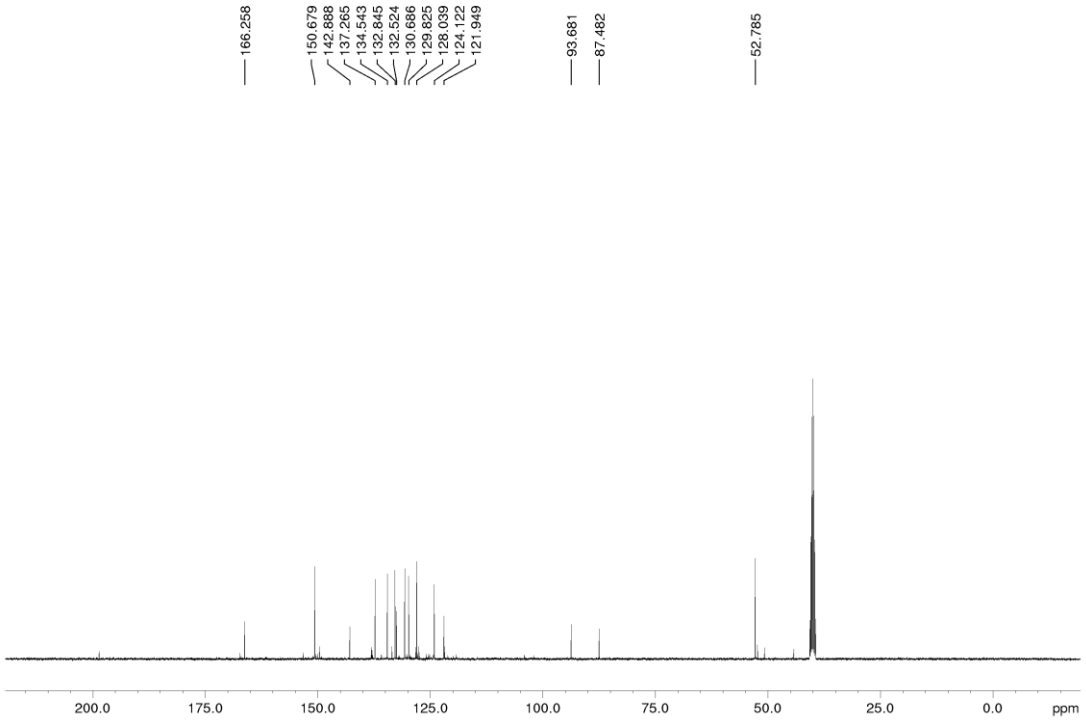
**$^{19}$F NMR (376.5 MHz), DMSO$d_6$**



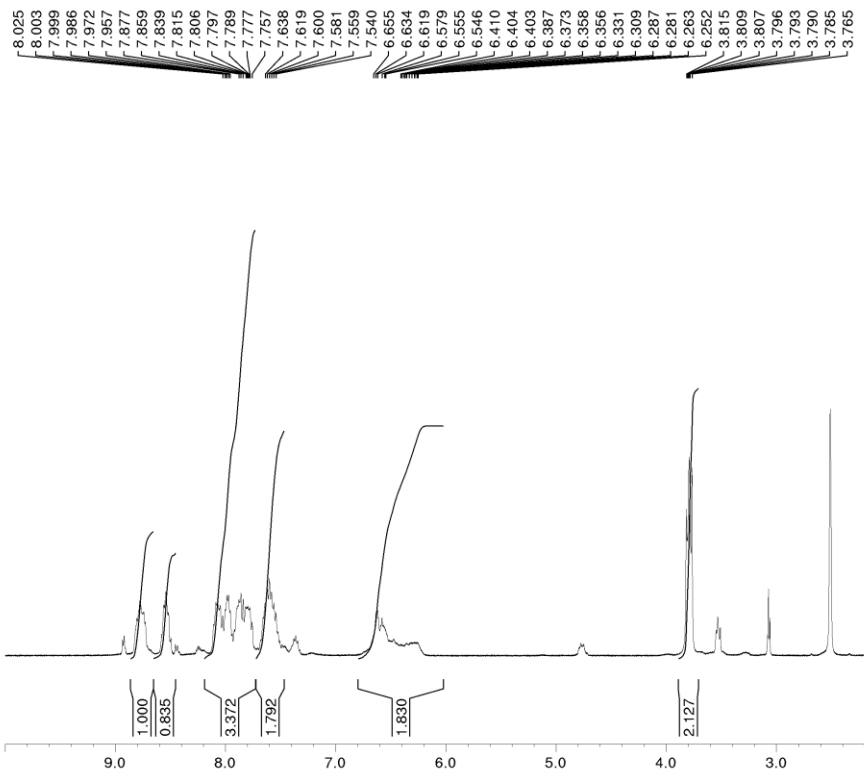
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: methyl 2-(pyridin-2-ylethynyl)benzoate (**1g**)

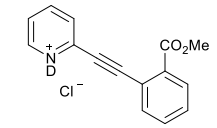



**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**

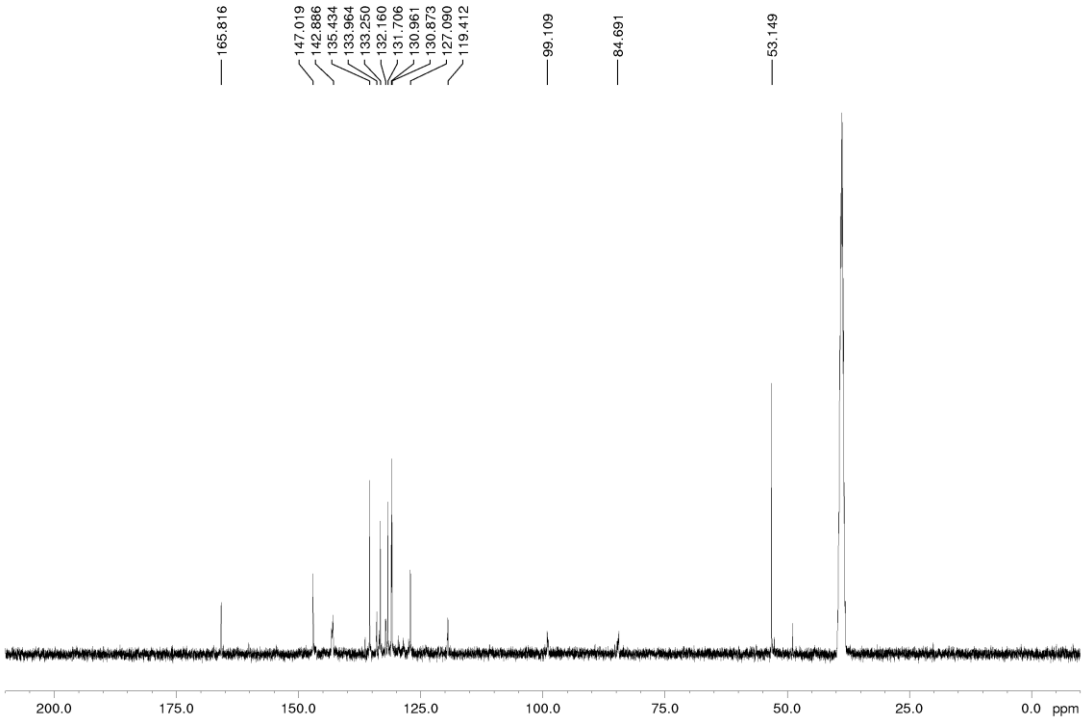


**$^{1}$H NMR (400.13 MHz), DMSO$d_6$/DCl/$D_2O$**: 2-((2-(methoxycarbonyl)phenyl)ethynyl)pyridinium chloride (**1g'**)

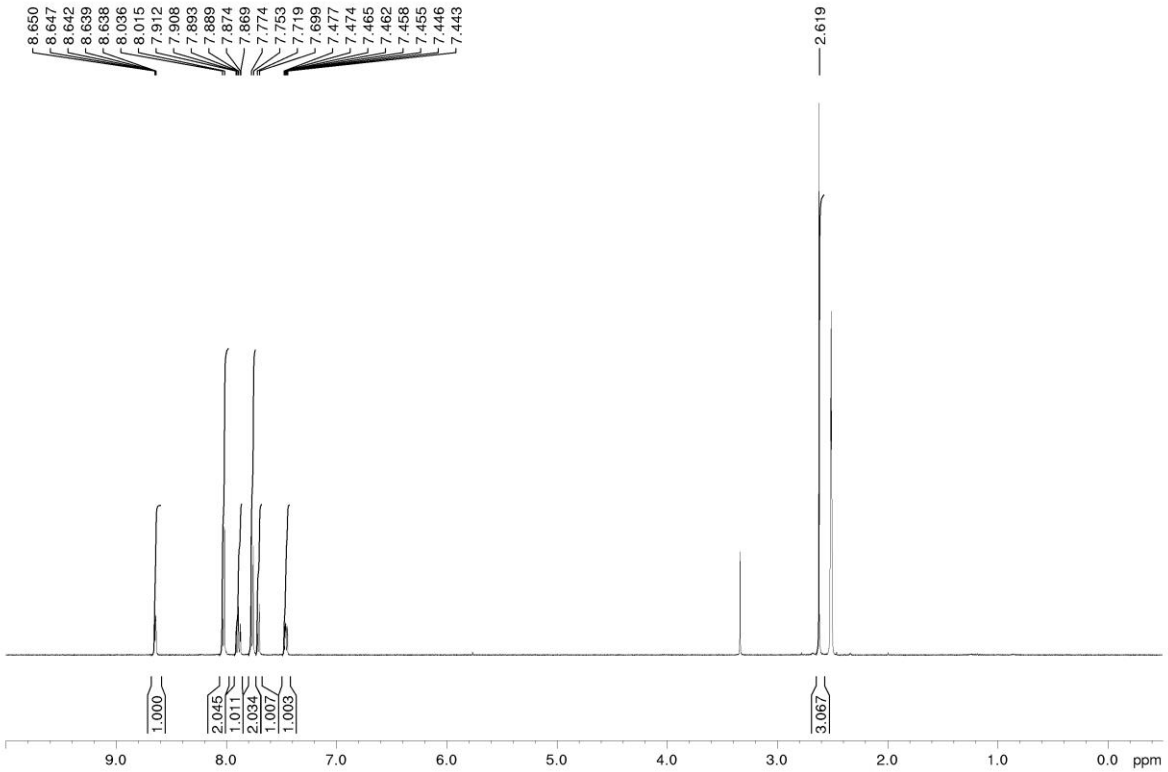


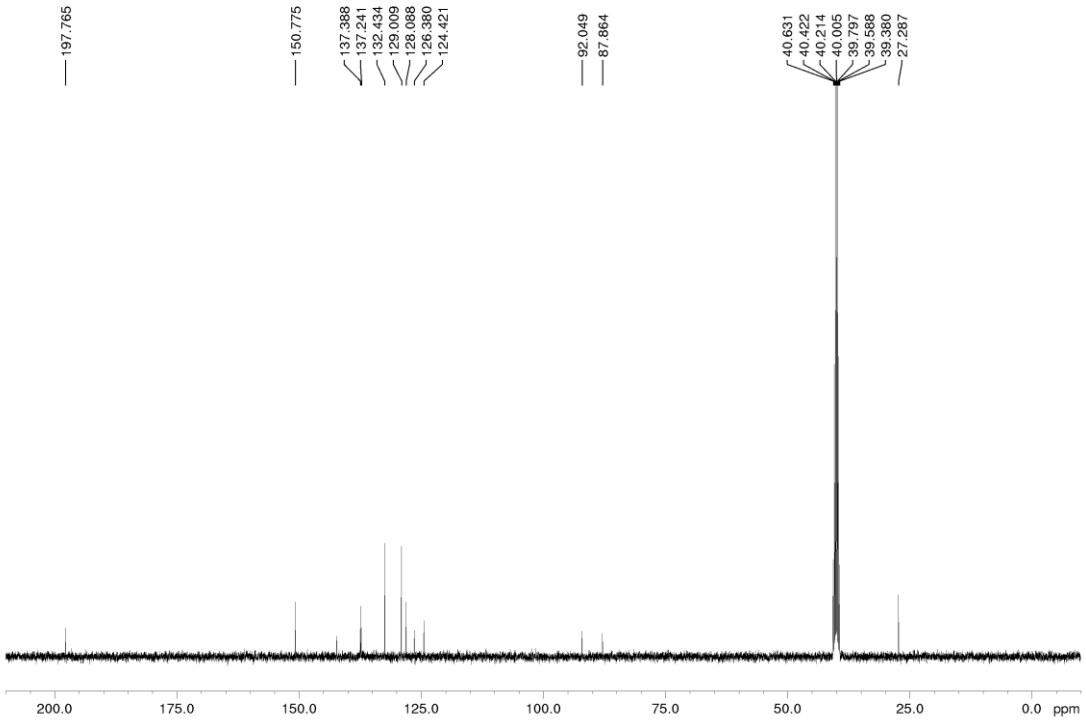

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$/DCl/$D_2O$**



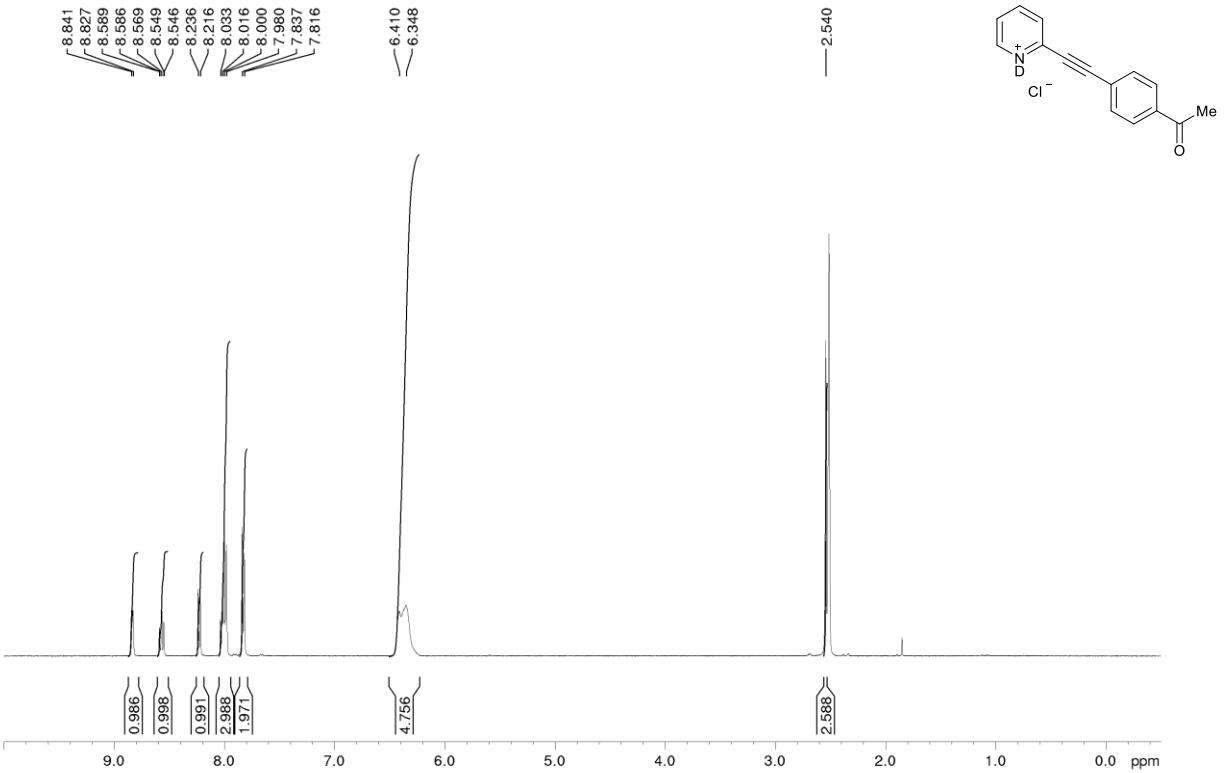
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$**: 1-(4-(pyridin-2-ylethynyl)phenyl)ethanone (**1h**)



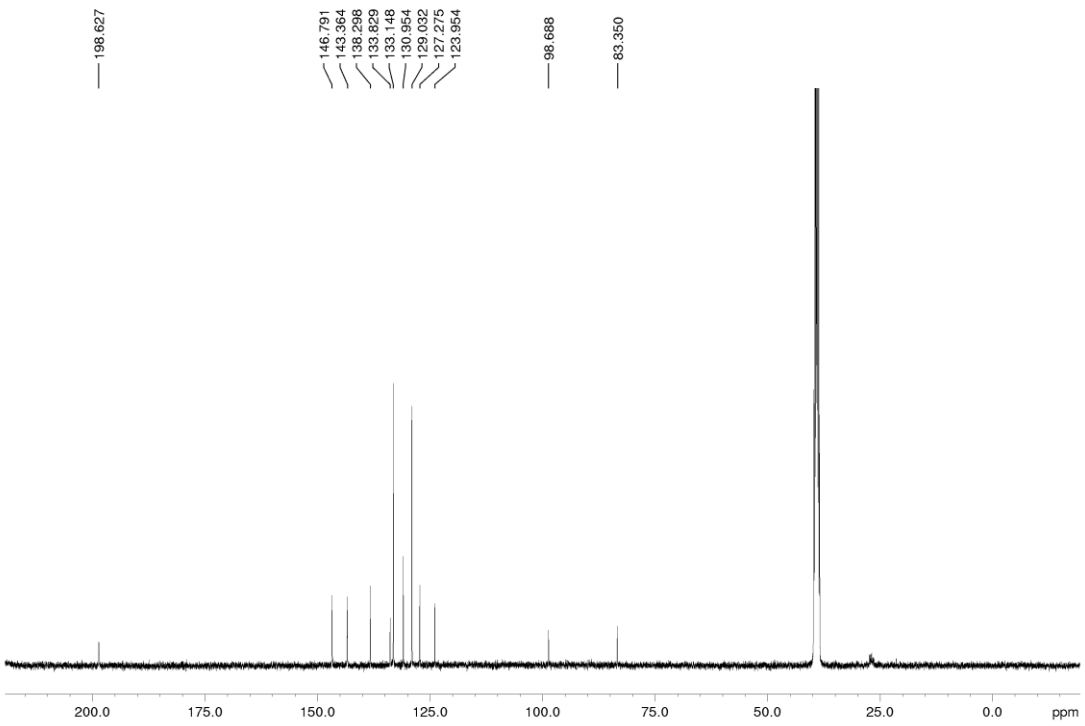

**$^{13}$C NMR (100.6 MHz), DMSO$d_6$**



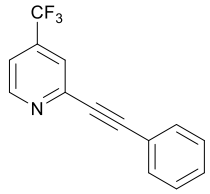
**$^{1}$H NMR (400.13 MHz), DMSO$d_6$/DCl/$D_2O$**: 2-((4-acetylphenyl)ethynyl)pyridinium chloride (**1h'**)

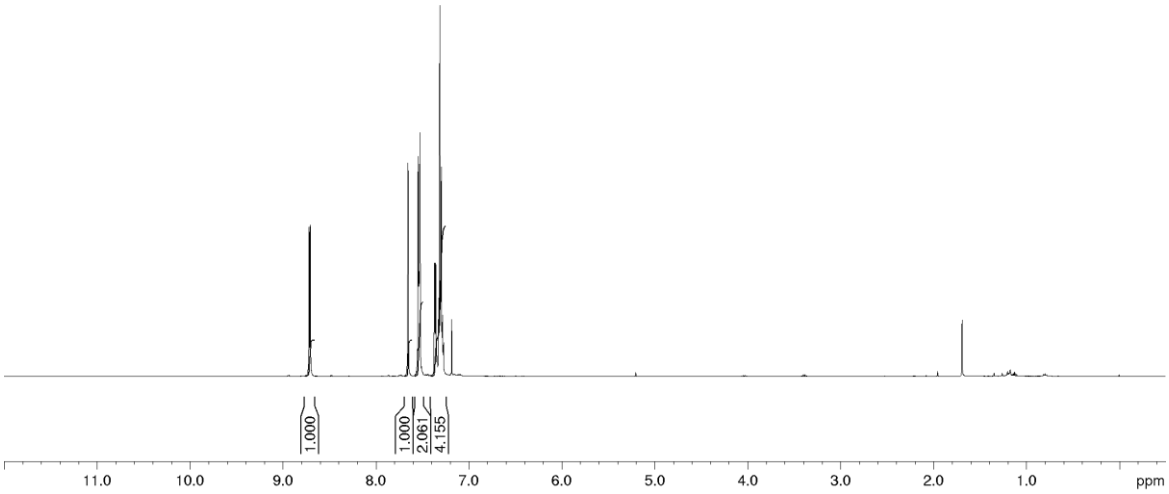



**$^{13}$C NMR (100.6 MHz), DMSO$d_6$/DCl/$D_2O$**

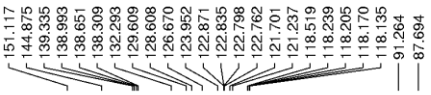


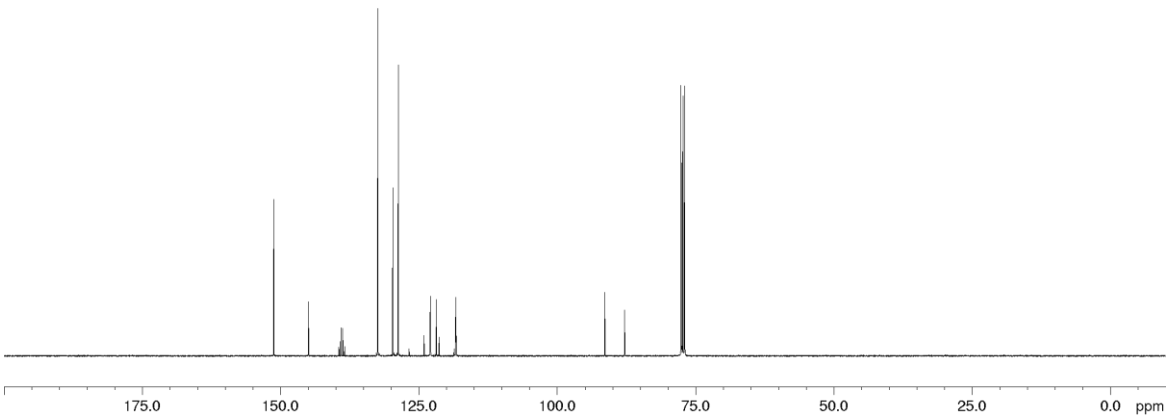
**$^{1}$H NMR (400.13 MHz), $CDCl_3$**: 2-(phenylethynyl)-4-(trifluoromethyl)pyridine (**6a**)

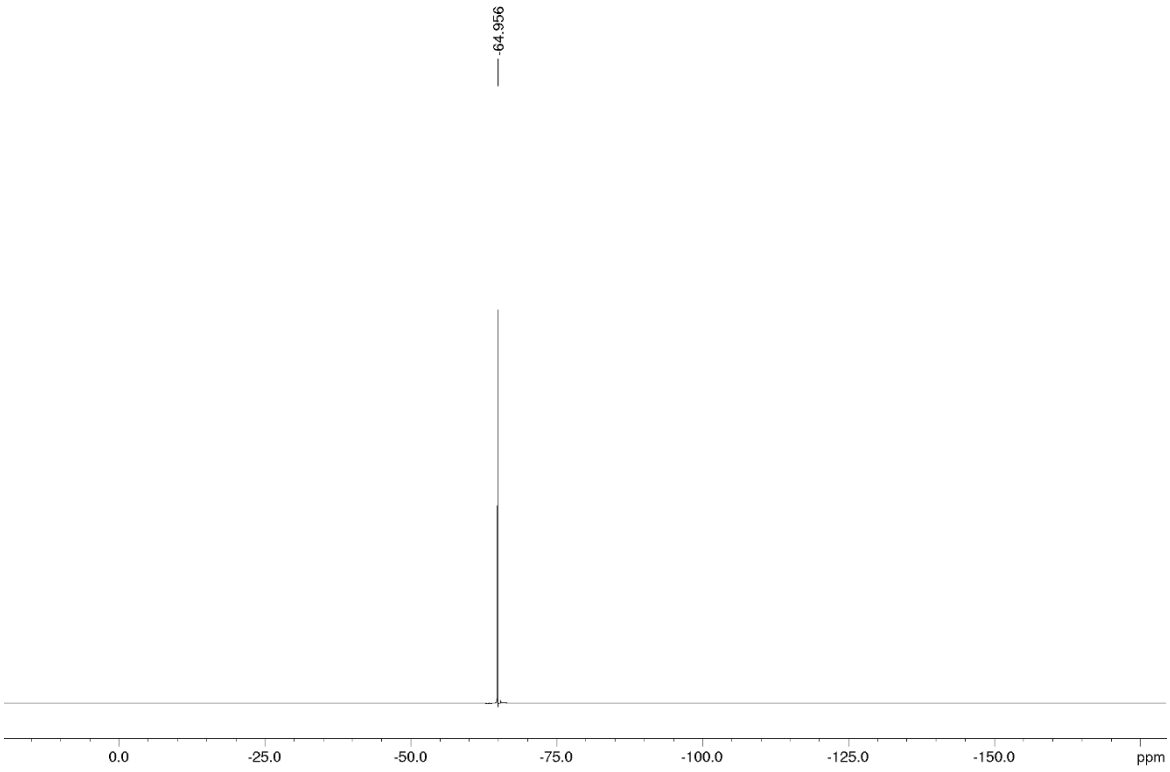




**$^{13}$C NMR (100.6 MHz), $CDCl_3$**

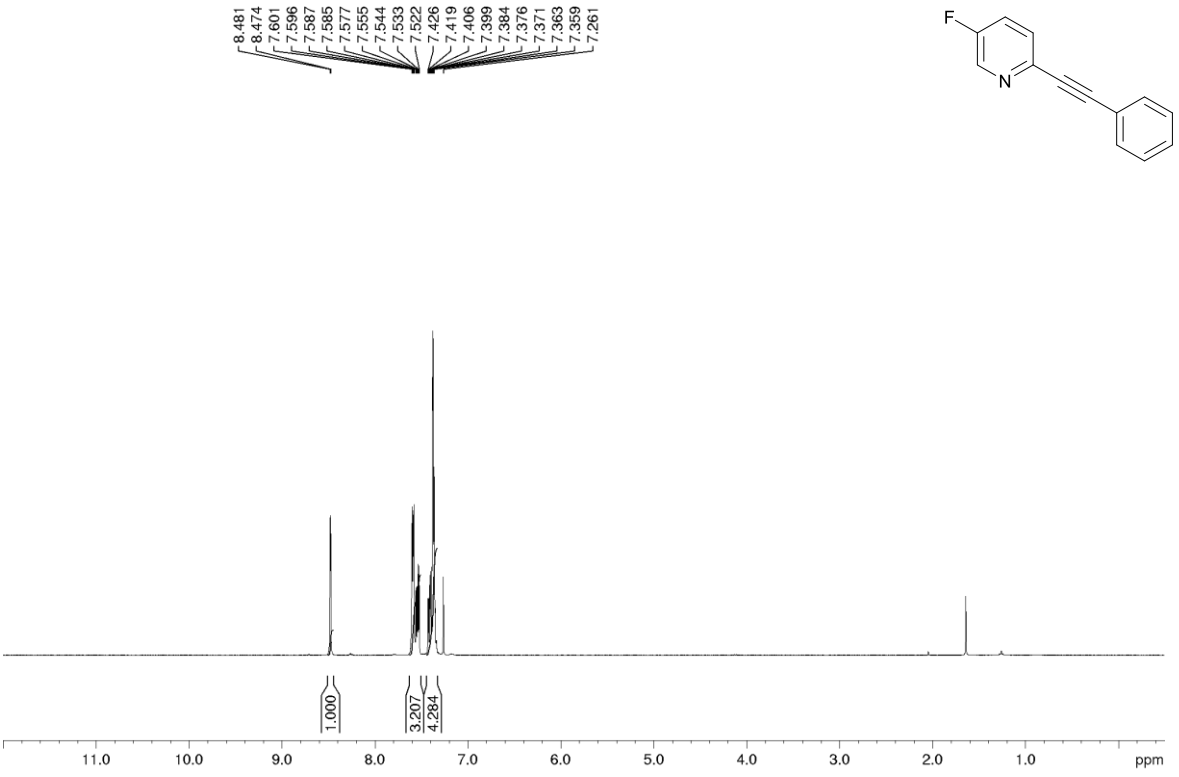


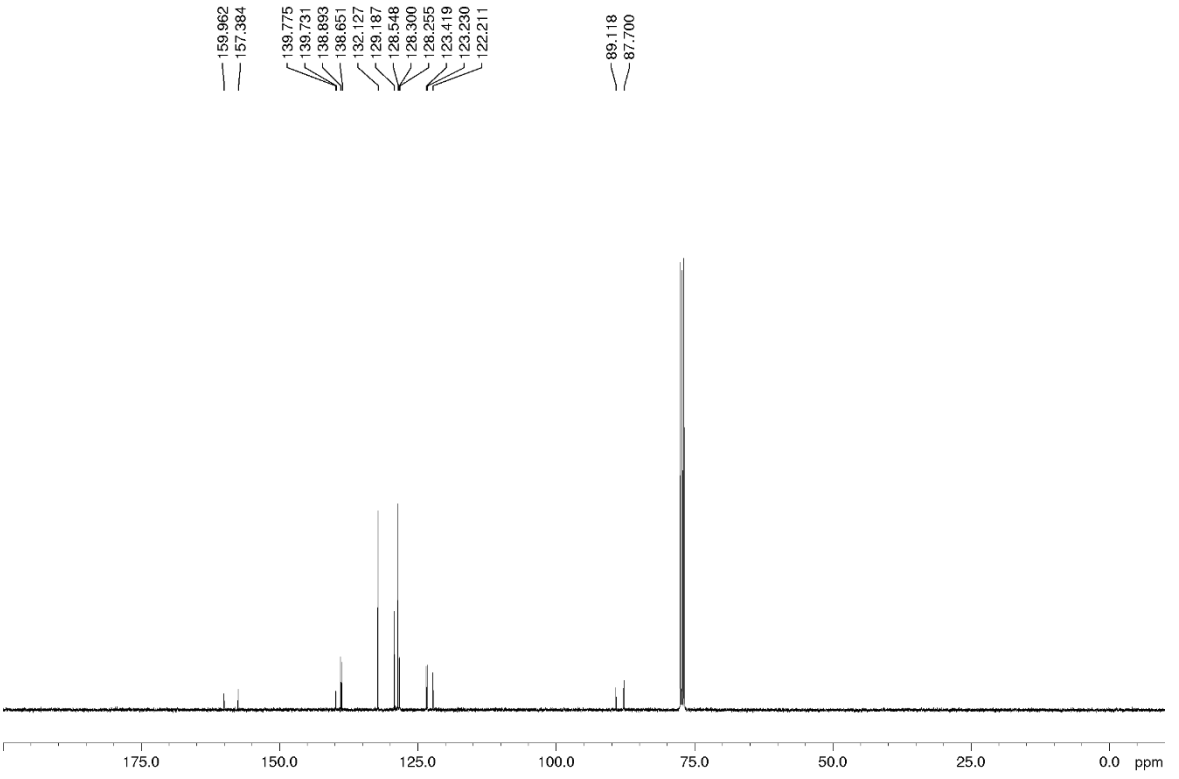
**$^{19}$F NMR (376.5 MHz MHz), $CDCl_3$**



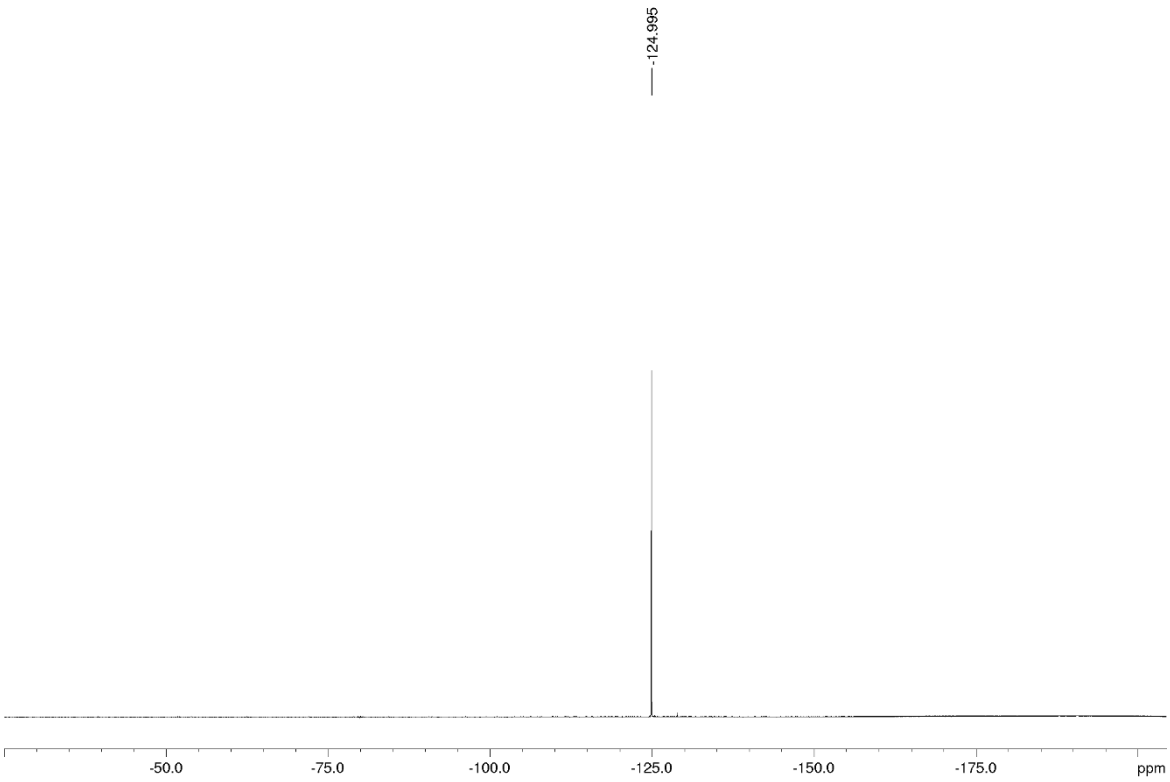
**$^{1}$H NMR (400.13 MHz), $CDCl_3$**: 5-fluoro-2-(phenylethynyl)pyridine (**6b**)



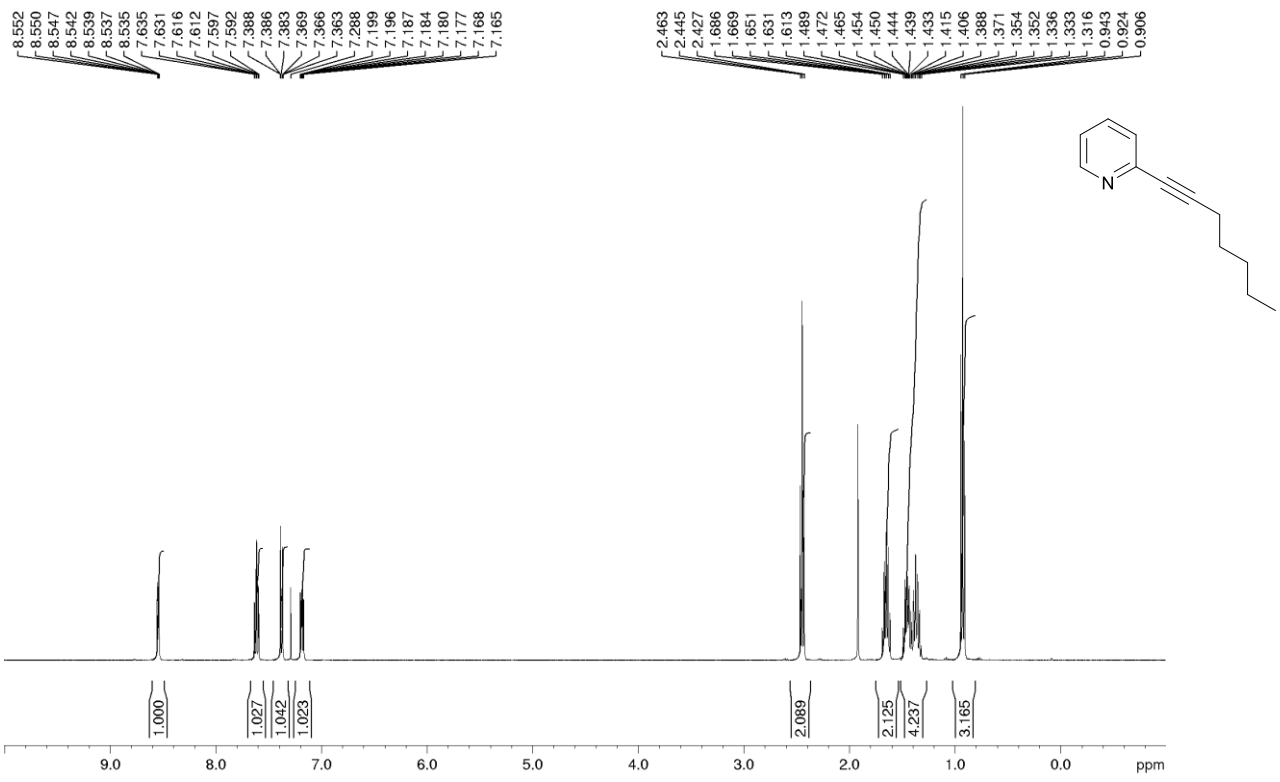

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



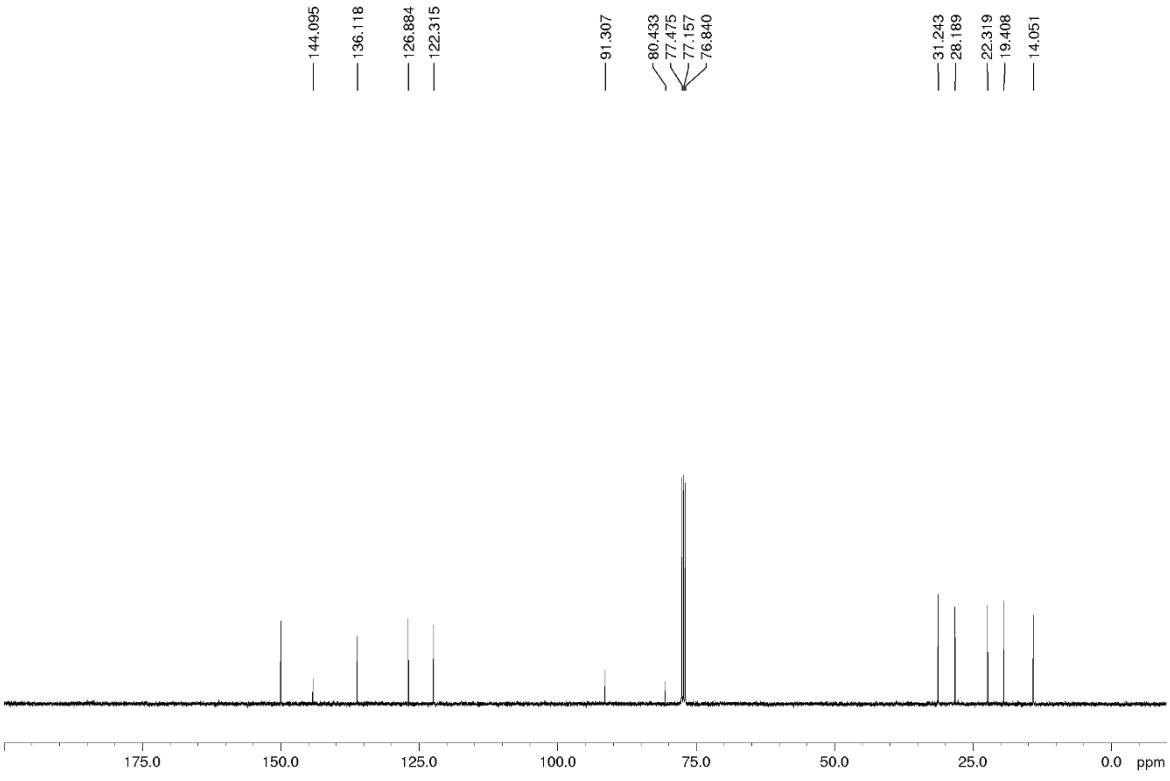
**$^{19}$F NMR (376.5 MHz MHz), $CDCl_3$**



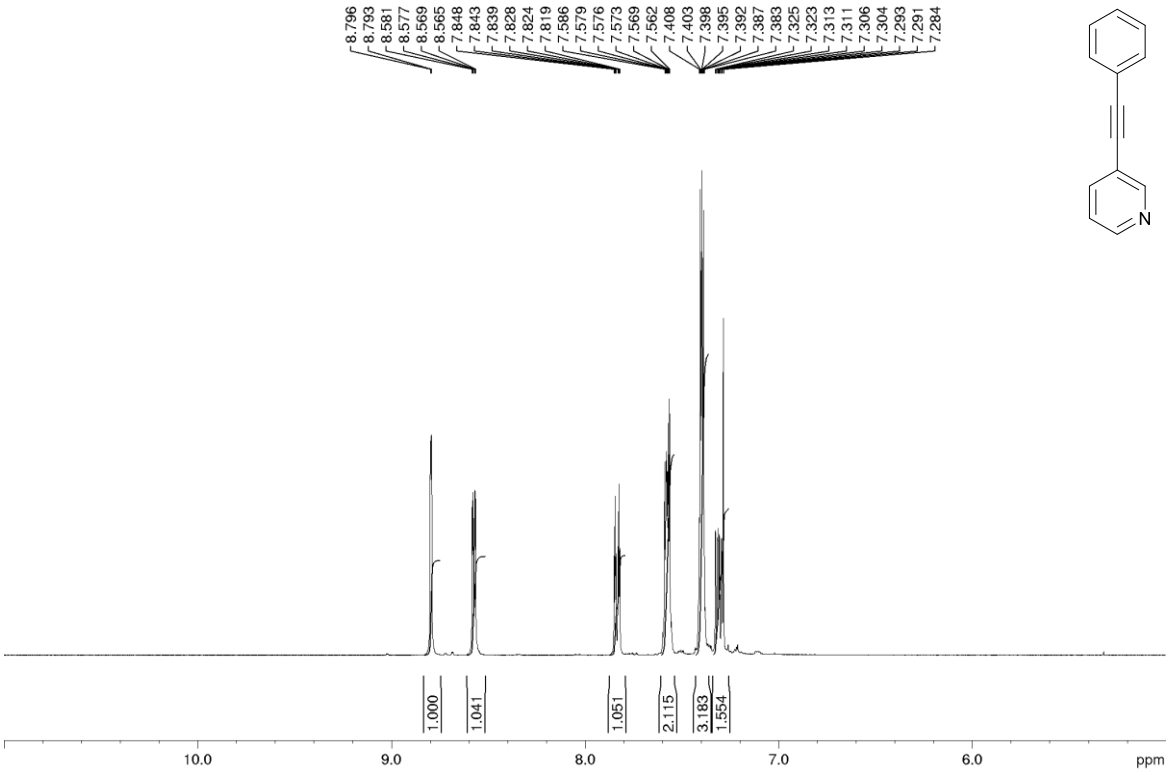
**$^{1}$H NMR (400.13 MHz), $CDCl_3$**: 2-(hept-1-yn-1-yl)pyridine (**6c**)



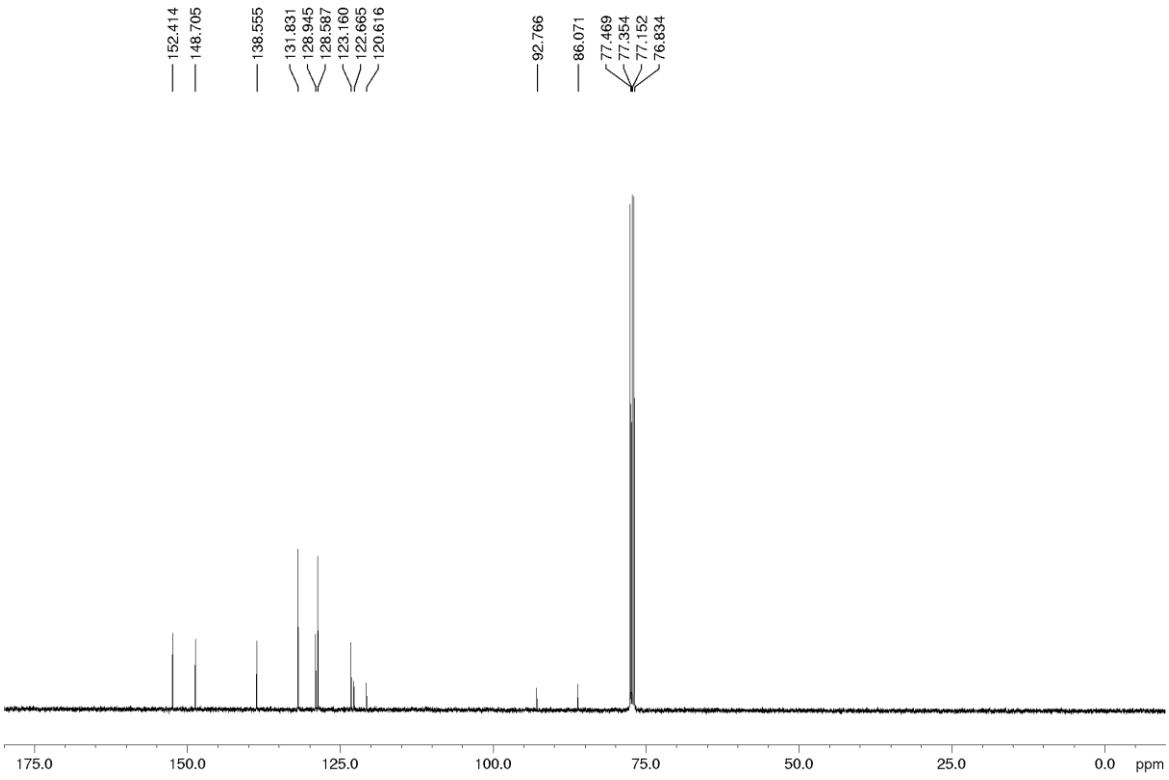

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



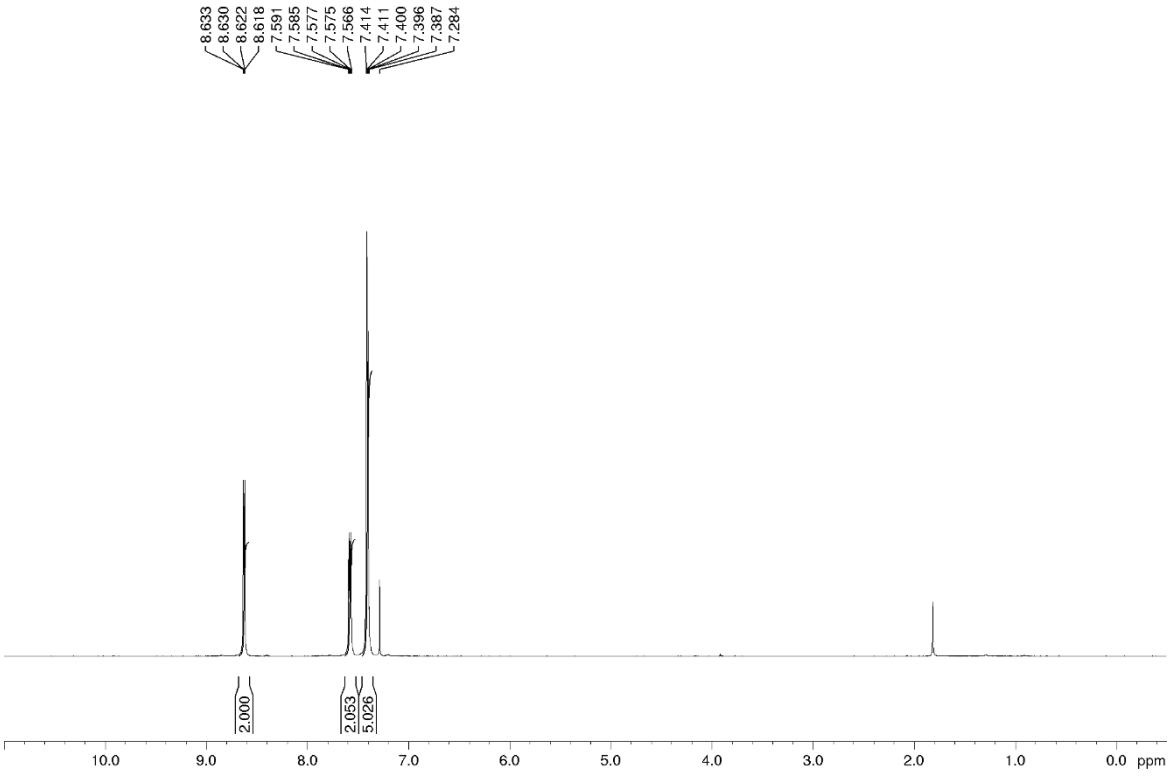
**$^{1}$H NMR (400.13 MHz), $CDCl_3$**: 3-(phenylethynyl)pyridine (**8**)



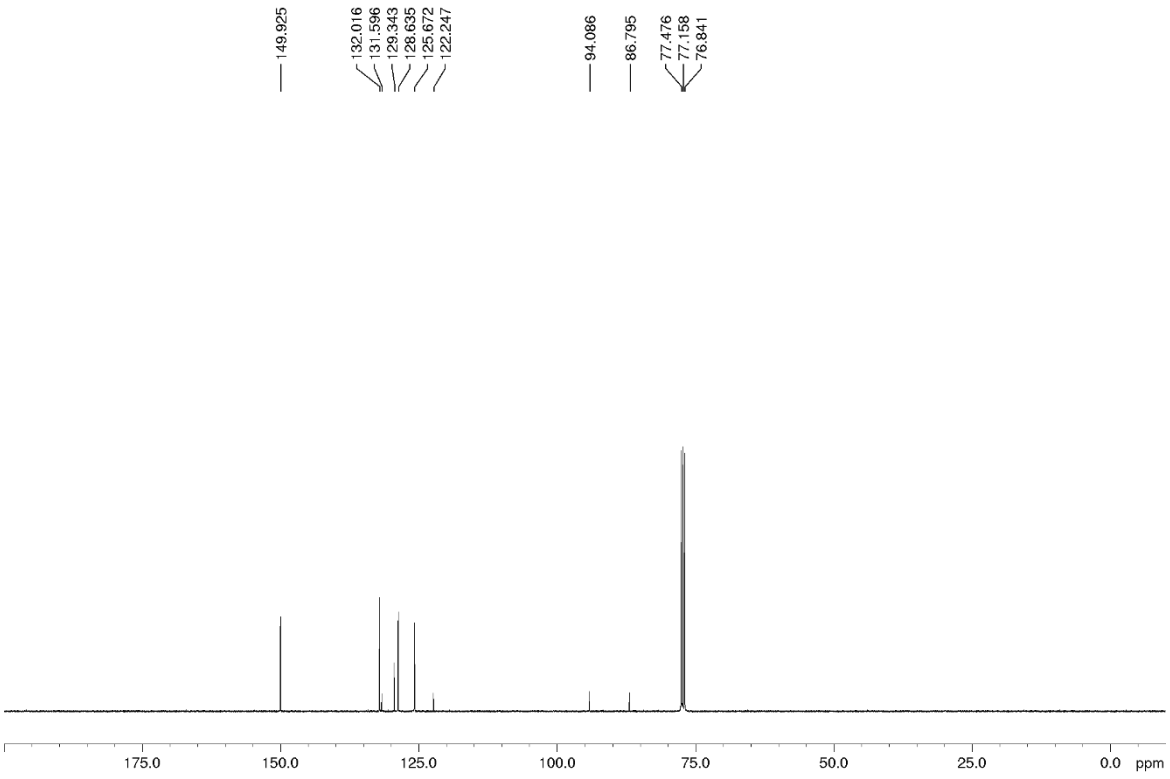

**$^{13}$C NMR (100.6 MHz), $CDCl_3$**



**$^{1}$H NMR (400.13 MHz), $CDCl_3$**: 4-(phenylethynyl)pyridine (**9**)

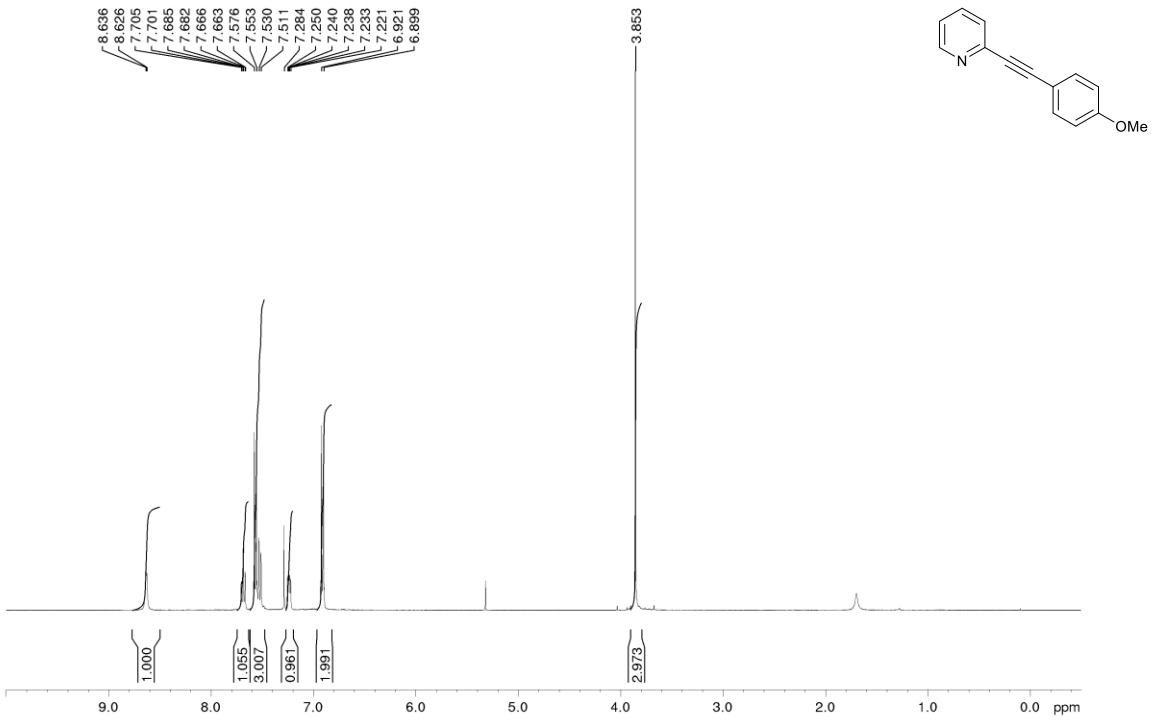



**$^{13}$C NMR (100.6 MHz), $CDCl_3$**

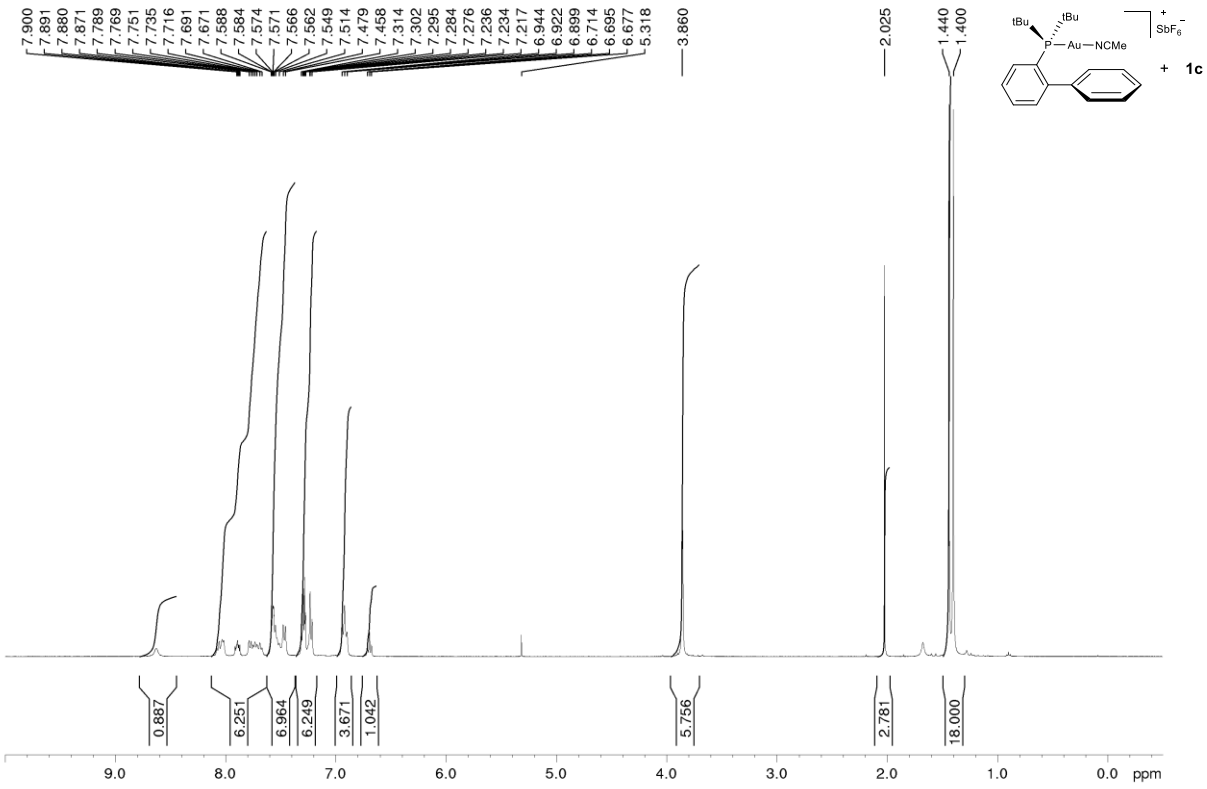


**$^{1}$H, $^{13}$C SPECTRA OF [(LIGAND)Au(2-(ARYLETHYNYL)PYRIDINE)]$^{+}$ COMPLEXES**

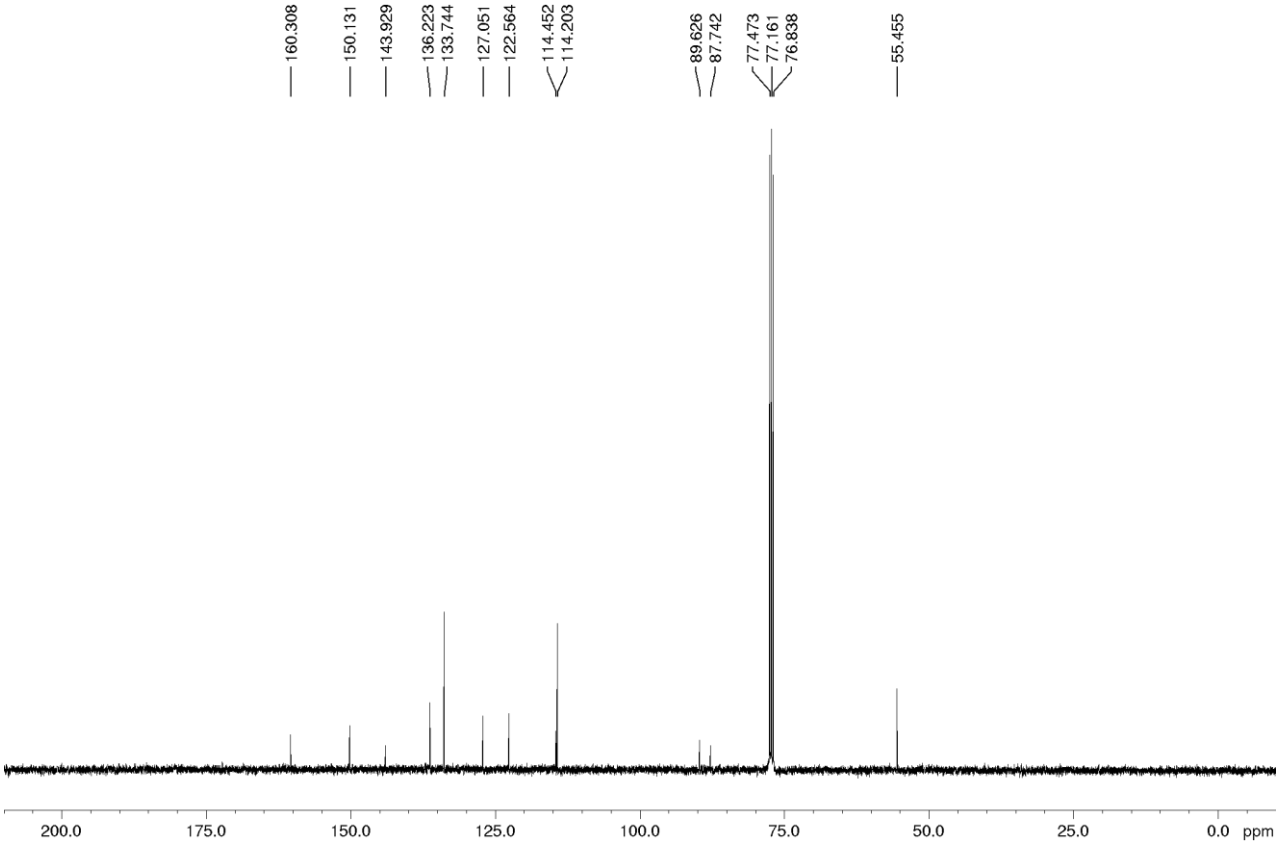
**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** 2-((4-methoxyphenyl)ethynyl)pyridine (**1c**)



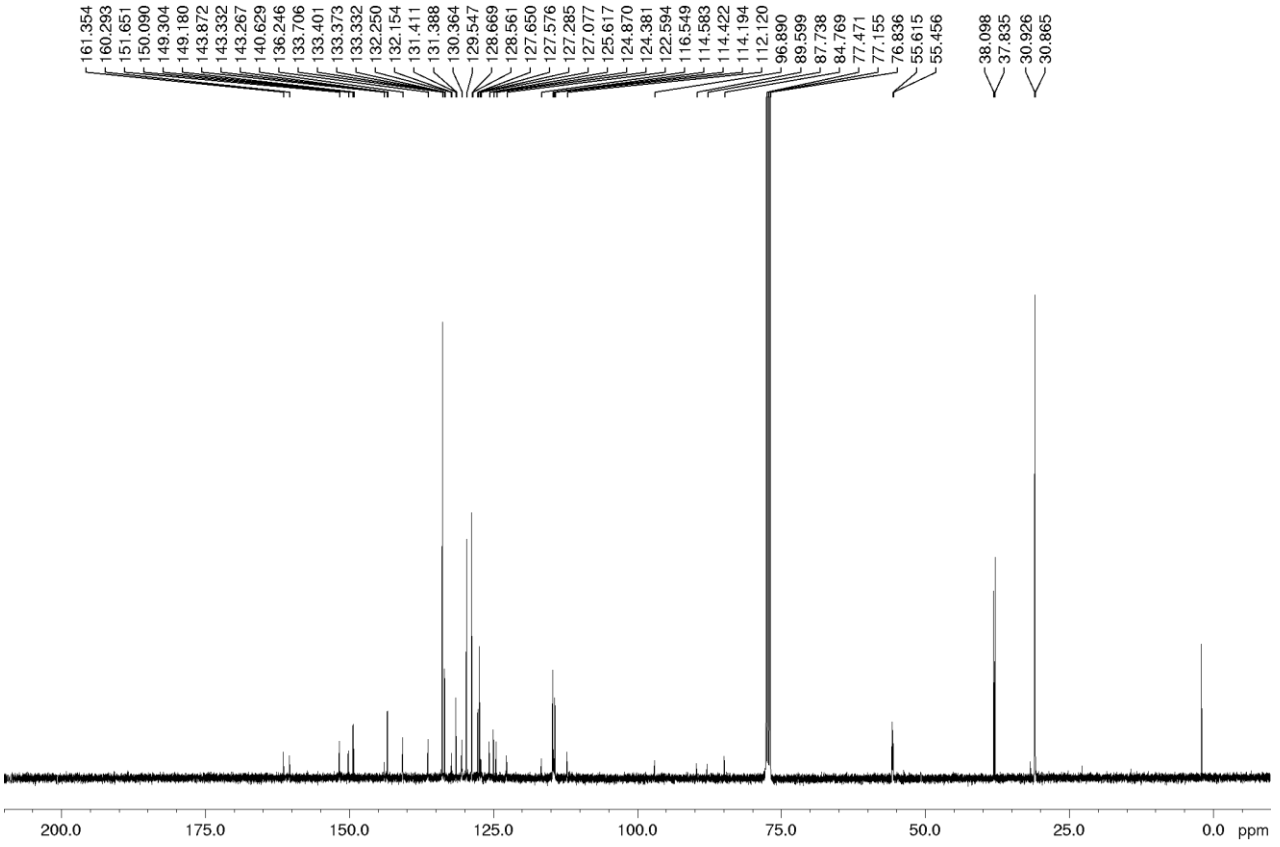

**$^{1}$H NMR (400.13 MHz), $CDCl_3$:** 2-((4-methoxyphenyl)ethynyl)pyridine (1c) + $JPAu(CH_3CN)SbF_6$



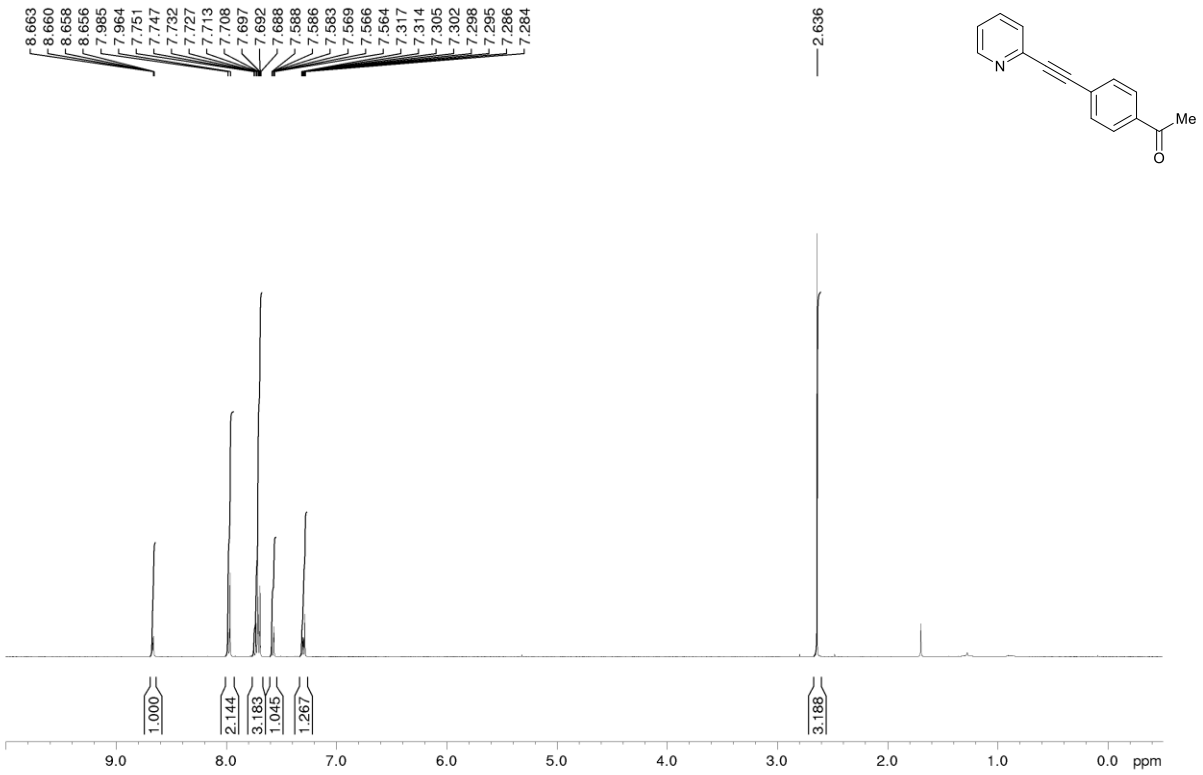
**$^{13}$C NMR (100.6 MHz), $CDCl_3$:** 2-((4-methoxyphenyl)ethynyl)pyridine (**1c**)



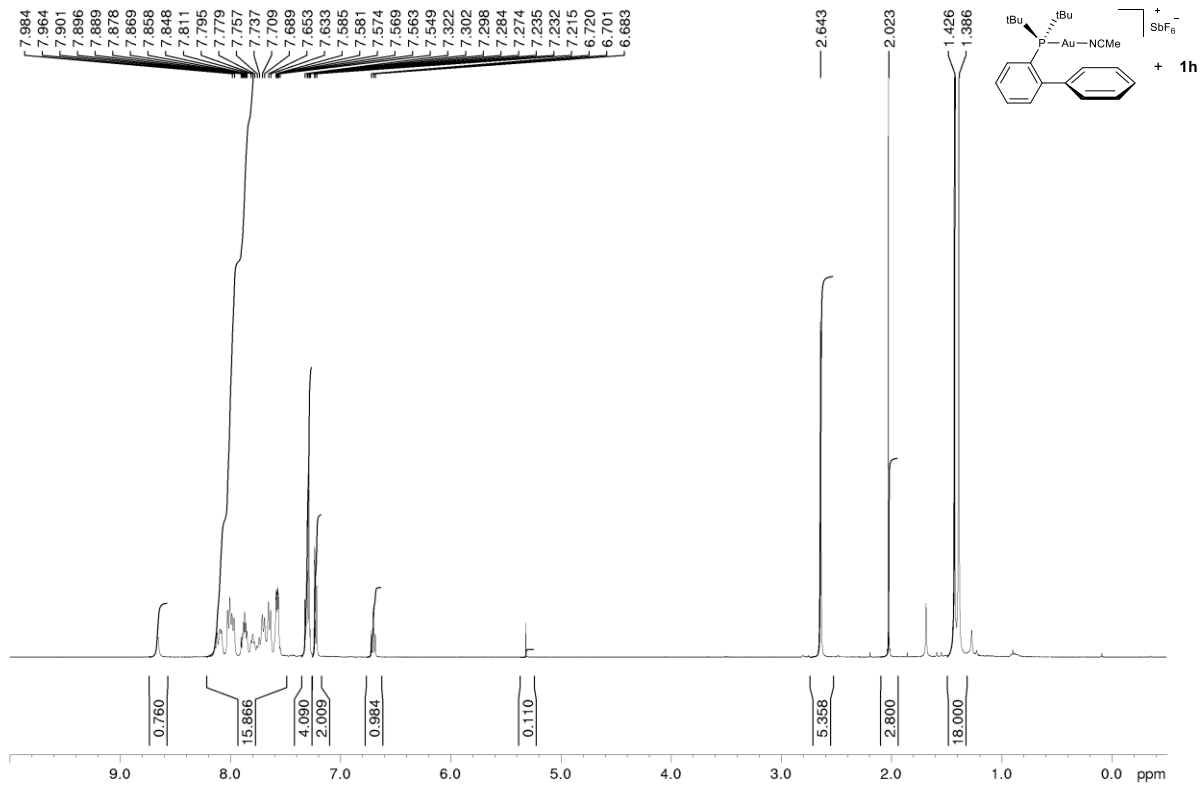

**$^{13}$C NMR (100.6 MHz), $CDCl_3$:** 2-((4-methoxyphenyl)ethynyl)pyridine (**1c**) + $JPAu(CH_3CN)SbF_6$



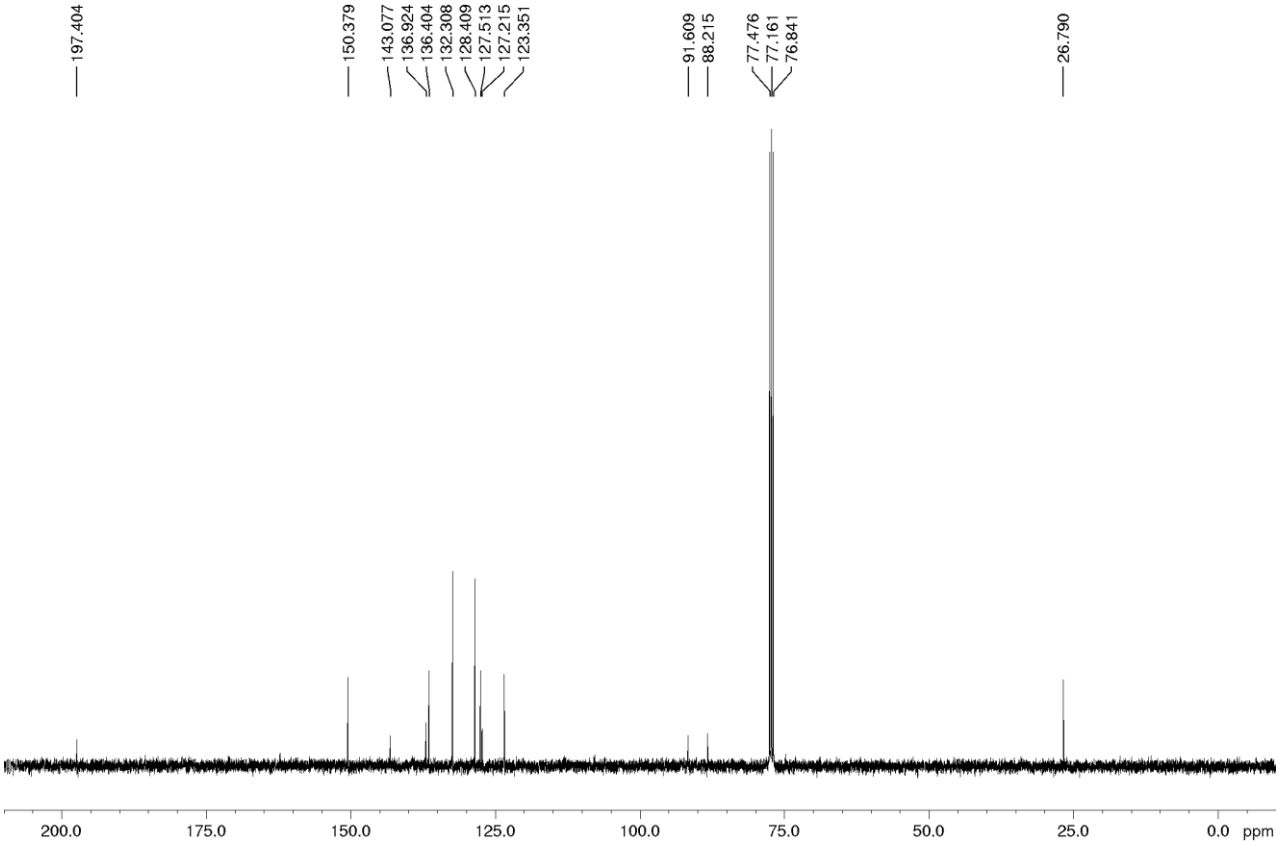
**$^1$H NMR (400.13 MHz), $CDCl_3$:** 1-(4-(pyridin-2-ylethynyl)phenyl)ethanone (**1h**)



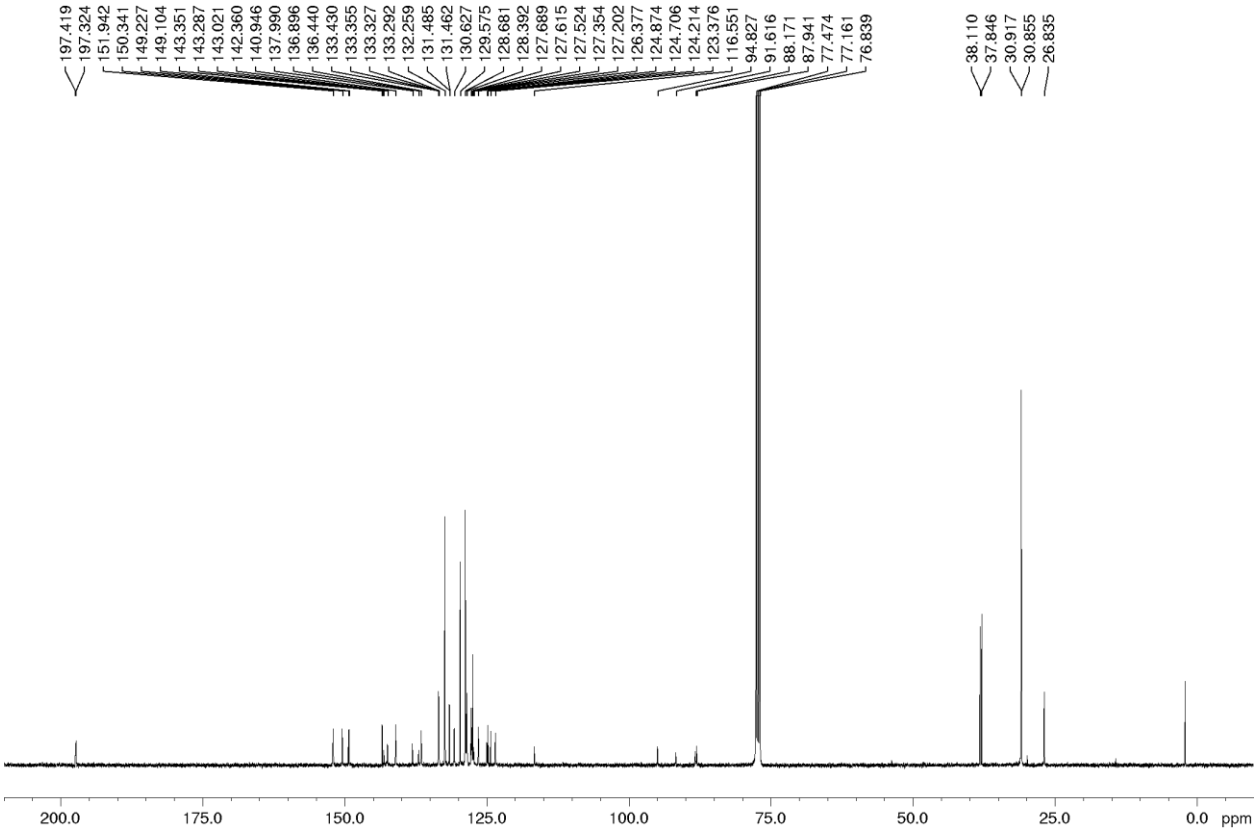

**$^1$H NMR (400.13 MHz), $CDCl_3$:** 1-(4-(pyridin-2-ylethynyl)phenyl)ethanone (**1h**)



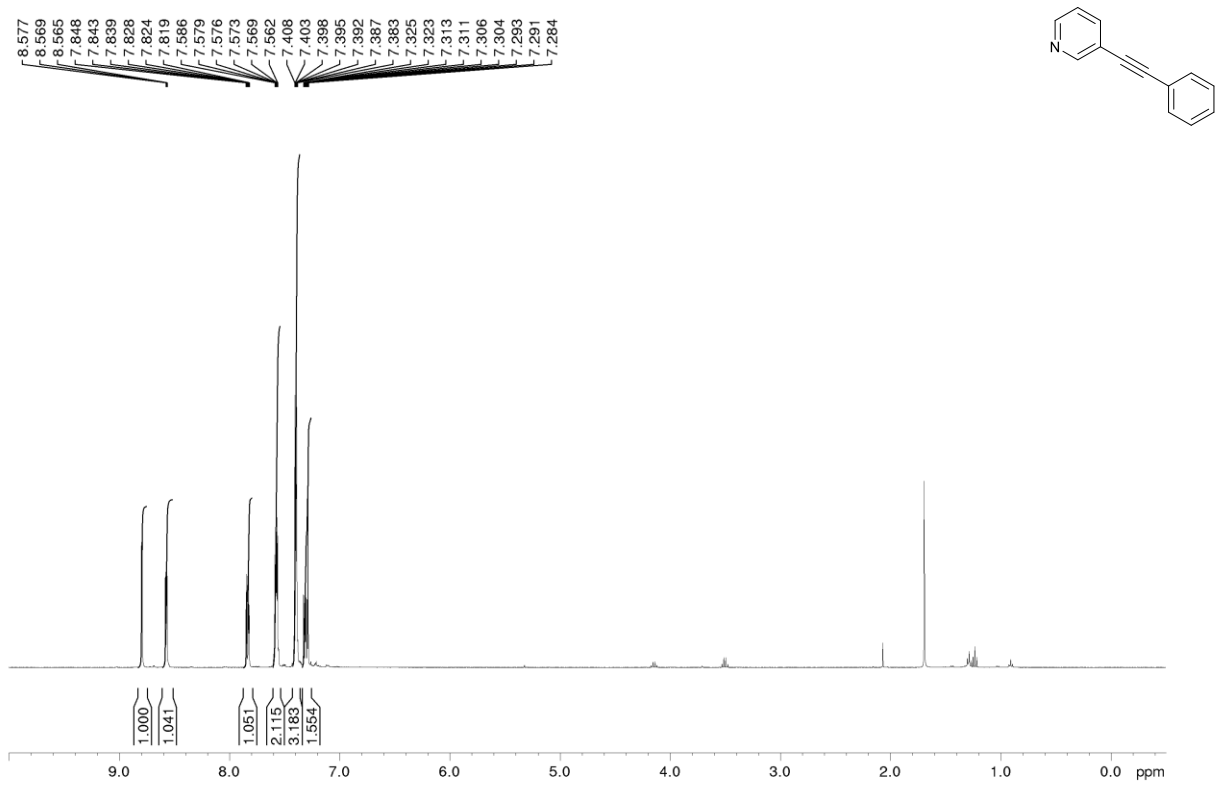
**$^{13}$C NMR (100.6 MHz), $CDCl_3$:** 1-(4-(pyridin-2-ylethynyl)phenyl)ethanone (**1h**)



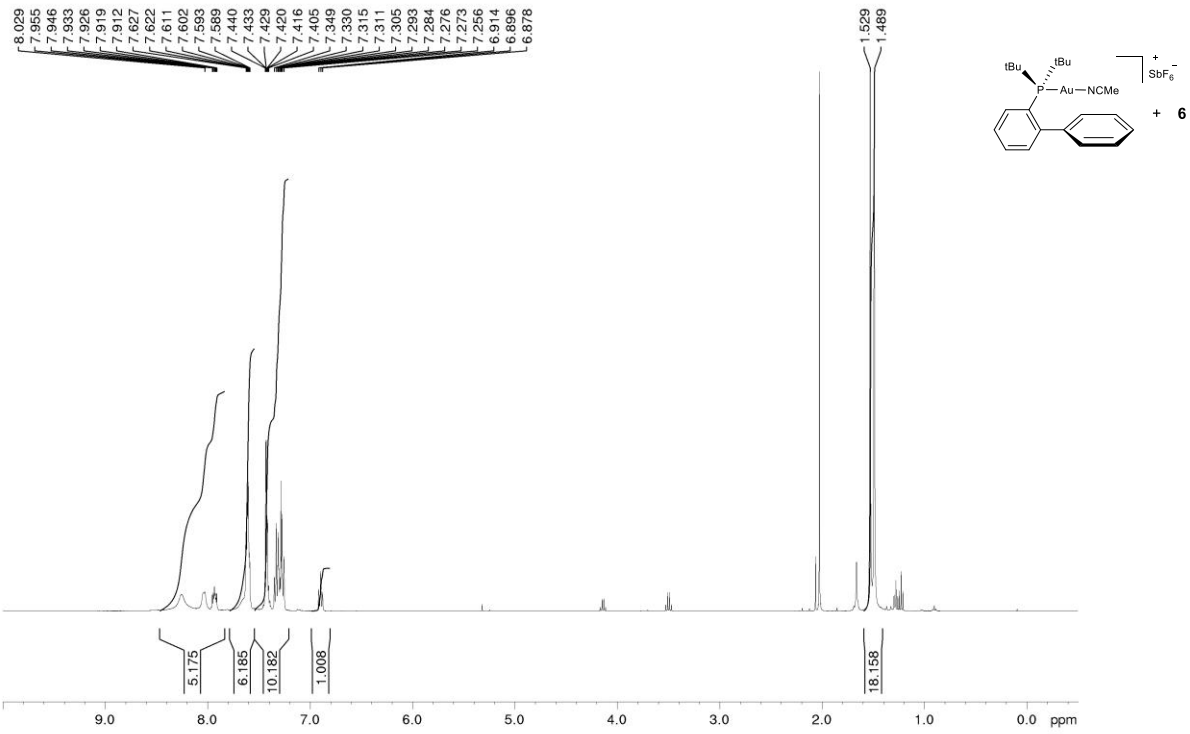

**$^{13}$C NMR (100.6 MHz), $CDCl_3$:** 1-(4-(pyridin-2-ylethynyl)phenyl)ethanone (**1h**) + $JPAu(CH_3CN)SbF_6$



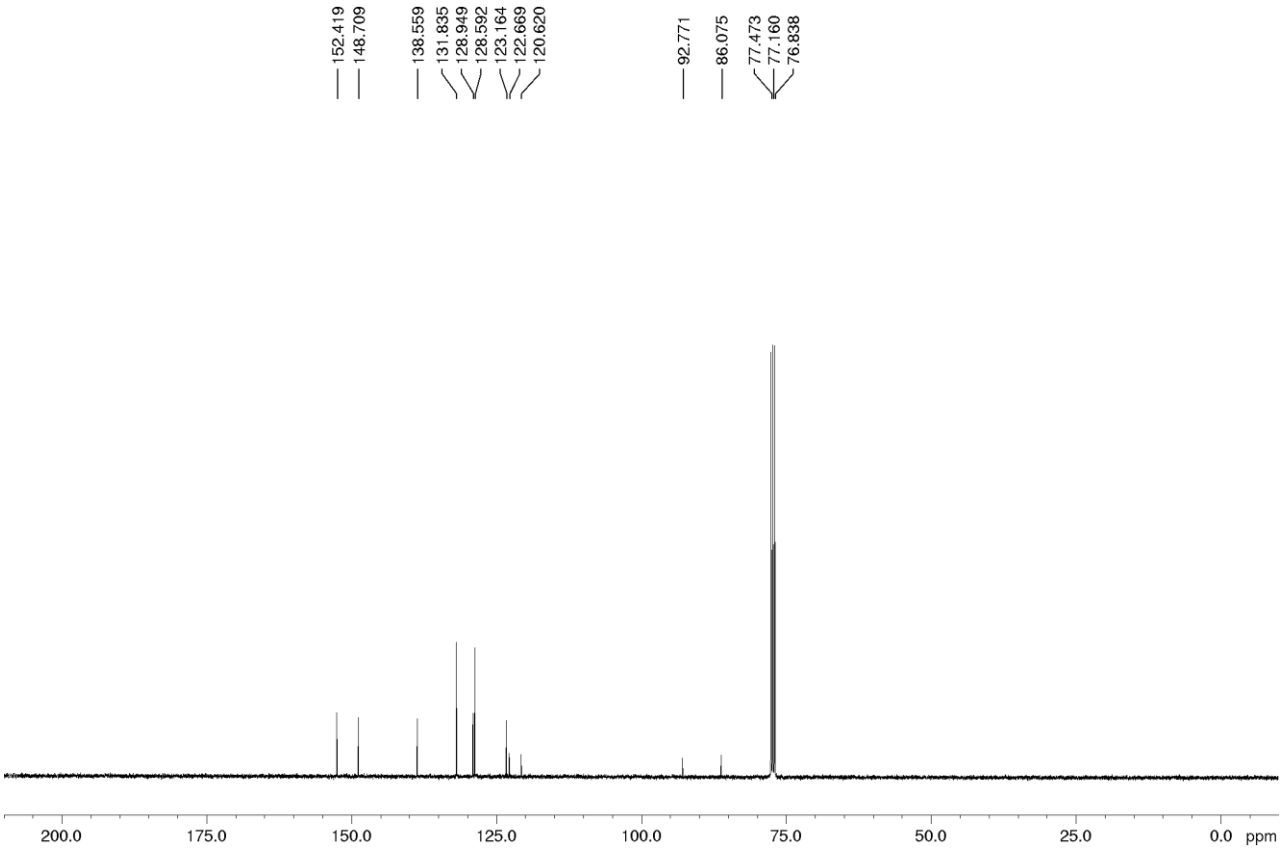
**$^1$H NMR (400.13 MHz), $CDCl_3$:** 3-(phenylethynyl)pyridine (**6**)



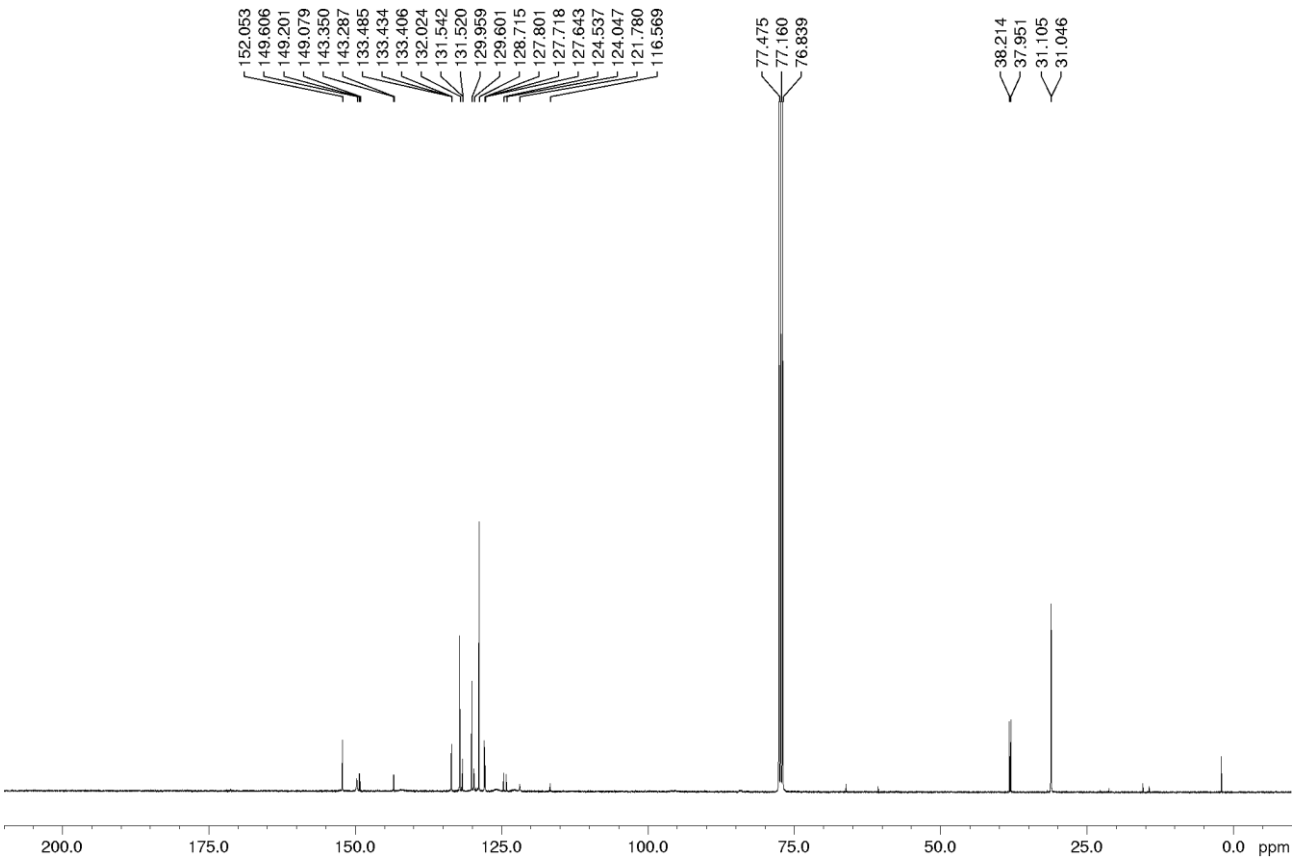

**$^1$H NMR (400.13 MHz), $CDCl_3$:** 3-(phenylethynyl)pyridine (**6**) + $JPAu(CH_3CN)SbF_6$



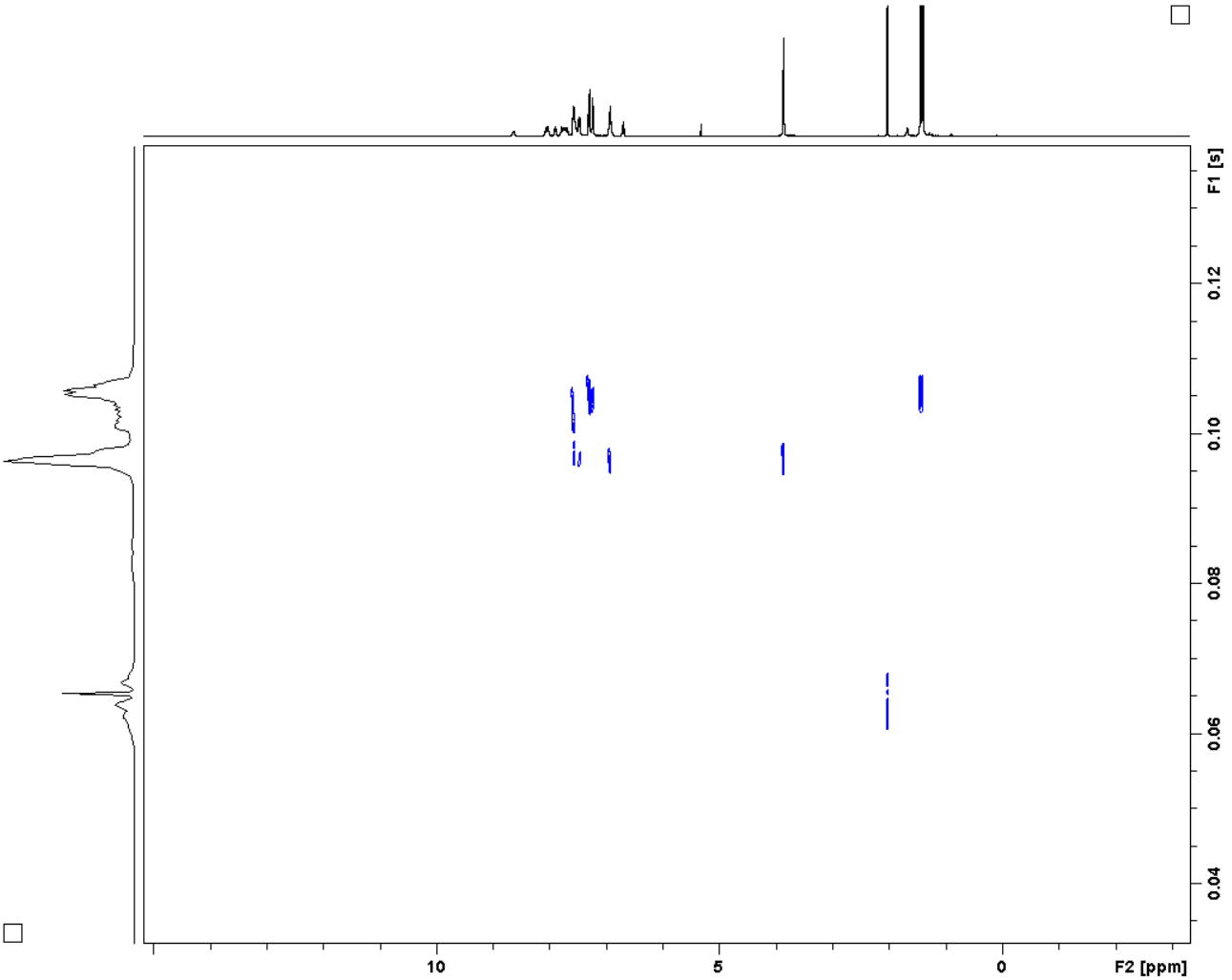
**$^{13}$C NMR (100.6 MHz), $CDCl_3$:** 3-(phenylethynyl)pyridine (**6**)




**$^{13}$C NMR (100.6 MHz), $CDCl_3$:** 3-(phenylethynyl)pyridine (**6**) + $JPAu(CH_3CN)SbF_6$



**DOSY, $CDCl_3$:** 2-((4-methoxyphenyl)ethynyl)pyridine **(1c)** + $JPAu(CH_3CN)SbF_6$



OUTPUTS CALCOLATION FOR **3a** *Z* isomer

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+-------------------------------------------------------------------+
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  |                                                                   |
  |  Use of this program should be acknowledged in publications as:   |
  |  Jaguar 3.5, Schrodinger, Inc., Portland, Oregon, 1998.           |
  +-------------------------------------------------------------------+

  start of program pre
  Job name: WF29836
  Executables used: C:\USERS\GIANCARLO\DOCUMENTS\1.
  Temporary files : LAVORO\C.

  Input file comments:
    Molecule001
    This file created by Spartan

  basis set:             6-31G**
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....          395

 Input geometry:
                              angstroms
  atom            x                y                z
  C3        0.5543850000     -1.2762350000     -2.4395500000
  C1        0.6152290000     -1.3969400000     -0.9915580000
  C2        0.4857320000     -0.4264550000     -0.0382740000
  H3        0.7994000000     -2.4268240000     -0.6376890000
  N1        0.4025910000      0.9382840000     -0.2966610000
  C9        0.5613240000     -0.8726740000      1.3758640000
  H7        0.6097430000      1.2234090000     -1.2336360000
  C5       -0.4435910000      1.8200590000      0.3979150000
  C4        0.4260130000     -1.1831790000     -5.2065090000
  C6        0.5963150000     -2.4825670000     -3.1911500000
  C7        0.5304180000     -2.4265990000     -4.5800100000
  C8        0.3941080000     -0.0373770000     -4.3935330000
  H10       0.6793880000     -3.4469690000     -2.6725740000
  H11       0.5605480000     -3.3504960000     -5.1760230000
  H12       0.3138760000      0.9698580000     -4.8414960000
  H13       0.3711390000     -1.0958190000     -6.2982980000
  N3        0.4564740000     -0.0655830000     -3.0523640000
  C10       0.7644830000     -1.8029430000      4.0046140000
  C11      -0.2441460000     -1.9332560000      1.8124590000
  C12       1.4689120000     -0.2805520000      2.2624980000
  C13       1.5679420000     -0.7482820000      3.5725190000
  C14      -0.1416760000     -2.3938070000      3.1234510000
  H20      -0.9582560000     -2.3983140000      1.1160140000
  H21       2.1041730000      0.5527780000      1.9255920000
  H22       2.2832340000     -0.2813160000      4.2655810000
  H23      -0.7771810000     -3.2249650000      3.4625480000
  H24       0.8444040000     -2.1686250000      5.0387670000
  C15      -2.0521730000      3.6875900000      1.7628900000
  C16      -1.4420680000      1.3912440000      1.2985050000
  C17      -0.2825370000      3.2118550000      0.1823640000
  C18      -1.0809510000      4.1234020000      0.8619750000
  C19      -2.2259280000      2.3217270000      1.9741260000
  H1       -1.6051030000      0.3166400000      1.4754180000
  H2        0.4762800000      3.5784970000     -0.5252050000
  H4       -0.9413210000      5.2005840000      0.6851970000
  H5       -2.9944920000      1.9680340000      2.6778020000
  H6       -2.6766900000      4.4158160000      2.2984320000

  Molecular weight:    272.13 amu

  Stoichiometry:        C19N2H16
  Molecular Point Group: C1
```

```
 Point Group used: C1
 nuclear repulsion energy.......  1478.021441331 hartrees

Non-default options chosen:
  Geometry will be optimized in redundant internal coordinates
  Initial Hessian: from previous calculation

 end of program pre


 start of program onee
 smallest eigenvalue of S:    4.381E-04
 number of canonical orbitals.....          393
 end of program onee


 start of program hfig
 initial wavefunction generated automatically from atomic wavefunctions

 Irreducible     Total no   No of occupied orbitals
 representation  orbitals   Shell_1  Shell_2    ...
 No Symm          393         72
 ------------------------
 Orbital occupation/shell    1.000

 end of program hfig


 start of program probe
 end of program probe


 start of program grid

 number of gridpoints:
    atom        C3     C1     C2     H3     N1     C9     H7     C5
 grid # 1       86     87     86     69     97     92     67     88
 grid # 2       94     95     97    111    104    100    108     97
 grid # 3      191    187    191    208    201    193    190    197
 grid # 4      327    329    328    213    377    341    195    331

 number of gridpoints:
    atom        C4     C6     C7     C8    H10    H11    H12    H13
 grid # 1       89     89     89     83     73     73     73     73
 grid # 2       97     97     97     94    114    118    118    118
 grid # 3      186    186    186    183    216    224    224    224
 grid # 4      334    333    332    319    223    232    232    232

 number of gridpoints:
    atom        N3    C10    C11    C12    C13    C14    H20    H21
 grid # 1      105     89     87     88     89     88     70     73
 grid # 2      113     97     95     96     97     96    113    115
 grid # 3      229    186    183    186    185    185    216    221
 grid # 4      412    331    329    330    330    331    222    226

 number of gridpoints:
    atom       H22    H23    H24    C15    C16    C17    C18    C19
 grid # 1       73     73     73     89     88     89     89     89
 grid # 2      118    118    118     97     96     96     97     97
 grid # 3      224    224    224    187    185    184    185    184
 grid # 4      232    231    232    332    331    332    329    328

 number of gridpoints:
    atom        H1     H2     H4     H5     H6  total
 grid # 1       69     72     73     73     73   3026
 grid # 2      111    116    118    118    118   3899
 grid # 3      210    217    223    223    224   7472
 grid # 4      213    225    232    232    232  10670

 end of program grid


 start of program rwr
 end of program rwr
```

```
 start of program scf
 number of electrons.........        144
 number of alpha electrons....         72
 number of beta electrons.....         72
 number of orbitals, total....        393
 number of core orbitals......         72
 number of open shell orbs....          0
 number of occupied orbitals..         72
 number of virtual orbitals...        321
 number of hamiltonians.......          1
 number of shells.............          1
 SCF type: HF

       i  u  d  i  g                                          RMS    maximum
       t  p  i  c  r                              energy  density   DIIS
       e  d  i  u  i                total energy  change  change    error

etot   1  N  N  5  M  -835.08439182672           4.1E-03  9.8E-02
etot   2  Y  Y  6  M  -837.50669340712  2.4E+00  1.5E-03  3.6E-02
etot   3  Y  Y  6  M  -837.69644392560  1.9E-01  6.2E-04  1.2E-02
etot   4  N  Y  2  U  -837.70362660994  7.2E-03  3.1E-04  1.4E-02
etot   5  Y  Y  6  M  -837.71134317223  7.7E-03  1.5E-03  1.1E-02
etot   6  N  Y  2  U  -837.72403573531  1.3E-02  1.9E-04  2.4E-03
etot   7  Y  Y  6  M  -837.72524500821  1.2E-03  5.6E-05  5.8E-04
etot   8  Y  Y  6  M  -837.72535002794  1.1E-04  1.4E-05  3.1E-04
etot   9  N  Y  2  U  -837.72507345400 -2.8E-04  8.5E-06  1.4E-04
etot  10  Y  Y  6  M  -837.72508049397  7.0E-06  7.9E-06  9.1E-05
etot  11  Y  Y  6  M  -837.72508311296  2.6E-06  1.5E-06  2.2E-05
etot  12  Y  N  6  M  -837.72507461584 -8.5E-06  0.0E+00  0.0E+00


 Energy components, in hartrees:
   (A)  Nuclear repulsion.............  1478.02144133125
   (E)  Total one-electron terms..... -4072.15428937863
   (I)  Total two-electron terms.....  1756.40777343154
   (L)  Electronic energy............. -2315.74651594708  (E+I)
   (N)  Total energy.................  -837.72507461584  (A+L)

 SCFE: SCF energy: HF    -837.72507461584 hartrees   iterations:  12


 HOMO energy:    -0.26214
 LUMO energy:     0.08644

  Orbital energies:
 -15.57797  -15.56537  -11.29179  -11.28519  -11.27938  -11.27810
 -11.25861  -11.24616  -11.24010  -11.23933  -11.23863  -11.23832
 -11.23802  -11.23794  -11.23764  -11.23158  -11.23067  -11.22588
 -11.22229  -11.21974  -11.21961   -1.26004   -1.24289   -1.15366
  -1.12768   -1.07769   -1.07035   -1.03358   -1.01226   -1.00232
  -0.99271   -0.95613   -0.87561   -0.84882   -0.82798   -0.81976
  -0.81508   -0.80279   -0.75713   -0.71105   -0.69840   -0.68688
  -0.66980   -0.65308   -0.64731   -0.63156   -0.62307   -0.60700
  -0.59873   -0.59012   -0.58188   -0.57529   -0.57158   -0.56111
  -0.55329   -0.53699   -0.51984   -0.51731   -0.50319   -0.49613
  -0.49113   -0.48856   -0.47653   -0.45875   -0.40957   -0.39215
  -0.37419   -0.34349   -0.33473   -0.32642   -0.29923   -0.26214
   0.08644    0.12829    0.13579    0.14497    0.15709    0.16552
   0.23430    0.23606    0.23785    0.24992

 end of program scf


 start of program der1a
 end of program der1a


 start of program rwr
 end of program rwr


 start of program der1b
```

forces (hartrees/bohr) : total

| atom | label | x | y | z |
|---|---|---|---|---|
| 1 | C3 | -1.542875E-03 | 3.646308E-03 | -2.906296E-02 |
| 2 | C1 | -2.324435E-04 | 4.792924E-03 | 2.414893E-02 |
| 3 | C2 | 5.335123E-03 | -1.389357E-02 | -2.716176E-02 |
| 4 | H3 | -3.307716E-03 | 2.186555E-02 | -4.271514E-03 |
| 5 | N1 | -2.860477E-03 | -5.449803E-03 | 3.260275E-03 |
| 6 | C9 | 2.202102E-03 | -3.881972E-03 | 1.100600E-02 |
| 7 | H7 | -2.167217E-03 | -7.635024E-03 | 9.732142E-04 |
| 8 | C5 | -7.952156E-03 | 1.535489E-02 | 9.490476E-03 |
| 9 | C4 | -8.303780E-04 | 1.118600E-02 | 4.438588E-04 |
| 10 | C6 | 2.395493E-05 | 4.434787E-03 | 1.356033E-04 |
| 11 | C7 | 3.049618E-04 | -3.676661E-03 | 1.788950E-03 |
| 12 | C8 | -3.762192E-05 | -2.429385E-03 | 5.871002E-03 |
| 13 | H10 | -1.312318E-03 | 1.523448E-02 | -7.752719E-03 |
| 14 | H11 | -4.521867E-04 | 1.401801E-02 | 9.256511E-03 |
| 15 | H12 | 1.559827E-03 | -1.878091E-02 | 7.291051E-03 |
| 16 | H13 | 8.326388E-04 | -4.289418E-04 | 1.613293E-02 |
| 17 | N3 | 2.505258E-03 | -2.548728E-02 | -1.025266E-02 |
| 18 | C10 | 5.323462E-05 | -3.101873E-03 | 7.571697E-03 |
| 19 | C11 | -1.073400E-03 | -4.551145E-03 | -1.239650E-03 |
| 20 | C12 | 2.569482E-03 | 5.443399E-03 | 7.195323E-04 |
| 21 | C13 | 5.290639E-03 | 3.953008E-03 | 3.527297E-03 |
| 22 | C14 | -3.958366E-03 | -6.188202E-03 | 2.654124E-03 |
| 23 | H20 | 1.136265E-02 | 8.570429E-03 | 1.161285E-02 |
| 24 | H21 | -1.135958E-02 | -1.382589E-02 | 4.629758E-03 |
| 25 | H22 | -1.096300E-02 | -7.453607E-03 | -1.082575E-02 |
| 26 | H23 | 9.625166E-03 | 1.287094E-02 | -5.121827E-03 |
| 27 | H24 | -1.309925E-03 | 5.763879E-03 | -1.588890E-02 |
| 28 | C15 | -5.921954E-03 | 5.751779E-03 | 5.732774E-03 |
| 29 | C16 | 3.575054E-03 | -9.592031E-03 | -5.136667E-03 |
| 30 | C17 | 3.432719E-03 | -8.424406E-03 | -2.741380E-03 |
| 31 | C18 | -3.091095E-04 | 6.915719E-03 | -2.164843E-03 |
| 32 | C19 | -4.375752E-03 | 9.379986E-04 | 3.948199E-03 |
| 33 | H1 | 1.845620E-03 | 2.290765E-02 | -4.082681E-03 |
| 34 | H2 | -1.034525E-02 | -7.856500E-03 | 1.110648E-02 |
| 35 | H4 | -1.984061E-03 | -1.679544E-02 | 2.517084E-03 |
| 36 | H5 | 1.198217E-02 | 5.173634E-03 | -1.124901E-02 |
| 37 | H6 | 9.359219E-03 | -1.087102E-02 | -7.934838E-03 |
| total | | -4.359610E-04 | -1.502282E-03 | -1.068571E-03 |

end of program der1b

start of program onee
smallest eigenvalue of S: 4.070E-04
number of canonical orbitals..... 393
end of program onee

start of program probe
end of program probe

start of program grid

number of gridpoints:

| atom | C3 | C1 | C2 | H3 | N1 | C9 | H7 | C5 |
|---|---|---|---|---|---|---|---|---|
| grid # 1 | 89 | 87 | 86 | 71 | 95 | 92 | 67 | 86 |
| grid # 2 | 97 | 96 | 94 | 112 | 103 | 100 | 106 | 93 |
| grid # 3 | 189 | 187 | 192 | 207 | 201 | 194 | 186 | 192 |
| grid # 4 | 329 | 327 | 325 | 203 | 374 | 341 | 191 | 326 |

number of gridpoints:

| atom | C4 | C6 | C7 | C8 | H10 | H11 | H12 | H13 |
|---|---|---|---|---|---|---|---|---|
| grid # 1 | 89 | 88 | 89 | 83 | 73 | 73 | 73 | 73 |
| grid # 2 | 97 | 97 | 97 | 94 | 115 | 118 | 118 | 118 |
| grid # 3 | 184 | 184 | 183 | 178 | 216 | 224 | 224 | 224 |
| grid # 4 | 330 | 328 | 328 | 314 | 215 | 224 | 222 | 224 |

```
 number of gridpoints:
    atom        N3    C10    C11    C12    C13    C14    H20    H21
 grid # 1      103     89     87     88     89     89     70     71
 grid # 2      111     97     95     96     97     96    114    115
 grid # 3      228    183    183    183    184    184    216    216
 grid # 4      411    327    328    327    327    327    214    214

 number of gridpoints:
    atom       H22    H23    H24    C15    C16    C17    C18    C19
 grid # 1       73     73     73     89     88     86     89     88
 grid # 2      118    118    118     97     96     96     97     97
 grid # 3      222    223    224    184    184    182    184    183
 grid # 4      223    224    224    327    327    328    328    328

 number of gridpoints:
    atom        H1     H2     H4     H5     H6  total
 grid # 1       71     72     73     73     73   3021
 grid # 2      114    115    118    118    118   3896
 grid # 3      215    218    223    223    224   7431
 grid # 4      211    219    224    222    224  10485

 end of program grid


 start of program rwr
 end of program rwr


 start of program scf

      i  u  d  i  g                                          RMS    maximum
      t  p  i  c  r                                 energy  density   DIIS
      e  d  i  u  i                    energy       change  change    error

etot  1  N  N  1  U  -837.74121023218                1.8E-05  3.0E-04
etot  2  Y  Y  4  M  -837.74123212478  2.2E-05       5.5E-06  1.2E-04
etot  3  Y  Y  4  M  -837.74123480401  2.7E-06       1.5E-06  2.9E-05
etot  4  Y  N  4  M  -837.74123364537 -1.2E-06       0.0E+00  0.0E+00


 Energy components, in hartrees:
   (A)  Nuclear repulsion.............  1488.84968506246
   (E)  Total one-electron terms..... -4093.77507732388
   (I)  Total two-electron terms.....  1767.18415861605
   (L)  Electronic energy............. -2326.59091870783  (E+I)
   (N)  Total energy.................  -837.74123364537  (A+L)

 SCFE: SCF energy: HF    -837.74123364537 hartrees   iterations:   4


 HOMO energy:    -0.26441
 LUMO energy:     0.09507

 Orbital energies:
 -15.56564  -15.55761  -11.28504  -11.27874  -11.26878  -11.26845
 -11.25124  -11.24092  -11.23198  -11.23142  -11.23037  -11.22999
 -11.22901  -11.22892  -11.22876  -11.22721  -11.22650  -11.22023
 -11.21979  -11.21926  -11.20544   -1.26726   -1.24901   -1.15620
  -1.13630   -1.08356   -1.07063   -1.03642   -1.01437   -1.00885
  -1.00029   -0.96172   -0.87441   -0.85598   -0.83235   -0.82413
  -0.82136   -0.80823   -0.76173   -0.71934   -0.70280   -0.69136
  -0.67729   -0.65621   -0.65285   -0.63351   -0.62560   -0.61483
  -0.60620   -0.59685   -0.58463   -0.57935   -0.57444   -0.56550
  -0.55788   -0.54479   -0.51836   -0.51424   -0.50417   -0.50168
  -0.49346   -0.48872   -0.48308   -0.46208   -0.40626   -0.38803
  -0.37528   -0.34585   -0.33338   -0.32815   -0.30467   -0.26441
   0.09507    0.13343    0.14116    0.14718    0.15991    0.16603
   0.24102    0.24241    0.24564    0.25801

 end of program scf


 start of program der1a
 end of program der1a
```

```
 start of program rwr
 end of program rwr


 start of program der1b

 forces (hartrees/bohr) : total
```

| atom | label | x | y | z |
|---|---|---|---|---|
| 1 | C3 | -2.021163E-05 | 5.280463E-05 | 1.684405E-05 |
| 2 | C1 | -1.984294E-05 | -1.547557E-05 | -4.943061E-05 |
| 3 | C2 | -1.846917E-05 | -9.625238E-05 | -1.177382E-04 |
| 4 | H3 | 2.676077E-05 | -7.478640E-05 | 1.119782E-05 |
| 5 | N1 | -2.726502E-05 | -6.570470E-05 | -1.200928E-04 |
| 6 | C9 | -1.591567E-05 | -1.020228E-06 | -8.355042E-05 |
| 7 | H7 | 1.569481E-06 | -5.204811E-05 | -2.436672E-05 |
| 8 | C5 | -3.859705E-05 | 8.232874E-06 | 2.456303E-05 |
| 9 | C4 | -1.108142E-05 | -6.038182E-05 | -4.304977E-05 |
| 10 | C6 | 9.076312E-06 | -9.601413E-05 | -3.920904E-05 |
| 11 | C7 | 6.104584E-06 | -6.027015E-05 | 8.669350E-07 |
| 12 | C8 | -1.065334E-05 | 9.540286E-07 | 4.079139E-05 |
| 13 | H10 | 6.355058E-06 | -4.750746E-05 | -2.919421E-05 |
| 14 | H11 | -7.276552E-06 | -1.009745E-04 | -3.370954E-05 |
| 15 | H12 | -3.689606E-05 | -1.007186E-04 | -4.605551E-05 |
| 16 | H13 | -2.881020E-05 | -8.792266E-05 | -4.049425E-05 |
| 17 | N3 | -4.809336E-05 | -9.571790E-05 | -1.444937E-04 |
| 18 | C10 | 7.714203E-05 | 4.319996E-05 | 5.802132E-05 |
| 19 | C11 | -3.261100E-06 | -1.339159E-05 | -3.422662E-05 |
| 20 | C12 | 1.089018E-05 | -3.085249E-05 | -5.377819E-05 |
| 21 | C13 | -2.686455E-05 | -6.615379E-05 | -2.517352E-05 |
| 22 | C14 | -2.504870E-05 | -6.867181E-06 | -4.480960E-05 |
| 23 | H20 | -6.179840E-05 | -9.658877E-05 | -9.383987E-05 |
| 24 | H21 | 4.056638E-05 | 6.240829E-05 | -6.721947E-05 |
| 25 | H22 | 7.690476E-05 | 9.533908E-05 | 2.986209E-05 |
| 26 | H23 | -3.221663E-05 | -7.888804E-05 | -2.456498E-06 |
| 27 | H24 | 6.614136E-06 | 1.550125E-05 | -3.755216E-05 |
| 28 | C15 | 9.313368E-05 | 4.242534E-05 | -1.580565E-04 |
| 29 | C16 | 2.803974E-05 | -8.816430E-05 | -8.368042E-05 |
| 30 | C17 | 7.116703E-05 | 1.081799E-04 | -9.985564E-05 |
| 31 | C18 | -7.889525E-05 | -1.700266E-04 | -5.062186E-05 |
| 32 | C19 | 3.416835E-05 | -4.831333E-05 | -3.735926E-05 |
| 33 | H1 | 4.644763E-05 | 3.681081E-05 | -3.922043E-05 |
| 34 | H2 | -1.843033E-04 | -9.436454E-05 | 4.516645E-05 |
| 35 | H4 | 3.383358E-05 | 9.796160E-05 | -7.042531E-05 |
| 36 | H5 | 6.597464E-06 | -3.360714E-05 | -8.414884E-05 |
| 37 | H6 | 3.989012E-05 | -1.694735E-05 | -9.664292E-05 |
| total | | -8.023905E-05 | -1.135142E-03 | -1.623139E-03 |

```
 end of program der1b


 start of program geopt  19

 geometry optimization step 19
 reading input hessian of dimension   111
  in five columns format
 reading input hessian of dimension   111
  in five columns format


 energy change:          -1.3371E-05 *  (  5.0000E-05 )
 gradient maximum:        2.2255E-04 *  (  4.5000E-04 )
 gradient rms:            5.5272E-05 #  (  3.0000E-04 )
 step size:   0.00937  trust radius:   0.30000
 displacement maximum:    4.2185E-03 .  (  1.8000E-03 )
 displacement rms:        8.0094E-04 *  (  1.2000E-03 )
 predicted energy change:    -9.8903E-07    geom step:   9.3747E-03    full step:   9.3747E-03

 *****************************************************
 **           Geometry optimization complete          **
 *****************************************************
```

```
 center of mass moved by:
    x:     0.0000E+00     y:     0.0000E+00     z:     0.0000E+00

 final geometry:
                                angstroms
 atom            x                 y                 z
 C3         0.5196620952     -1.3247128884     -2.4605946789
 C1         0.5664128189     -1.4720346837     -1.0030935993
 C2         0.4043668536     -0.5219300365     -0.0624755040
 H3         0.8001922234     -2.4593578374     -0.6531021855
 N1         0.2506313758      0.8151383791     -0.3520383484
 C9         0.5284036460     -0.9068119190      1.3781227692
 H7         0.3434822496      1.0187804556     -1.3262512830
 C5        -0.5017921379      1.7521375168      0.3884554991
 C4         0.4434978263     -1.0757935870     -5.1922971123
 C6         0.5997200790     -2.4719994983     -3.2627843986
 C7         0.5605346507     -2.3424712180     -4.6323565356
 C8         0.3749344668     -0.0039324534     -4.3273718913
 H10        0.6894148658     -3.4391245267     -2.8029920993
 H11        0.6204242325     -3.2141327827     -5.2606900484
 H12        0.2879465154      0.9993440613     -4.7096351779
 H13        0.4102887996     -0.9268224080     -6.2555148525
 N3         0.4145108754     -0.1166079313     -3.0095140928
 C10        0.8479260197     -1.6664872282      4.0423489757
 C11       -0.1220643252     -2.0304861081      1.8761630672
 C12        1.3353702113     -0.1611073284      2.2341575875
 C13        1.4979907003     -0.5424552643      3.5540300606
 C14        0.0360134133     -2.4080327709      3.2005039665
 H20       -0.7641304221     -2.6000534738      1.2288000004
 H21        1.8380005108      0.7118985605      1.8607326117
 H22        2.1307176762      0.0380268809      4.2019722297
 H23       -0.4793886386     -3.2758841955      3.5728940847
 H24        0.9708065855     -1.9580244131      5.0707274424
 C15       -1.9378558019      3.7105661443      1.7677921049
 C16       -1.6149632930      1.4058079353      1.1467905397
 C17       -0.1236088988      3.0901358647      0.3170289183
 C18       -0.8423668046      4.0605138409      0.9929045771
 C19       -2.3150817636      2.3798999632      1.8404125051
 H1        -1.9343761671      0.3819998227      1.1950239388
 H2         0.7417044151      3.3584318989     -0.2641470925
 H4        -0.5360192043      5.0897970406      0.9251443728
 H5        -3.1684792735      2.0937061582      2.4303780490

 H6        -2.4892088712      4.4627480262      2.3037405754

 nuclear repulsion energy.......  1488.849685062 hartrees
 -------------------------------------------------
/  end of geometry optimization iteration  19   /
-------------------------------------------------

 end of program geopt


 start of program post
 Writing a SPARTAN archive file
 end of program post

Total cpu seconds     user:    2375.094   user+sys:    2375.094
```

OUTPUTS CALCOLATION FOR **3a** *E* isomer

```
+-------------------------------------------------------------------+
  |  Jaguar version 3.5, release  42                                  |
  |                                                                   |
  |  Copyright 1991-1998 Schrodinger, Inc.                            |
  |  All Rights Reserved.                                             |
  |                                                                   |
  |  Use of this program should be acknowledged in publications as:   |
  |  Jaguar 3.5, Schrodinger, Inc., Portland, Oregon, 1998.           |
  +-------------------------------------------------------------------+

  start of program pre
  Job name: WF13223
  Executables used: C:\USERS\GIANCARLO\DOCUMENTS\1.
  Temporary files : LAVORO\C.

  Input file comments:
    Molecule001
    This file created by Spartan

  basis set:             6-31G**
  net molecular charge:    0
  multiplicity:            1

  number of basis functions....          395

 Input geometry:
                                angstroms
  atom           x                 y                 z
  C1        1.3160650000     -1.3742920000     -0.6127530000
  C2        0.9278180000     -0.1173390000     -0.2737740000
  C3        0.7832540000     -2.6062330000     -0.0213730000
  N1        1.6497640000      1.0076460000     -0.7316570000
  C9       -0.1806120000      0.1280750000      0.6728710000
  H7        2.5363490000      0.7719070000     -1.1342250000
  C15       1.0250190000      2.0828560000     -1.3981520000
  C10      -2.2753080000      0.5529870000      2.4769010000
  C11      -1.4334020000     -0.4604840000      0.4504920000
  C12       0.0146750000      0.9353190000      1.8006760000
  C13      -1.0313950000      1.1424710000      2.6992600000
  C14      -2.4745600000     -0.2473720000      1.3516790000
  H20      -1.5871440000     -1.0955340000     -0.4360190000
  H21       0.9926970000      1.4085280000      1.9758450000
  H22      -0.8728030000      1.7759900000      3.5842810000
  H23      -3.4552000000     -0.7122560000      1.1730150000
  H24      -3.0988620000      0.7198530000      3.1863930000
  H9        2.1003030000     -1.5451770000     -1.3715000000
  C4       -0.1097410000     -4.9746630000      1.0781730000
  C6        0.9468770000     -2.8348760000      1.3648600000
  C7        0.4923760000     -4.0341750000      1.9131750000
  C8       -0.2316790000     -4.6656580000     -0.2894210000
  H13       1.4217690000     -2.0690340000      1.9927280000
  H14       0.6088520000     -4.2324360000      2.9886080000
  H15      -0.7032140000     -5.3799140000     -0.9888330000
  H16      -0.4801010000     -5.9308240000      1.4680970000
  N2        0.1984960000     -3.5196740000     -0.8431100000
  C16      -0.1184910000      4.3329480000     -2.6486220000
  C17       1.8295720000      3.1798400000     -1.7941650000
  C18      -0.3596490000      2.1360640000     -1.6606370000
  C19      -0.9168990000      3.2556080000     -2.2717550000
  C20       1.2544760000      4.2854370000     -2.4087300000
  H25       2.9148170000      3.1659950000     -1.6128020000
  H26      -1.0108780000      1.2938200000     -1.3780810000
  H27      -2.0006450000      3.2816610000     -2.4615120000
```

```
 H28       1.8928370000      5.1308100000     -2.7068430000
 H29      -0.5654340000      5.2121290000     -3.1330930000

 Molecular weight:    272.13 amu

 Stoichiometry:        C19N2H16
 Molecular Point Group: C1
 Point Group used: C1
 nuclear repulsion energy.......  1499.115451548 hartrees

Non-default options chosen:
  Geometry will be optimized in redundant internal coordinates
  Initial Hessian: from previous calculation

 end of program pre


 start of program onee
 smallest eigenvalue of S:    4.427E-04
 number of canonical orbitals.....          393
 end of program onee


 start of program hfig
 initial wavefunction generated automatically from atomic wavefunctions

 Irreducible     Total no   No of occupied orbitals
 representation  orbitals   Shell_1  Shell_2    ...
 No Symm          393         72
 ------------------------
 Orbital occupation/shell    1.000

 end of program hfig


 start of program probe
 end of program probe


 start of program grid

 number of gridpoints:
    atom        C1     C2     C3     N1     C9     H7    C15    C10
 grid # 1       87     87     87     97     92     70     86     89
 grid # 2       94     96     96    105    100    111     98     97
 grid # 3      185    194    191    201    193    195    193    185
 grid # 4      331    324    329    378    341    206    328    330

 number of gridpoints:
    atom       C11    C12    C13    C14    H20    H21    H22    H23
 grid # 1       87     87     89     89     69     73     73     73
 grid # 2       95     95     96     95    113    114    118    118
 grid # 3      183    185    184    184    215    220    224    222
 grid # 4      329    330    329    328    217    225    232    230

 number of gridpoints:
    atom       H24     H9     C4     C6     C7     C8    H13    H14
 grid # 1       73     72     89     88     89     83     72     73
 grid # 2      118    116     97     96     96     93    115    118
 grid # 3      224    218    185    185    185    182    219    223
 grid # 4      232    225    331    331    331    318    224    231

 number of gridpoints:
    atom       H15    H16     N2    C16    C17    C18    C19    C20
 grid # 1       73     73    104     89     89     88     89     89
 grid # 2      118    118    114     97     97     96     97     97
 grid # 3      224    224    233    187    184    185    185    185
```

```
 grid # 4      232    232    418    332    331    331    328    329

 number of gridpoints:
    atom       H25    H26    H27    H28    H29  total
 grid # 1       72     69     73     73     73   3028
 grid # 2      116    111    118    118    118   3905
 grid # 3      218    208    223    223    224   7478
 grid # 4      226    210    232    232    232  10675

 end of program grid


 start of program rwr
 end of program rwr


 start of program scf
number of electrons..........        144
number of alpha electrons....         72
number of beta electrons.....         72
number of orbitals, total....        393
number of core orbitals......         72
number of open shell orbs....          0
number of occupied orbitals..         72
number of virtual orbitals...        321
number of hamiltonians.......          1
number of shells.............          1
SCF type: HF

      i  u  d  i  g
      t  p  i  c  r                                  RMS    maximum
      e  d  i  u  i                      energy  density   DIIS
      r  t  s  t  d     total energy     change  change    error

etot   1  N  N  5  M  -835.05316109430            4.3E-03  1.2E-01
etot   2  Y  Y  6  M  -837.49477884410  2.4E+00   1.5E-03  3.6E-02
etot   3  Y  Y  6  M  -837.68340752646  1.9E-01   6.2E-04  1.2E-02
etot   4  N  Y  2  U  -837.69057794326  7.2E-03   4.9E-04  1.4E-02
etot   5  Y  Y  6  M  -837.69885498153  8.3E-03   1.8E-03  1.1E-02
etot   6  N  Y  2  U  -837.71013652769  1.1E-02   2.3E-04  2.5E-03
etot   7  Y  Y  6  M  -837.71119785386  1.1E-03   6.1E-05  5.6E-04
etot   8  Y  Y  6  M  -837.71127152325  7.4E-05   1.1E-05  1.7E-04
etot   9  N  Y  2  U  -837.71105402332 -2.2E-04   5.5E-06  9.7E-05
etot  10  Y  Y  6  M  -837.71106116970  7.1E-06   4.4E-06  4.9E-05
etot  11  Y  N  6  M  -837.71106509012  3.9E-06   0.0E+00  0.0E+00


 Energy components, in hartrees:
   (A)  Nuclear repulsion.............  1499.11545154768
   (E)  Total one-electron terms..... -4114.33422019094
   (I)  Total two-electron terms.....  1777.50770355315
   (L)  Electronic energy............. -2336.82651663780  (E+I)
   (N)  Total energy.................  -837.71106509012  (A+L)

 SCFE: SCF energy: HF    -837.71106509012 hartrees   iterations:  11


 HOMO energy:    -0.27977
 LUMO energy:     0.10104

  Orbital energies:
  -15.58331  -15.56230  -11.28651  -11.27985  -11.27965  -11.27413
  -11.25499  -11.24502  -11.23953  -11.23896  -11.23864  -11.23806
  -11.23764  -11.23690  -11.23624  -11.23427  -11.23293  -11.22891
  -11.22806  -11.22440  -11.22213   -1.25817   -1.24225   -1.15361
   -1.12967   -1.07501   -1.07358   -1.02644   -1.01135   -1.00458
   -0.99574   -0.95681   -0.87142   -0.84358   -0.82725   -0.82305
```

```
  -0.81774   -0.80168   -0.75609   -0.71379   -0.68922   -0.68761
  -0.66441   -0.65501   -0.64541   -0.63562   -0.62493   -0.61552
  -0.60105   -0.59207   -0.58228   -0.57758   -0.57396   -0.56673
  -0.55090   -0.52942   -0.52168   -0.50866   -0.50522   -0.49704
  -0.48980   -0.48754   -0.47725   -0.45727   -0.40671   -0.37801
  -0.36554   -0.34503   -0.33289   -0.32865   -0.30235   -0.27977
   0.10104    0.12910    0.13459    0.14646    0.15143    0.15772
   0.21300    0.23419    0.24368    0.24530

 end of program scf


 start of program der1a
 end of program der1a


 start of program rwr
 end of program rwr


 start of program der1b

 forces (hartrees/bohr) : total

atom  label          x             y             z
----  -----   -------------  -------------  -------------
  1    C1      2.630444E-03   3.109732E-02  -1.423350E-02
  2    C2      2.597317E-02  -3.014770E-02  -1.485961E-02
  3    C3     -1.213302E-02  -3.365286E-02   1.389391E-02
  4    N1     -5.094356E-03  -5.496506E-03  -4.299005E-03
  5    C9     -1.144541E-02   3.512291E-03   1.090766E-02
  6    H7     -4.289779E-03   1.475398E-04   3.093485E-03
  7    C15    -5.133622E-03   1.868782E-02  -6.281287E-03
  8    C10    -5.684629E-03   1.159525E-03   5.045989E-03
  9    C11    -2.231432E-03  -4.443870E-03  -1.063272E-03
 10    C12     3.743678E-03   4.226272E-03   4.766037E-04
 11    C13     1.609276E-03   4.451288E-03   6.136883E-03
 12    C14    -6.640197E-03  -3.804574E-03  -1.974408E-03
 13    H20     2.652840E-03   1.121532E-02   1.501640E-02
 14    H21    -1.577193E-02  -8.028384E-03  -4.133369E-03
 15    H22    -2.446909E-03  -9.881469E-03  -1.352232E-02
 16    H23     1.509670E-02   7.271584E-03   2.674826E-03
 17    H24     1.262647E-02  -2.435675E-03  -1.091675E-02
 18    H9     -1.330114E-02   8.113315E-03   1.052495E-02
 19    C4     -2.755515E-03  -1.730516E-03  -8.731948E-03
 20    C6     -1.036901E-03  -7.578122E-04  -5.449722E-03
 21    C7      2.997199E-04   1.203987E-03   2.810823E-03
 22    C8      2.578465E-03   6.530586E-03  -2.200171E-03
 23    H13    -7.354264E-03  -1.271574E-02  -1.088184E-02
 24    H14    -1.692608E-03   2.872641E-03  -1.637878E-02
 25    H15     8.417814E-03   1.232205E-02   1.352266E-02
 26    H16     5.275173E-03   1.383716E-02  -6.372756E-03
 27    N2      9.143374E-03   3.170863E-04   3.266538E-02
 28    C16    -5.762583E-03   7.405390E-03  -3.917737E-03
 29    C17     2.039215E-04  -7.537377E-03   4.068141E-03
 30    C18     2.006899E-03  -1.211894E-02   4.393745E-03
 31    C19    -4.719670E-03   3.320375E-03  -2.564979E-03
 32    C20     4.645023E-03   4.522173E-03  -3.432856E-03
 33    H25    -1.673904E-02  -1.500656E-03  -8.834457E-04
 34    H26     1.349930E-02   1.845471E-02  -7.449234E-03
 35    H27     1.709736E-02  -8.470896E-04   2.970633E-03
 36    H28    -9.692512E-03  -1.330912E-02   4.650844E-03
 37    H29     6.704612E-03  -1.316460E-02   7.383534E-03
-----------   -------------  -------------  -------------
   total       2.787116E-04  -9.044464E-04   6.894980E-04

 end of program der1b
```

```
  start of program onee
  smallest eigenvalue of S:    4.190E-04
  number of canonical orbitals.....          393
  end of program onee


  start of program probe
  end of program probe


  start of program grid

  number of gridpoints:
     atom        C1     C2     C3     N1     C9     H7    C15    C10
  grid # 1       88     86     86     96     92     71     86     89
  grid # 2       94     96     94    104    100    111     93     97
  grid # 3      182    192    186    202    193    196    193    184
  grid # 4      322    317    323    377    340    208    327    326

  number of gridpoints:
     atom       C11    C12    C13    C14    H20    H21    H22    H23
  grid # 1       87     87     89     89     70     73     73     73
  grid # 2       95     95     96     96    113    114    118    118
  grid # 3      182    182    183    183    216    217    222    222
  grid # 4      326    326    326    326    215    215    224    223

  number of gridpoints:
     atom       H24     H9     C4     C6     C7     C8    H13    H14
  grid # 1       73     72     89     88     89     81     71     73
  grid # 2      118    115     97     96     97     91    114    118
  grid # 3      223    216    184    182    183    178    218    223
  grid # 4      224    212    329    327    328    313    211    223

  number of gridpoints:
     atom       H15    H16     N2    C16    C17    C18    C19    C20
  grid # 1       73     73    103     89     86     88     88     89
  grid # 2      118    118    111     97     96     96     97     97
  grid # 3      224    224    233    184    182    184    183    185
  grid # 4      222    224    417    328    328    327    328    329

  number of gridpoints:
     atom       H25    H26    H27    H28    H29  total
  grid # 1       72     71     73     73     73   3022
  grid # 2      115    114    118    118    118   3893
  grid # 3      218    214    223    223    224   7443
  grid # 4      218    211    223    224    224  10491

  end of program grid


  start of program rwr
  end of program rwr


  start of program scf

       i  u  d  i  g                                          RMS    maximum
       t  p  i  c  r                                       density   DIIS
       e  d  i  u  i                      energy  energy   change    error
       r  t  s  t  d     total energy     change  change    error

etot   1  N  N  1  U  -837.72875434650           3.5E-05  1.3E-03
etot   2  Y  Y  4  M  -837.72898488926  2.3E-04  1.7E-05  5.1E-04
```

```
etot   3  Y  Y  4  M  -837.72901857434  3.4E-05  5.1E-06  1.2E-04
etot   4  Y  Y  4  M  -837.72902168341  3.1E-06  2.4E-06  6.0E-05
etot   5  Y  N  4  M  -837.72901996426 -1.7E-06  0.0E+00  0.0E+00


 Energy components, in hartrees:
   (A)  Nuclear repulsion.............  1499.01705276839
   (E)  Total one-electron terms..... -4114.00125267898
   (I)  Total two-electron terms.....  1777.25517994633
   (L)  Electronic energy............. -2336.74607273266  (E+I)
   (N)  Total energy.................  -837.72901996426  (A+L)

 SCFE: SCF energy: HF    -837.72901996426 hartrees   iterations:   5


 HOMO energy:    -0.27693
 LUMO energy:     0.10056

  Orbital energies:
 -15.57643  -15.55011  -11.28203  -11.27255  -11.27204  -11.26090
 -11.24559  -11.24182  -11.23424  -11.23305  -11.23280  -11.23173
 -11.23142  -11.23067  -11.22960  -11.22728  -11.22578  -11.22412
 -11.22276  -11.22190  -11.21585   -1.26049   -1.25381   -1.15846
  -1.13902   -1.07950   -1.07248   -1.03021   -1.01604   -1.01228
  -1.00453   -0.96330   -0.87259   -0.84864   -0.83274   -0.82818
  -0.82656   -0.80799   -0.76237   -0.72220   -0.69885   -0.69381
  -0.67008   -0.66093   -0.64661   -0.63845   -0.62803   -0.62107
  -0.60819   -0.59968   -0.58749   -0.58379   -0.58164   -0.56980
  -0.54895   -0.53236   -0.52343   -0.51065   -0.50727   -0.50256
  -0.49360   -0.49027   -0.48362   -0.45839   -0.40069   -0.38595
  -0.36724   -0.34843   -0.33330   -0.33158   -0.30779   -0.27693
   0.10056    0.13068    0.14241    0.14793    0.15462    0.16082
   0.22799    0.24264    0.24895    0.25407

 end of program scf


 start of program der1a
 end of program der1a


 start of program rwr
 end of program rwr


 start of program der1b

 forces (hartrees/bohr) : total

 atom  label          x             y             z
 ----  -----   -------------  -------------  -------------
   1    C1      7.986386E-05  -8.753600E-05  -1.325119E-04
   2    C2      7.744534E-05   6.602647E-05  -2.561828E-06
   3    C3      1.723764E-04   2.838905E-04   3.497936E-04
   4    N1      2.041631E-04  -1.594347E-04  -2.534863E-05
   5    C9     -3.502879E-05   6.703332E-05   1.410291E-04
   6    H7     -1.523555E-04   1.114477E-06   7.805942E-05
   7    C15    -6.919679E-05  -1.711158E-05  -6.257239E-05
   8    C10    -1.341867E-05  -3.116849E-05  -7.896304E-05
   9    C11     5.812720E-05   4.758275E-05   4.993117E-05
  10    C12    -2.938052E-05  -1.127346E-04  -9.999172E-05
  11    C13     6.705963E-05   3.355296E-05   1.746523E-05
  12    C14     6.085397E-05   7.521205E-05   4.231705E-05
  13    H20     2.612211E-05   5.030862E-05   1.213717E-04
  14    H21    -8.582909E-05  -3.506808E-05  -4.865307E-05
  15    H22    -1.099783E-05   8.710297E-07  -8.259217E-05
  16    H23     7.767185E-05   4.468633E-05   4.365762E-05
```

```
  17    H24     4.064644E-05   3.747487E-05  -2.495552E-05
  18    H9     -8.511383E-05   4.060075E-05   2.751741E-04
  19    C4     -6.579702E-05  -1.152633E-04  -3.523254E-04
  20    C6      7.402946E-05   2.579128E-04  -1.499552E-05
  21    C7      1.166242E-04   1.234496E-04   3.973756E-04
  22    C8      6.271631E-06  -2.969263E-04   3.035171E-04
  23    H13     2.039987E-05   2.864532E-05  -2.440987E-05
  24    H14     2.358110E-05   7.167173E-05  -1.705182E-04
  25    H15    -7.455694E-06  -1.265121E-04   1.044940E-04
  26    H16    -7.001959E-06  -8.795837E-05   5.141291E-05
  27    N2     -5.435847E-05  -1.207543E-04   3.593817E-05
  28    C16     1.320666E-04   4.606037E-05   5.238811E-05
  29    C17    -2.236293E-04  -1.724962E-04  -7.482440E-05
  30    C18     9.616181E-05  -2.387495E-04   7.324105E-05
  31    C19    -2.905264E-04  -9.721351E-05  -2.287451E-04
  32    C20     9.657132E-05   6.874428E-05  -9.764024E-05
  33    H25     4.376494E-05  -2.231027E-06   3.265464E-05
  34    H26     2.677806E-04   2.459688E-04   3.242475E-05
  35    H27     6.417499E-05  -5.057001E-05  -4.365005E-05
  36    H28    -2.360051E-05  -4.371760E-05  -4.887513E-05
  37    H29     3.379375E-06  -2.713077E-05  -6.804695E-05
 -----------   -------------  -------------  -------------
    total       6.554454E-04  -2.317694E-04   5.200643E-04

  end of program der1b


  start of program geopt  23

  geometry optimization step 23
  reading input hessian of dimension   111
   in five columns format
  reading input hessian of dimension   111
   in five columns format
  reading input hessian of dimension   111
   in five columns format


  energy change:          -1.6816E-06 #  (  5.0000E-05 )
  gradient maximum:        3.8542E-04 *  (  4.5000E-04 )
  gradient rms:            1.2044E-04 *  (  3.0000E-04 )
  step size:   0.00915  trust radius:   0.07500
  displacement maximum:    5.4741E-03 .  (  1.8000E-03 )
  displacement rms:        7.9667E-04 *  (  1.2000E-03 )
  predicted energy change:    -2.7668E-06    geom step:   9.1531E-03    full step:
9.1531E-03

  ***************************************************
  **           Geometry optimization complete          **
  ***************************************************

  center of mass moved by:
     x:     0.0000E+00     y:     0.0000E+00     z:     0.0000E+00

  final geometry:
                               angstroms
  atom           x                 y                 z
  C1        1.1435995465     -1.4446779688     -0.6630201310
  C2        0.8196208055     -0.1930563197     -0.3290428281
  C3        0.7355333759     -2.7154069863     -0.0211886325
  N1        1.5246127727      0.8800316367     -0.8897465093
  C9       -0.2106378125      0.1806756523      0.6877665623
  H7        2.3800563469      0.6159078076     -1.3264799168
  C15       0.9333961178      2.0358882554     -1.4477425631
  C10      -2.1199210636      0.8761512716      2.5948557874
  C11      -1.4854986071     -0.3755464430      0.6466353200
  C12       0.0919422642      1.1029950908      1.6852031971
```

```
 C13      -0.8547802082      1.4414576082      2.6381500989
 C14      -2.4345942239     -0.0299490528      1.5936799164
 H20      -1.7317820833     -1.0758911206     -0.1312004430
 H21       1.0691158780      1.5502929530      1.7111222190
 H22      -0.6060862595      2.1486076886      3.4100589201
 H23      -3.4176672900     -0.4648353614      1.5471952788
 H24      -2.8569600191      1.1443523008      3.3315011246
 H9        1.8044459992     -1.5853755852     -1.5025261918
 C4        0.0566842165     -5.1642652385      0.9819014912
 C6        0.6015648104     -2.8721541914      1.3595498005
 C7        0.2519417502     -4.1100797207      1.8598354907
 C8        0.2380996961     -4.9157161778     -0.3664929394
 H13       0.7723386788     -2.0426565717      2.0174337123
 H14       0.1422991221     -4.2525264193      2.9212259982
 H15       0.1127006637     -5.7060016992     -1.0876991338
 H16      -0.2137986320     -6.1449677259      1.3276201819
 N2        0.5712477209     -3.7354029929     -0.8557143251
 C16      -0.1191358724      4.3778840224     -2.5406829191
 C17       1.7158411287      3.1835306512     -1.5484581653
 C18      -0.3770223954      2.0676417251     -1.9083199897
 C19      -0.8984606188      3.2389009883     -2.4363242441
 C20       1.1962961043      4.3394505476     -2.1013363268
 H25       2.7271401146      3.1625842667     -1.1806961480
 H26      -0.9868545265      1.1852629685     -1.8580966089
 H27      -1.9184594508      3.2513757845     -2.7793082229
 H28       1.8154818198      5.2167316912     -2.1737018285
 H29      -0.5277492680      5.2812913989     -2.9571947330

 nuclear repulsion energy.......  1499.017052768 hartrees
 ------------------------------------------------
/  end of geometry optimization iteration  23   /
------------------------------------------------

 end of program geopt


 start of program post
 Writing a SPARTAN archive file
 end of program post

Total cpu seconds     user:    3249.938   user+sys:    3249.938
```

## REFERENCES


[i] Yang, F.; Cui, X.; Li, Y.; Zhang, J.; Ren, G.; Wu, Y. *Tetrahedron* **2007**, *63*, 1963.

[ii] Jahangir, J.; Wang,. Smith, R. W;. MacLean, D. B; Holland, H. L.; *Can. J. Chem*. **1990**, *68*, 587.

[iii] Muir, C. W.; Kennedy, A. R.; Joanna M.; Redmond; Watson, A. J. B. *Org. Biomol. Chem*., **2013**, *11*, 3337