# Dramatic Enhancing Effect of $InBr_3$ Towards the Oxidative Sonogashira Cross-Coupling Reaction of 2-Ethynylanilines

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## Supporting Information

**Experimental Section**

**Synthesis of starting acetylenes**

**Iodination of aniline derivatives**

**Method A[1];** In a round bottom flask equipped with a magnetic stir bar aniline derivative (5.0 mmol) was added iodine (635 mg, 5.0 mmol) and $Ag_2SO_4$ (1.56 g, 5.0 mmol) and dissolved in ethanol (15 mL). The mixture was stirred until the substrate was disappeared and then the solids were removed by filtration with celite and the filtrate was concentrated under reduced pressure. The crude was dissolved in $CHCl_3$ (15 mL) and washed with $Na_2S_2O_3$ (790 mg, 5.0 mmol) and water (5 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered the solid off. After evaporation of the solvent, the crude was purified by silica gel column chromatography to provide the iodoaniline derivative **5**.

**Method B[2];** To aniline derivative (5.0 mmol) in 50 mL of $H_2O$ was added $NaHCO_3$ (630 mg, 7.5 mmol) and iodine (635 mg, 5.0 mmol). The mixture was stirred until the substrate was disappeared and then $Na_2S_2O_3$ (790 mg, 5.0 mmol) was added. The reaction was extracted with $CHCl_3$, the combined organic layer was dried over anhydrous $MgSO_4$ and filtered the solid off. The crude was purified by silica gel column chromatography to provide the iodoaniline derivative **5**.

**Sonogashira cross-coupling reaction and desilylation[3,4]**

To a mixture of aryl iodide (5.0 mmol), $PdCl_2(PPh_3)_2$ (175 mg, 5 mol%), CuI (48 mg, 5 mol%) and $Et_3N$ (1.04 mL, 7.5 mmol) in dry THF (7.5 mL) was slowly added trimethylsilylacetylene (1.04 mL, 7.5 mmol). After the reaction mixture was stirred at room temperature for overnight, the reaction was quenched by addition of water and the whole mixture was extracted with $Et_2O$. The organic layer was dried over anhydrous $MgSO_4$ and filtered the solid off. After evaporation of the solvent, the crude was purified by silica gel column chromatography to afford the silylated arylacetylenes. The mixture of silylated arylacetylenes and $K_2CO_3$ (691 mg, 5.0 mmol) in MeOH and $H_2O$ was stirred at room temperature until silylated acetylenes were disappeared. Then, the mixture was extracted with $CHCl_3$ and dried over anhydrous $MgSO_4$. After filtration of the solid, the organic layer was concentrated under reduced pressure. The residue was purified by silica gel chromatography to provide the arylacetylenes **2**.

**Different approach to 2-iodo-4-methoxybenzenamine[5,6,7]**

Under argon atmosphere, to the solution of *p*-anisidine (12.3 g, 100.0 mmol) in $CH_2Cl_2$ was added $Et_3N$ (15.4 mL, 110.0 mmol) and $Boc_2O$ (25.3 mL, 110.0 mmol) slowly at 0 °C. After the reaction mixture was stirred at same temperature for overnight, the reaction was quenched by addition of water and the whole mixture was extracted with $CH_2Cl_2$. The organic layer was dried over anhydrous $MgSO_4$ and filtered the solid off. After evaporation of the solvent, the *tert*-butyl 4-methoxyphenylcarbamate **6i** was isolated as a white solid (21.9 g, 98%).

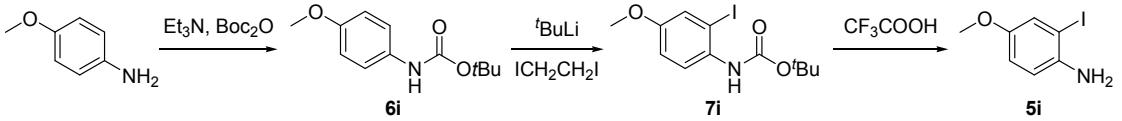
mp 95-96 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 1.51 (9H, s), 3.77 (3H, s), 6.37 (1H, br s), 6.8 (2H, d, *J* 8.3Hz),

7.26 (2H, d, *J* 8.3Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 28.4, 55.5, 80.2, 114.1, 120.5, 131.3, 153.0, 155.6; *m/z* (EI) 223.1201 ($M^+$. $C_{12}H_{17}NO_3$ requires 223.1208).

Under argon atmosphere, to a magnetically stirred solution of *tert*-butyl 4-methoxyphenylcarbamate **6i** (17.9 g, 80.0 mmol) in anhydrous $Et_2O$ (150 mL) was slowly added *tert*-butyllithium (88.4 mL of a 1.9M solution in hexane, 168.0 mmol) at -20 °C. After stirring for 3 hours, the reaction mixture was cooled to -78 °C, and 1,2-diiodoethane (45.1 g, 160.0 mmol) dissolved in anhydrous $Et_2O$ (300 mL) was added. Then the reaction mixture was gradually warmed to room temperature and stirred for overnight. After addition of $Na_2S_2O_3$ (150 mL of a saturated aqueous solution), the whole mixture was extracted with $Et_2O$ and dried over anhydrous $MgSO_4$. The solid was filtered off, and the organic layer was concentrated under reduced pressure. The residue was purified by silica gel chromatography (AcOEt : hexane = 10 : 90) to provide *tert*-butyl 2-iodo-4-methoxyphenlcarbamate **7i** as a light yellow oil in 69% yield (19.3 g).

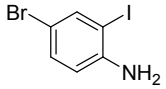
$\delta_H$ ($CDCl_3$, 400 MHz) 1.52 (9H, s), 3.76 (3H, s), 6.54 (1H, br s), 6.90 (1H, dd, *J* 3.0Hz, 8.8Hz), 7.30 (1H, d, *J* 3.0Hz), 7.81 (1H, d, *J* 8.8Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 28.4, 55.7, 80.7, 90.4, 114.8, 122.0, 123.6, 132.3, 153.0, 155.9; *m/z* (EI) 349.0182 ($M^+$. $C_{12}H_{16}INO_3$ requires 349.0175).

To the solution of *tert*-butyl 2-iodo-4-methoxyphenylcarbamate **7i** (17.5 g, 50.0 mmol) in $CH_2Cl_2$ (250 mL) was added $CF_3COOH$ (44.6 mL, 600.0 mmol) at room temperature. After the reaction mixture was stirred for overnight, 10% aqueous NaOH solution was added until pH of the solution became 7. The mixture was extracted with $CH_2Cl_2$, and the organic layer was dried over anhydrous $MgSO_4$. The solid was filtered off, and the organic layer was concentrated under reduced pressure. After purification by silica gel chromatography (AcOEt : hexane = 10 : 90), 2-iodo-4-methoxybenzenamine **5i** was isolated as a yellow oil in 98% (12.2 g).



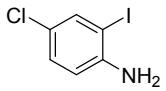

**Spectroscopic data of iodoaniline derivatives and aryl acetylenes**

4-bromo-2-iodobenzenamine **5c**



The title product **5c** was obtained as a light yellow solid (715 mg, 48%) after column chromatography (AcOEt : hexane = 10 : 90) using method A. mp 68-69 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 4.10 (2H, br s), 6.62 (1H, d, *J* 8.8Hz), 7.23 (1H, dd, *J* 2.2Hz, 8.6Hz), 7.74 (1H, d, *J* 2.5Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 84.0, 109.8, 115.5, 132.0, 140.3, 145.8; *m/z* (EI) 269.8659 ($M^+$. $C_6H_5BrIN$ requires 269.8650).

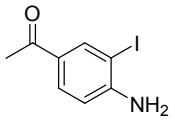
4-chloro-2-iodobenzenamine **5d**



The title product **5d** was obtained as a light yellow solid (811 mg, 64%) after column chromatography (AcOEt : hexane = 10 : 90) using method A. mp 39-40 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 4.08 (2H, br s), 6.66 (1H, d, *J* 8.3Hz), 7.11 (1H, dd, *J* 2.2Hz,

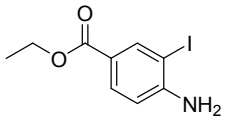
8.6Hz), 7.61 (1H, d, *J* 2.0Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 83.4, 114.9, 123.1, 129.2, 137.7, 145.4; *m/z* (EI) 252.9164 ($M^+$. $C_6H_5ClIN$ requires 252.9155).

1-(4-amino-3-iodophenyl)ethanone **5e**



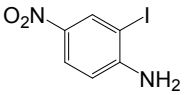
The title product **5e** was obtained as a white solid (744 mg, 57%) after column chromatography (AcOEt : hexane = 30 : 70) using method A. mp 45-46 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 2.49 (3H, s), 4.60 (2H, br s), 6.71 (1H, d, *J* 8.7Hz), 7.77 (1H, dd, *J* 1.4Hz, 8.2Hz), 8.28 (1H, d, *J* 1.4Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 26.0, 82.5, 113.1, 129.3, 130.3, 140.3, 150.9, 195.1; *m/z* (EI) 260.9653 ($M^+$. $C_8H_8INO$ requires 260.9651).

ethyl 4-amino-3-iodobenzoate **5f**



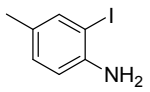
The title product **5f** was obtained as a white solid (1.22 g, 84%) after column chromatography (AcOEt : hexane = 30 : 70) using method A. mp 79-80 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 1.36 (3H, t, *J* 7.3Hz), 4.32 (2H, q, *J* 7.2Hz), 4.51 (2H, br s), 6.70 (1H, d, *J* 8.3Hz), 7.83 (1H, dd, *J* 2.0Hz, 8.3Hz), 8.34 (1H, d, *J* 2.0Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 14.4, 60.7, 82.1, 113.0, 121.5, 131.0, 140.9, 150.5, 165.2; *m/z* (EI) 290.9762 ($M^+$. $C_9H_{10}INO_2$ requires 290.9756).

2-iodo-4-nitrobenzene **5g**



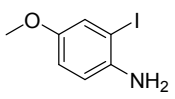
The title product **5g** was obtained as a yellow solid (1.10 g, 84%) after column chromatography ($CH_2Cl_2$ : hexane = 80 : 20) using method A. mp 106-107 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 4.85 (2H, br s), 6.71 (1H, d, *J* 8.8Hz), 8.06 (1H, dd, *J* 2.5Hz, 8.8Hz), 8.57 (1H, d, *J* 2.5Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 80.5, 112.2, 125.7, 135.4, 139.2, 152.2; *m/z* (EI) 263.9403 ($M^+$. $C_6H_5IN_2O_2$ requires 263.9394).

2-iodo-4-methylbenzenamine **5h**



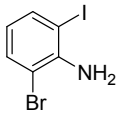
The title product **5h** was obtained as a light yellow solid (886 mg, 76%) after column chromatography (AcOEt : hexane = 5 : 95) using method B. mp 36-37 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 2.20 (3H, s), 3.93 (2H, br s), 6.66 (1H, d, *J* 8.2Hz), 6.94 (1H, dd, *J* 1.8Hz, 8.2Hz), 7.47 (1H, d, *J* 1.8Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 19.8, 84.3, 114.6, 129.5, 130.0, 139.0, 144.3; *m/z* (EI) 232.9704 ($M^+$. $C_7H_8IN$ requires 232.9701).

2-iodo-4-methoxybenzenamine **5i**



The title product **5i** was obtained as a light yellow oil. $\delta_H$ ($CDCl_3$, 400 MHz) 3.73 (3H, s), 3.79 (2H, br s), 6.70 (1H, d, *J* 8.3Hz), 6.77 (1H, dd, *J* 2.9Hz, 8.8Hz), 7.22 (1H, d, *J* 2.9Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 56.0, 84.3, 115.3, 116.1, 123.5, 140.7, 152.6; *m/z* (EI) 248.9655 ($M^+$. $C_7H_8INO$ requires 248.9651).

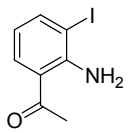
2-bromo-6-iodobenzenamine **5j**



The title product **5j** was obtained as a light yellow solid (655 mg, 44%) after column chromatography (AcOEt : hexane = 10 : 90) using method A. mp 83-84 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 4.17 (2H, br s), 6.58 (1H, d, *J* 8.3Hz), 7.41 (1H, dd, *J* 2.0Hz, 8.8Hz), 7.74

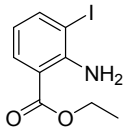
(1H, d, *J* 2.0Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 78.3, 110.0, 117.2, 136.9, 139.9, 143.8; *m/z* (EI) 269.8648 ($M^+$. $C_6H_5BrIN$ requires 297.8650).

1-(2-amino-3-iodophenyl)ethanone **5k**



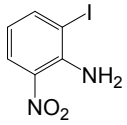
The title product **5k** was obtained as a light yellow solid (1.25 g, 96%) after column chromatography (AcOEt : hexane = 10 : 90) using method A. mp 93-94 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 2.55 (3H, s), 6.30 (2H, br s), 6.45 (1H, d, *J* 8.8Hz), 7.47 (1H, dd, *J* 1.9Hz, 8.8Hz), 7.97 (1H, d, *J* 2.0Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 27.7, 75.1, 119.4, 120.5, 140.5, 142.5, 149.7, 199.7; *m/z* (EI) 260.9651 ($M^+$. $C_8H_8INO$ requires 260.9651).

ethyl 2-amino-3-iodobenzoate **5l**



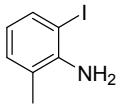
The title product **5l** was obtained as a white solid (1.19 g, 82%) after column chromatography (AcOEt : hexane = 10 : 90) using method A. mp 68-69 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 1.38 (3H, t, *J* 7.1Hz), 4.33 (2H, q, *J* 7.1Hz), 5.77 (2H, br s), 6.45 (1H, d, *J* 8.8Hz), 7.47 (dd, *J* 2.0Hz, 8.8Hz), 8.14 (1H, d, *J* 2.5Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 14.4, 60.4, 75.9, 113.1, 118.7, 139.3, 142.0, 149.7, 166.8; *m/z* (EI) 290.9760 ($M^+$. $C_9H_{10}INO_2$ requires 290.9756).

2-iodo-6-nitrobenzenamine **5m**



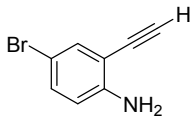
The title product **5m** was obtained as a yellow solid (1.16 g, 88%) after column chromatography (AcOEt : hexane = 20 : 80) using method A. mp 124-125 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 6.09 (2H, br s), 6.61 (1H, d, *J* 8.7Hz), 7.57 (1H, dd, *J* 2.0Hz, 8.8Hz), 8.43 (1H, d, *J* 2.3Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 75.9, 120.5, 133.1, 134.3, 143.6, 143.9; *m/z* (EI) 263.9399 ($M^+$. $C_6H_5IN_2O_2$ requires 263.9396).

2-iodo-6-methylbenzenamine **5n**



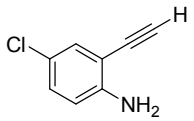
The title product **5n** was obtained as a light yellow solid (746 mg, 64%) after column chromatography (AcOEt : hexane = 10 : 90) using method B. mp 86-87 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 2.11 (3H, s), 3.61 (2H, br s), 6.45 (1H, d, *J* 8.2Hz), 7.29 (1H, dd, *J* 1.8Hz, 8.2Hz), 7.34 (1H, d, *J* 1.8Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 17.0, 79.5, 116.8, 124.9, 135.5, 138.6, 144.3; *m/z* (EI) 232.9701 ($M^+$. $C_7H_8IN$ requires 232.9701).

4-bromo-2-ethynylbenzenamine **2c**



The title product **2c** was obtained as a light yellow solid (892 mg, 91% for 2 steps) after column chromatography (AcOEt : hexane = 10 : 90). mp 65-66 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 3.41 (1H, s), 4.26 (2H, br s), 6.58 (1H, d, *J* 8.8Hz), 7.22 (1H, dd, *J* 2.4Hz, 8.8Hz), 7.43 (1H, d, *J* 2.4Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 79.2, 83.5, 108.4, 108.7, 115.7, 132.9, 134.6, 147.4; *m/z* (EI) 196.9670 ($M^+$. $C_8H_6BrN$ requires 196.9684).

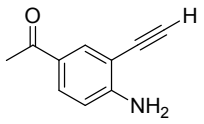
4-chloro-2-ethynylbenzenamine **2d**



The title product **2d** was obtained as a light yellow solid (531 mg, 70% for 2 steps) after column chromatography (AcOEt : hexane = 10 : 90). mp 53-54 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 3.41 (1H, s), 4.24 (2H, br s), 6.62 (1H, d, *J* 8.8Hz), 7.09

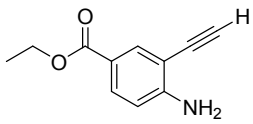
(1H, dd, *J* 2.5Hz, 8.8Hz), 7.28 (1H, d, *J* 2.4Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 79.4, 83.4, 107.9, 115.4, 122.0, 130.1, 131.8, 147.0; *m/z* (EI) 151.0180 ($M^+$. $C_8H_6ClN$ requires 151.0189).

1-(4-amino-3-ethynylphenyl)ethanone **2e**



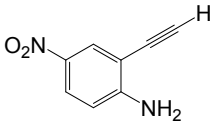
The title product **2e** was obtained as a white solid (661 mg, 83% for 2 steps) after column chromatography (AcOEt : hexane = 20 : 80). mp 76-77 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 2.50 (3H, s), 3.41 (1H, s), 4.74 (2H, br s), 6.69 (1H, d, *J* 8.6Hz), 7.80 (1H, dd, *J* 2.0Hz, 8.8Hz), 7.98 (1H, d, *J* 2.0Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 26.1, 79.5, 83.0, 105.6, 113.3, 127.4, 130.7, 134.2, 152.2, 195.5; *m/z* (EI) 159.0681 ($M^+$. $C_{10}H_9NO$ requires 159.0684).

ethyl 4-amino-3-ethynylbenzoate **2f**



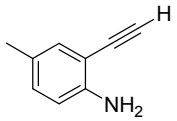
The title product **2f** was obtained as a white solid (870 mg, 92% for 2 steps) after column chromatography (AcOEt : hexane = 20 : 80). mp 105-106 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 1.36 (3H, t, *J* 7.3Hz), 3.40 (1H, s), 4.32 (2H, q, *J* 7.3Hz), 4.67 (2H, br s), 6.67 (1H, d, *J* 8.7Hz), 7.83 (1H, dd, *J* 1.8Hz, 8.7Hz), 8.04 (1H, d, *J* 2.3Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 14.4, 60.5, 79.6, 82.9, 105.7, 113.2, 119.7, 131.8, 134.8, 152.0, 166.0; *m/z* (EI) 189.0789 ($M^+$. $C_{11}H_{11}NO_2$ requires 189.0790).

2-ethynyl-4-nitrobenzenamine **2g**



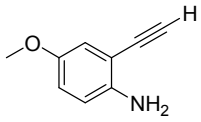
The title product **2g** was obtained as a yellow solid (609 mg, 75% for 2 steps) after column chromatography (AcOEt : hexane = 30 : 70). mp 128-129 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 3.47 (1H, s), 5.00 (2H, br s), 6.69 (1H, d, *J* 8.7Hz), 8.05 (1H, dd, *J* 2.4Hz, 8.8Hz), 8.26 (1H, d, *J* 2.9Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 78.1, 84.2, 105.7, 112.9, 126.3, 129.2, 138.3, 153.4; *m/z* (EI) 162.0423 ($M^+$. $C_8H_6N_2O_2$ requires 162.0429).

2-ethynyl-4-methylbenzenamine **2h**



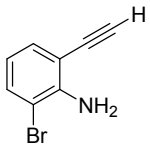
The title product **2h** was obtained as a light yellow solid (584 mg, 89% for 2 steps) after column chromatography (AcOEt : hexane = 5 : 95). mp 34-35 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 2.20 (3H, s), 3.35 (1H, s), 4.10 (2H, br s), 6.61 (1H, d, *J* 8.2Hz), 6.96 (1H, dd, *J* 1.8Hz, 8.2Hz), 7.13 (1H, d, *J* 1.6z); $\delta_C$ ($CDCl_3$, 400 MHz) 20.2, 80.8, 82.1, 106.6, 114.5, 127.1, 131.0, 132.6, 146.2; *m/z* (EI) 131.0730 ($M^+$. $C_9H_9N$ requires 131.0735).

2-ethynyl-4-methoxybenzenamine **2i**



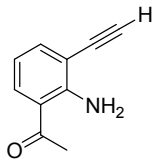
The title product **2i** was obtained as a light yellow oil (623 mg, 94% for 2 steps) after column chromatography (AcOEt : hexane = 10 : 90). $\delta_H$ ($CDCl_3$, 400 MHz) 3.38 (1H, s), 3.73 (3H, s), 3.98 (2H, br s), 6.65 (1H, d, *J* 8.8Hz), 6.79 (1H, dd, *J* 2.9Hz, 8.8Hz), 6.88 (1H, d, *J* 2.9Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 55.7, 80.6, 82.4, 107.1, 115.8, 116.2, 117.8, 142.7, 151.6; *m/z* (EI) 147.0687 ($M^+$. $C_9H_9NO$ requires 141.684).

2-bromo-6-ethynylbenzenamine **2j**



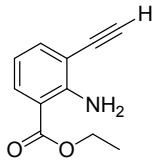
The title product **2j** was obtained as a light yellow solid (882 mg, 90% for 2 steps) after column chromatography (AcOEt : hexane = 20 : 80). mp 46-47 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 2.97 (1H, s), 4.25 (2H, br s), 6.67 (1H, d, *J* 8.3Hz), 7.24 (1H, dd, *J* 1.5Hz, 8.3Hz), 7.57 (1H, d, *J* 1.9Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 75.8, 82.8, 108.1, 112.5, 114.9, 132.3, 136.2, 144.7; *m/z* (EI) 196.9666 ($M^+$. $C_8H_6BrN$ requires 196.9684).

1-(2-amino-3-ethynylphenyl)ethanone **2k**



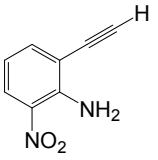
The title product **2k** was obtained as a light yellow solid (788 mg, 99% for 2 steps) after column chromatography (AcOEt : hexane = 20 : 80). mp 50-51 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 2.57 (3H,s), 2.97 (1H, s), 6.47 (2H, br s), 6.58 (1H, d, *J* 8.8Hz), 7.36 (1H, dd, *J* 1.9Hz, 8.3Hz), 7.89 (1H, d, *J* 1.9Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 27.6, 74.9, 83.6, 109.0, 117.3, 117.9, 136.6, 137.6, 150.5, 200.2; *m/z* (EI) 159.0688 ($M^+$. $C_{10}H_9NO$ requires 159.0684).

ethyl 2-amino-3-ethynylbenzoate **2l**



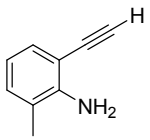
The title product **2l** was obtained as a white solid (539 mg, 57% for 2 steps) after column chromatography (AcOEt : hexane = 5 : 95). mp 65-66 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 1.39 (3H, t, *J* 7.3Hz), 2.95 (1H, s), 4.33 (2H, q, *J* 7.3Hz), 5.93 (2H, br s), 6.59 (1H, d, *J* 8.7Hz), 7.36 (1H, dd, *J* 1.8Hz, 8.7Hz), 8.05 (1H, d, *J* 1.8Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 14.3, 60.6, 74.8, 83.7, 109.3, 110.7, 116.6, 135.7, 137.2, 150.6, 167.4; *m/z* (EI) 189.0782 ($M^+$. $C_{11}H_{11}NO_2$ requires 189.0790).

2-ethynyl-6-methylbenzenamine **2m**



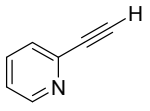
The title product **2m** was obtained as a yellow solid (800 mg, 99% for 2 steps) after column chromatography (AcOEt : hexane = 20 : 80). mp 119-120 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 3.00 (1H, s), 6.22 (2H, br s), 6.77 (1H, d, *J* 8.6Hz), 7.44 (1H, dd, *J* 2.0Hz, 8.8Hz), 8.29 (1H, d, *J* 2.0Hz) ; $\delta_C$ ($CDCl_3$, 400 MHz) 76.5, 81.8, 110.9, 118.9, 130.4, 131.9, 138.6, 144.6; *m/z* (EI) 162.0427($M^+$. $C_8H_6N_2O_2$ requires 162.0429).

2-ethynyl-6-methylbenzenamine **2n**



The title product **2n** was obtained as a yellow oil (151 mg, 23% for 2 steps) after column chromatography (AcOEt : hexane = 5 : 95). $\delta_H$ ($CDCl_3$, 400 MHz) 2.13 (3H, s), 2.94 (1H, s), 3.76 (2H, br s), 6.58 (1H, d, *J* 8.2Hz), 7.18 (1H, dd, *J* 1.8Hz, 8.2Hz), 7.21 (1H, d, *J* 1.8Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 17.1, 74.6, 84.6, 111.3, 114.4, 121.9, 131.2, 134.3, 145.3; *m/z* (EI) 131.0728 ($M^+$. $C_9H_9N$ requires 131.0735).

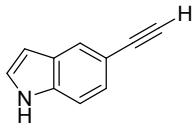
2-ethynylpyridine **2o**



The title product **2o** was obtained as a light yellow oil (382 mg, 74% for 2 steps) after column chromatography (AcOEt : hexane = 30 : 70). $\delta_H$ ($CDCl_3$, 400 MHz) 3.16 (1H, s), 7.25-7.29 (1H, m), 7.49 (1H, d, *J* 7.8Hz), 7.64-7.69 (1H, m), 8.60 (1H,

d, *J* 4.9Hz); $\delta_C$ ($CDCl_3$, 400 MHz) 77.1, 82.7, 123.3, 127.3, 136.0, 142.2, 149.9; *m/z* (EI) 103.0420 ($M^+$. $C_7H_5N$ requires 103.0422).

5-ethynyl-1*H*-indole **2p**



The title product **2p** was obtained as a light yellow solid (536 mg, 76% for 2 steps) after column chromatography (AcOEt : hexane = 10 : 90). mp 66-67 °C; $\delta_H$ ($CDCl_3$, 400 MHz) 3.00 (1H, s), 6.53-6.55 (1H, m), 7.21-7.23 (1H, m), 7.32 (2H, s), 7.84 (1H, s), 8.20 (1H, br s); $\delta_C$ ($CDCl_3$, 400 MHz) 74.6, 85.3, 102.9, 111.0, 113.1, 125.1, 125.3, 125.9, 127.6, 135.6; *m/z* (EI) 141.0579 ($M^+$. $C_{10}H_7N$ requires 141.0578).

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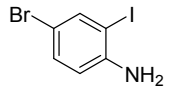
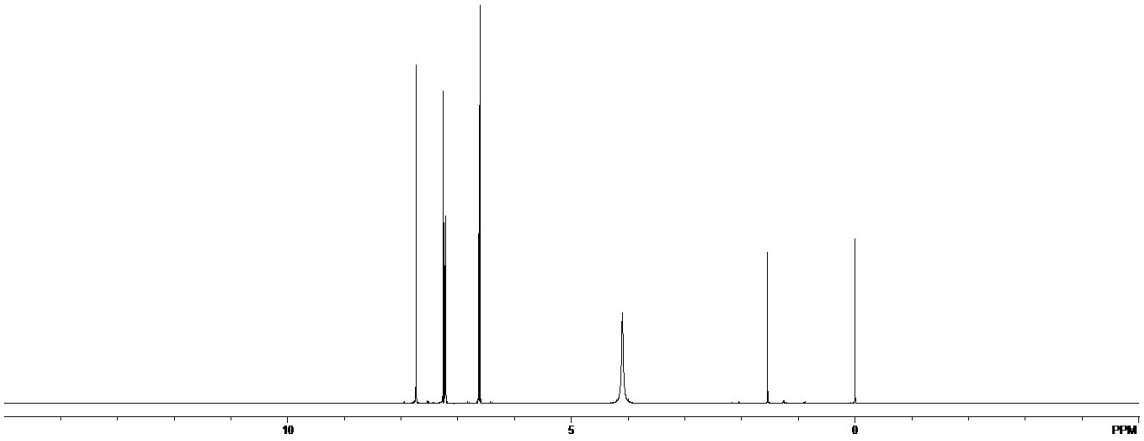
**$^{1}$H and $^{13}$C NMR Charts:**

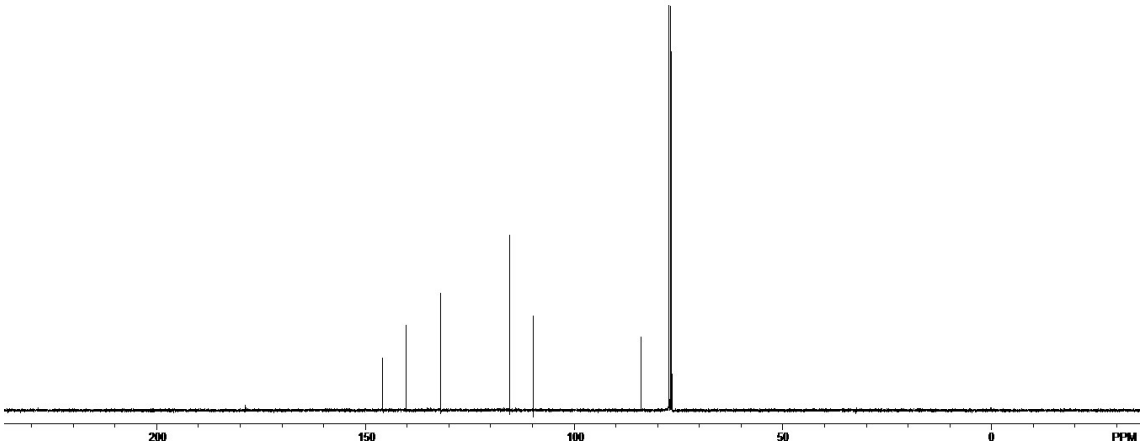
4-bromo-2-iodobenzenamine **5c**



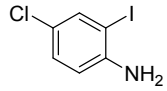

$^{1}$H NMR spectrum



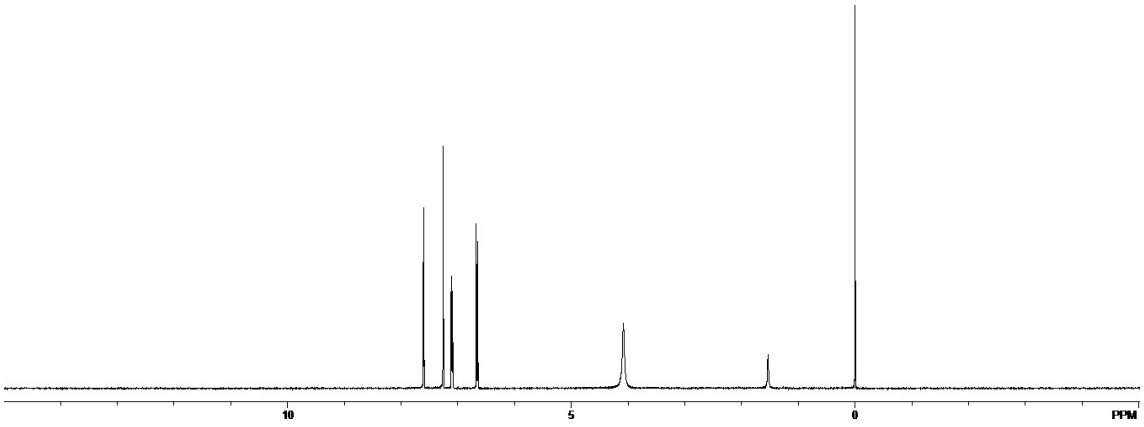

$^{13}$C NMR spectrum



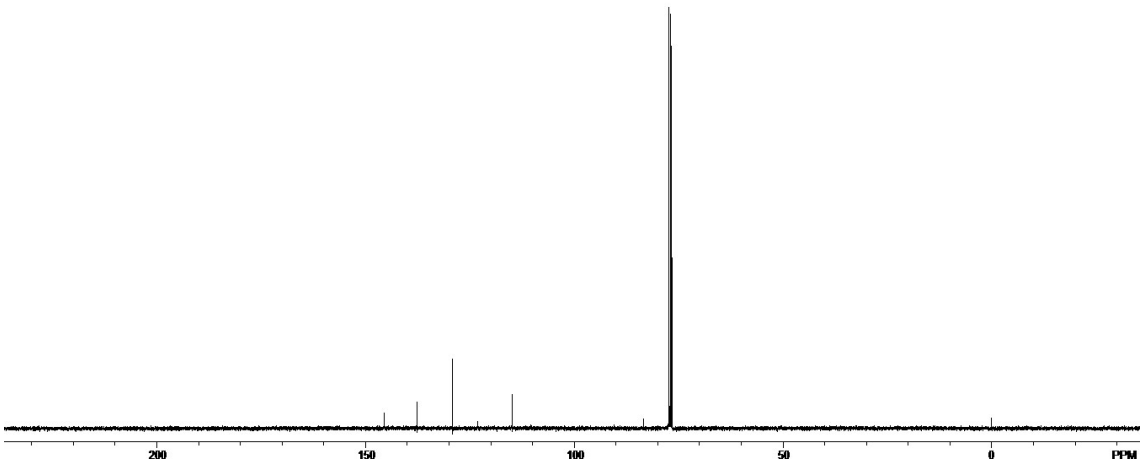
4-chloro-2-iodobenzenamine **5d**



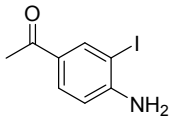

$^{1}$H NMR spectrum



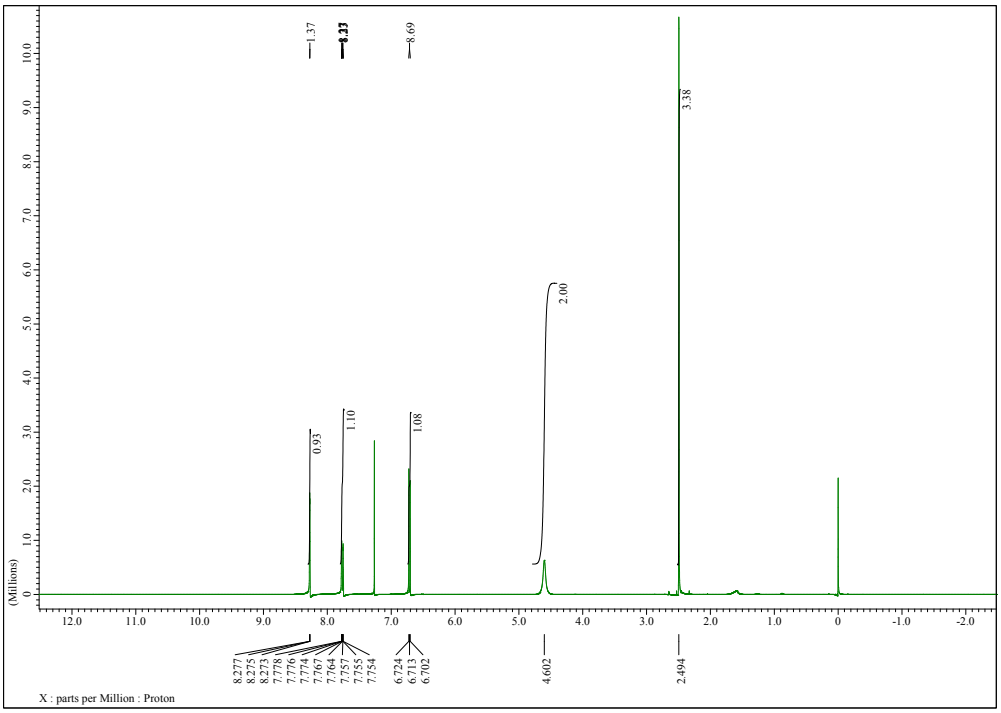

$^{13}$C NMR spectrum



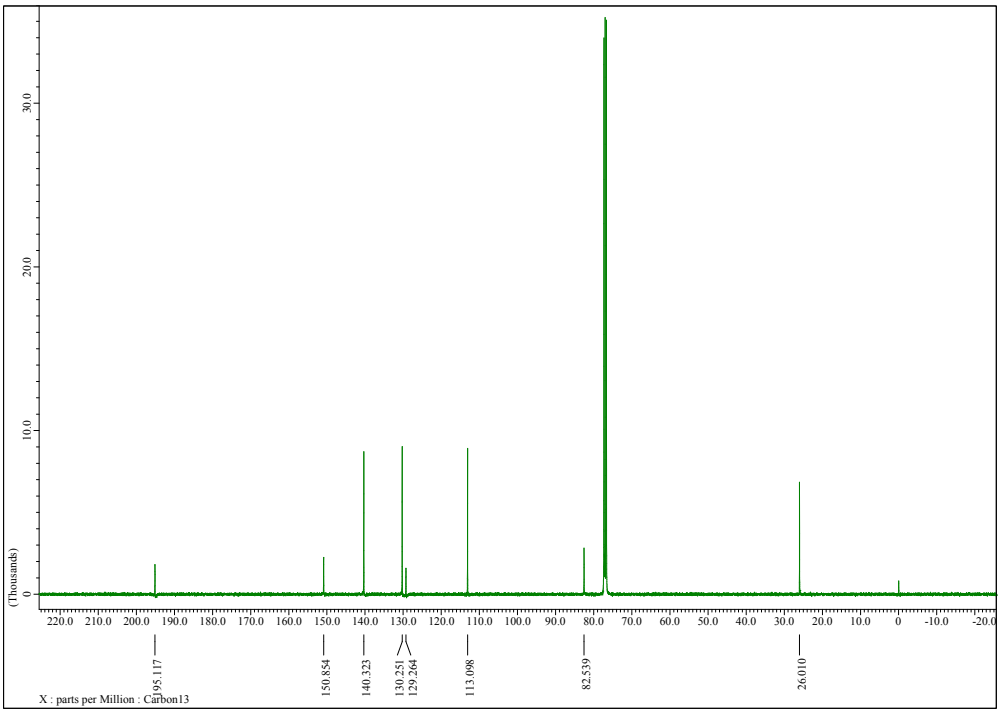
1-(4-amino-3-iodophenyl)ethanone **5e**



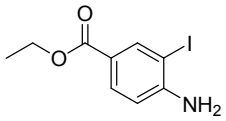

$^{1}$H NMR spectrum



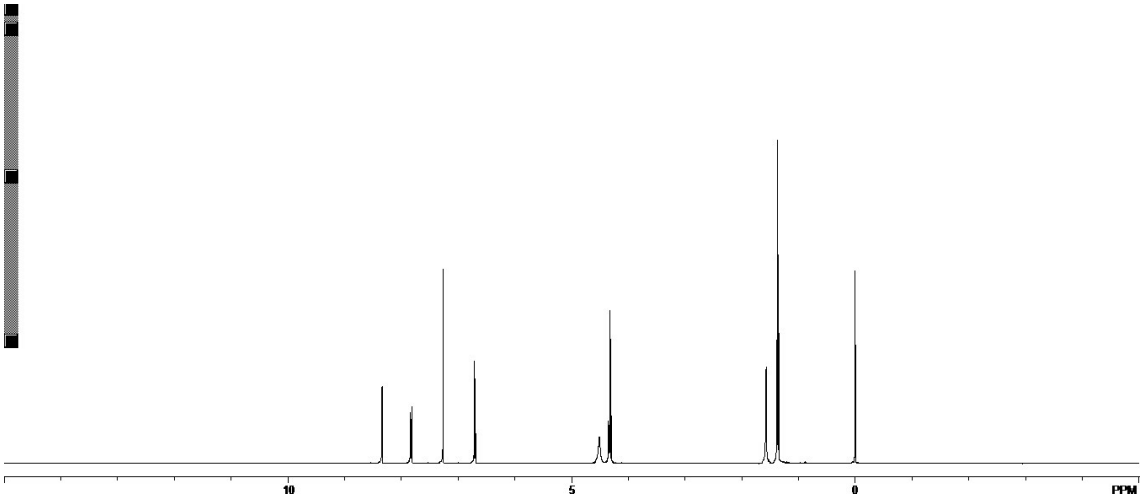

$^{13}$C NMR spectrum



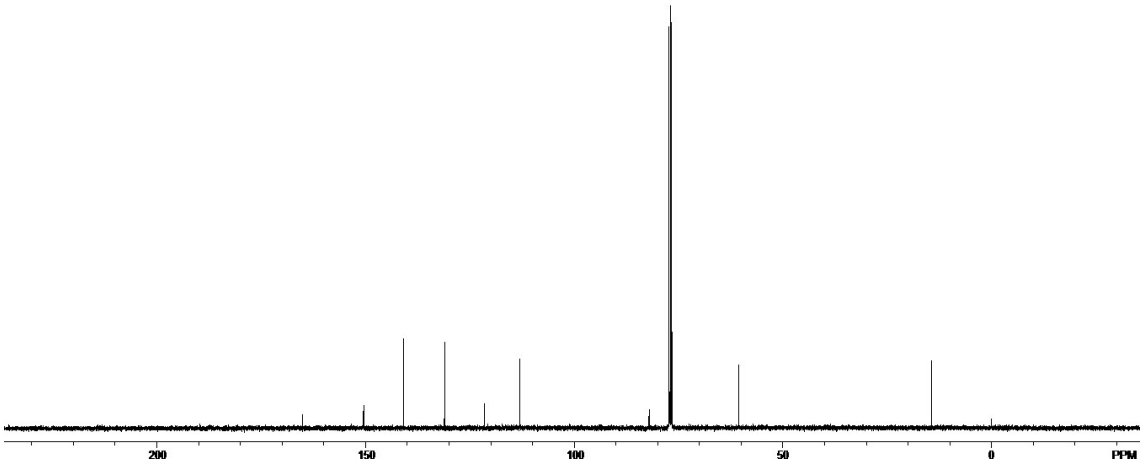
ethyl 4-amino-3-iodobenzoate **5f**



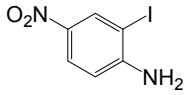

$^{1}$H NMR spectrum



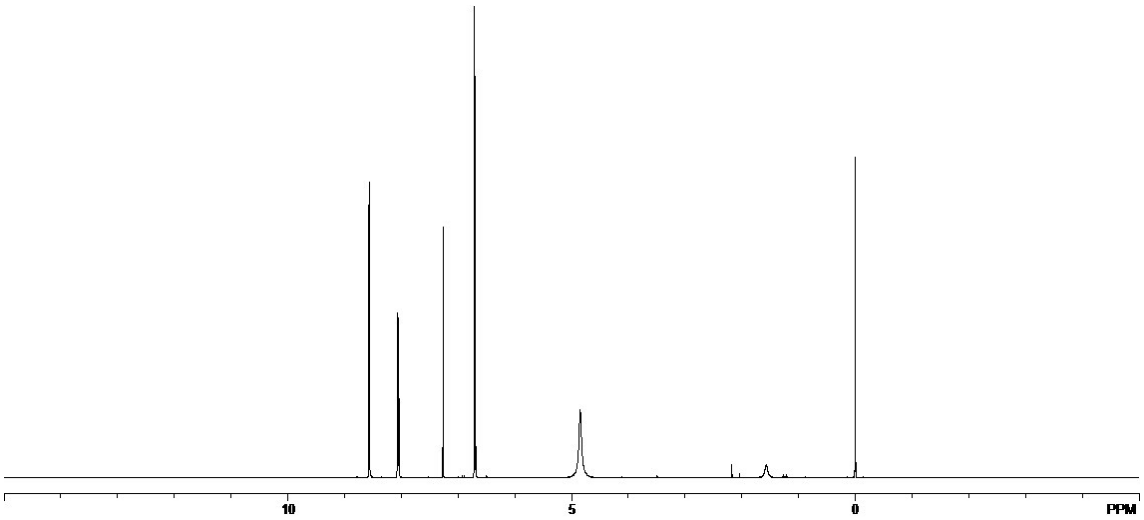

$^{13}$C NMR spectrum



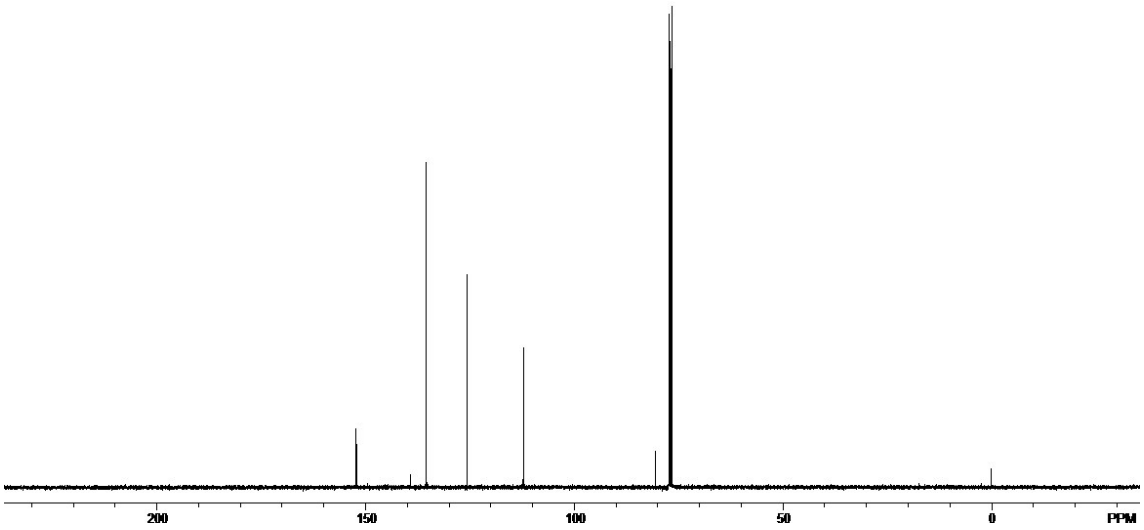
2-iodo-4-nitrobenzene **5g**



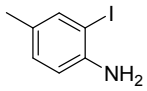

$^{1}$H NMR spectrum



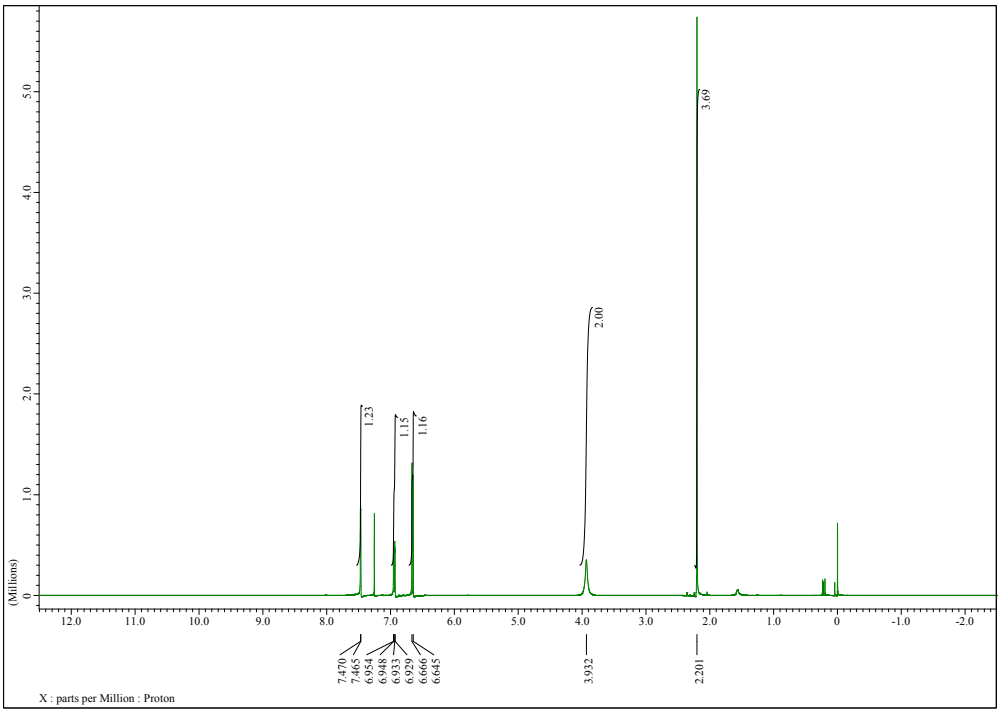

$^{13}$C NMR spectrum



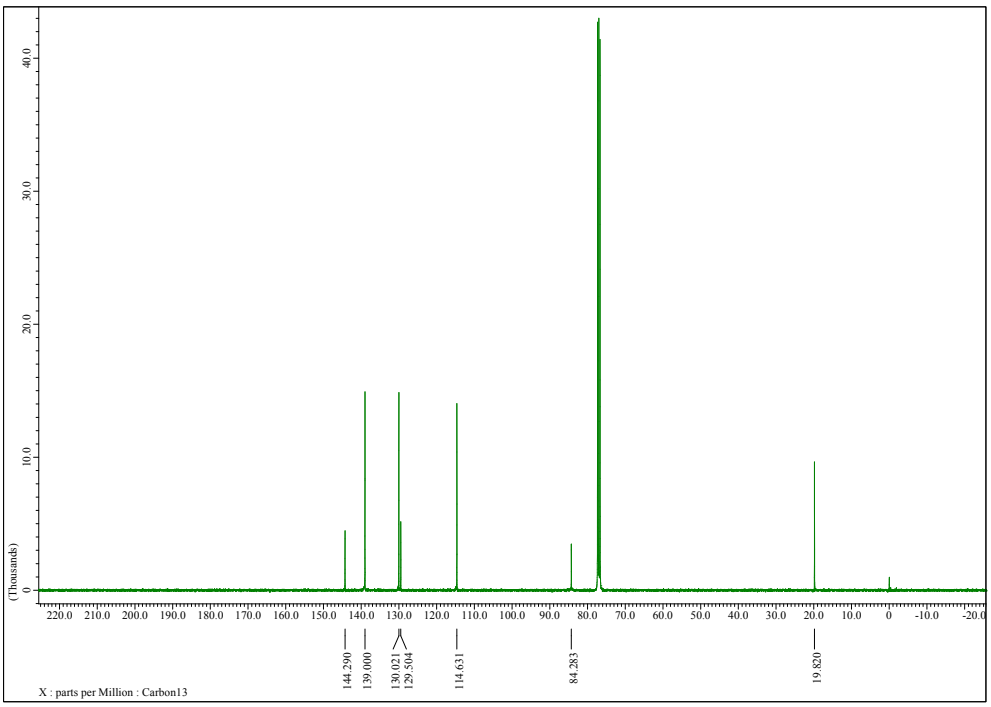
2-iodo-4-methylbenzenamine **5h**



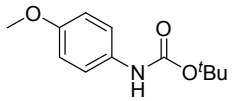

$^{1}$H NMR spectrum



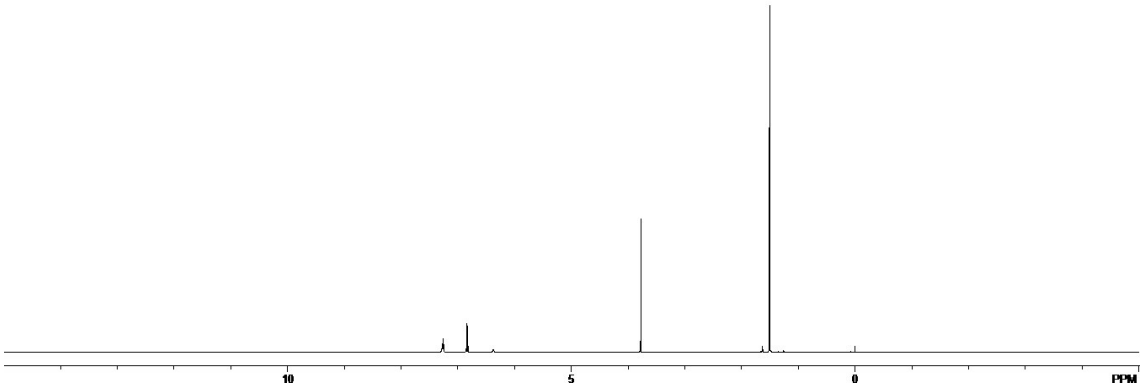

$^{13}$C NMR spectrum



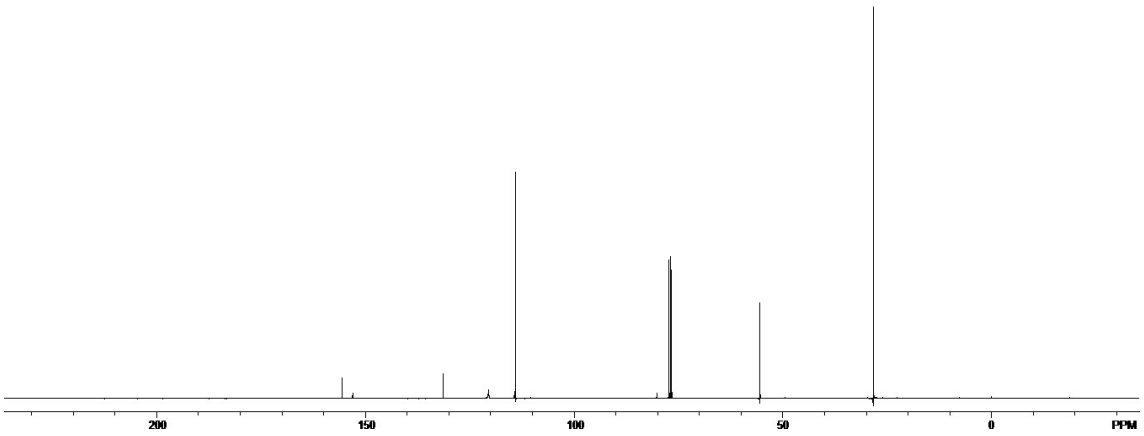
*tert*-butyl 4-methoxyphenylcarbamate **6i**



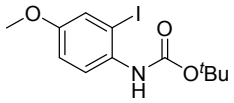

$^1$H NMR spectrum



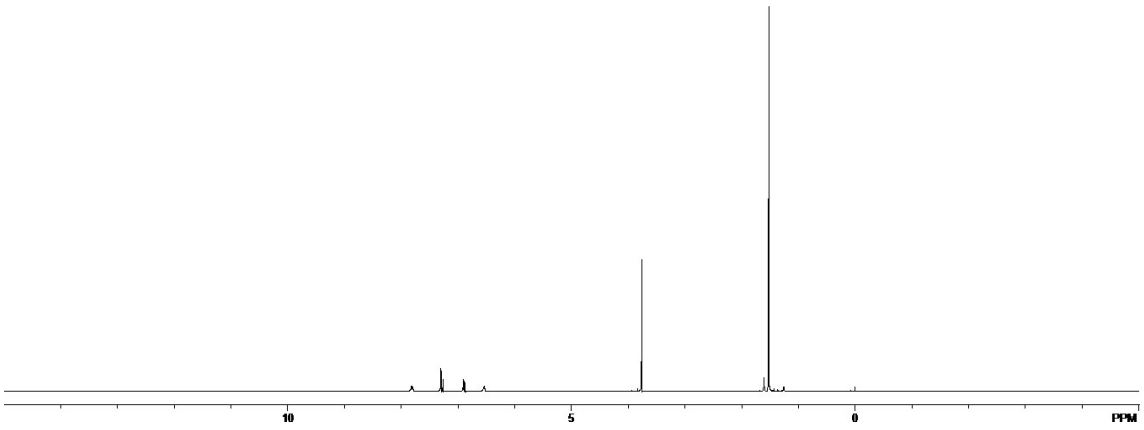

$^{13}$C NMR spectrum



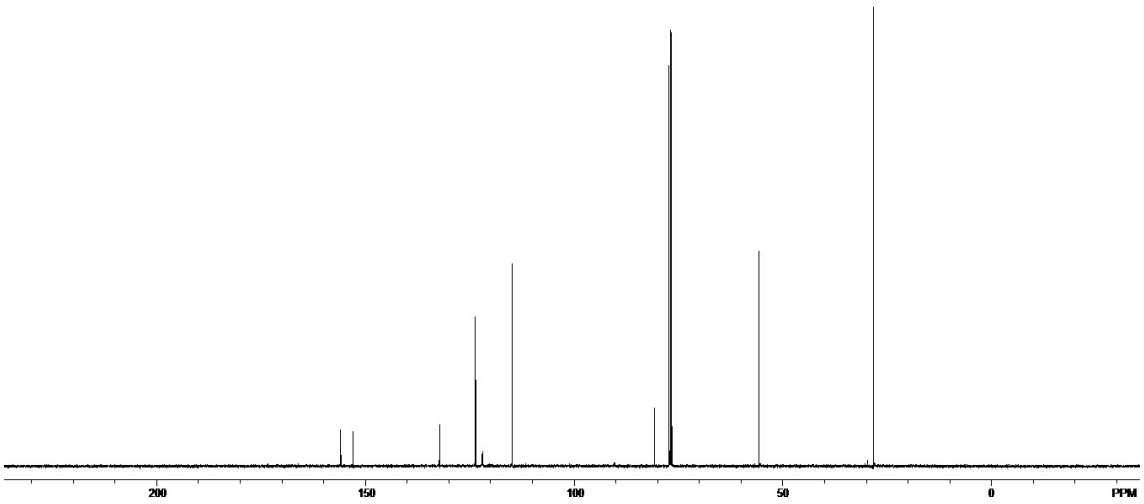
*tert*-butyl 2-iodo-4-methoxyphenlcarbamate **7i**



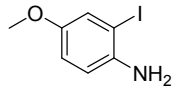

$^1$H NMR spectrum



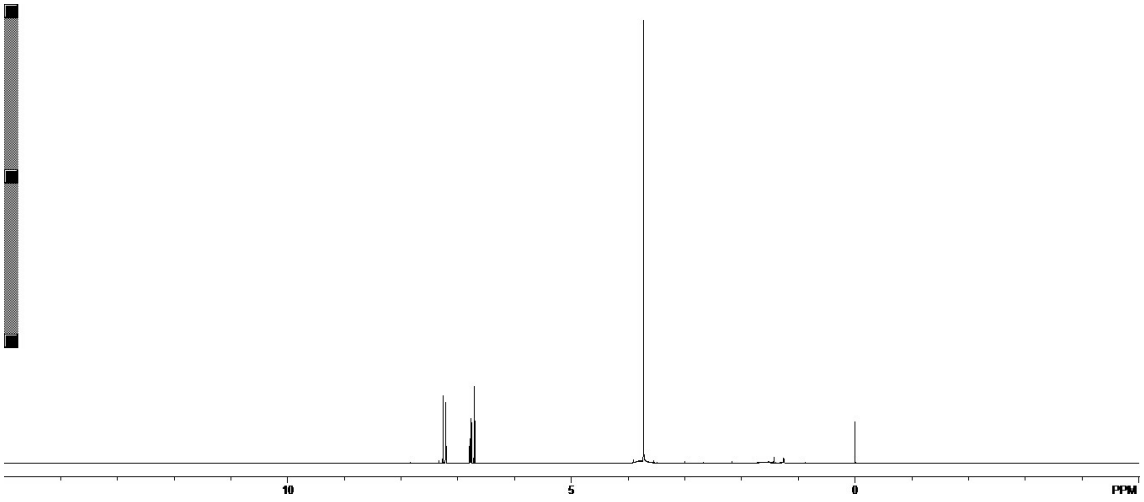

$^{13}$C NMR spectrum



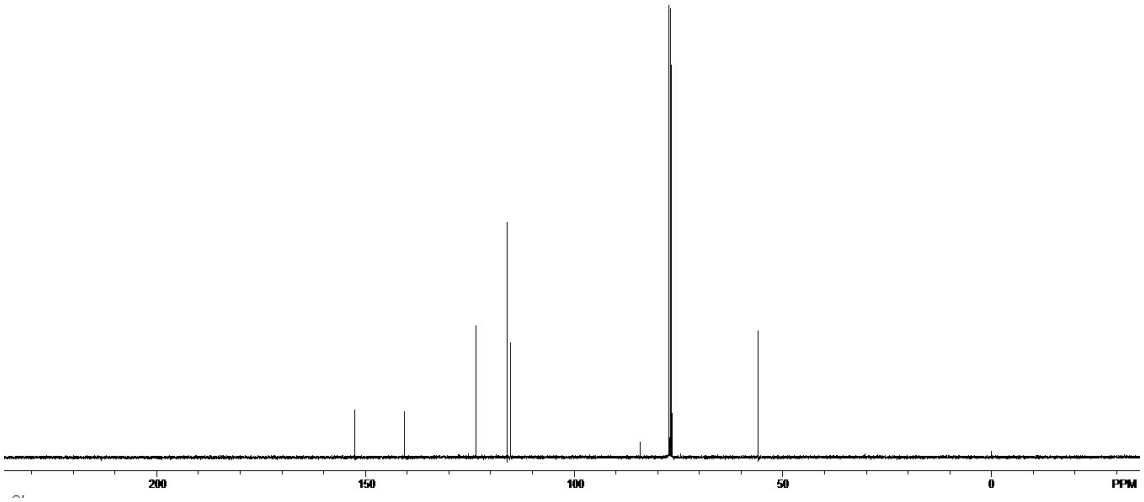
2-iodo-4-methoxybenzenamine **5i**



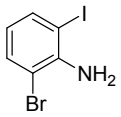

$^{1}$H NMR spectrum



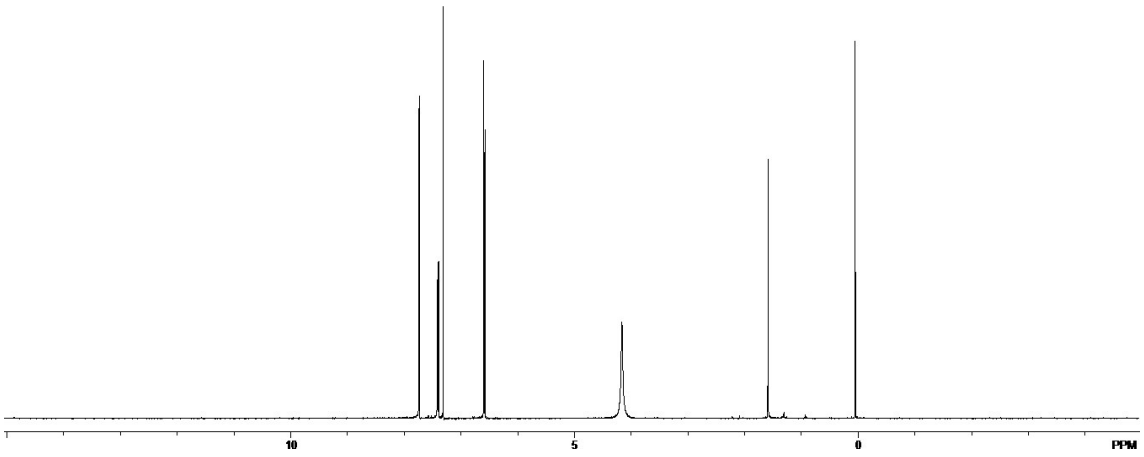

$^{13}$C NMR spectrum



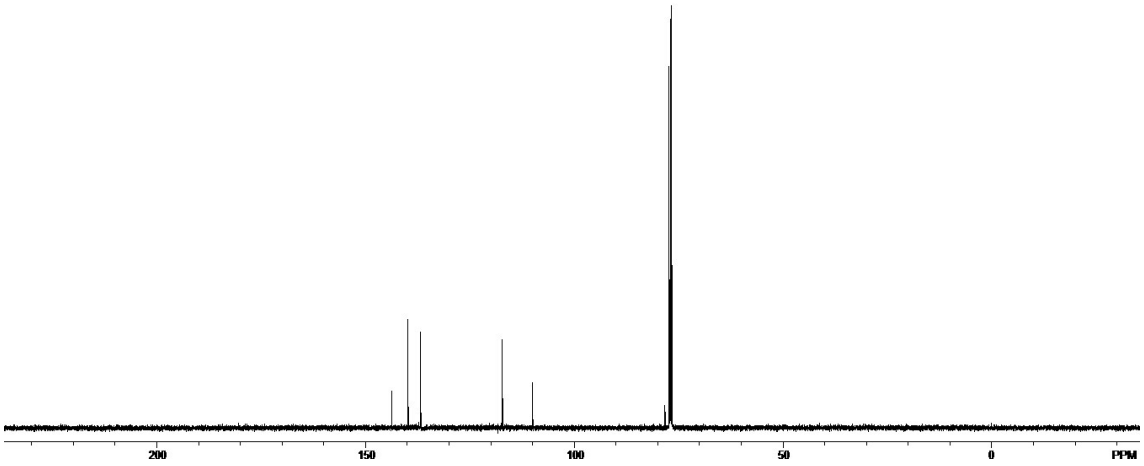
2-bromo-6-iodobenzenamine **5j**



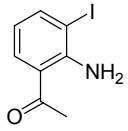

$^{1}$H NMR spectrum



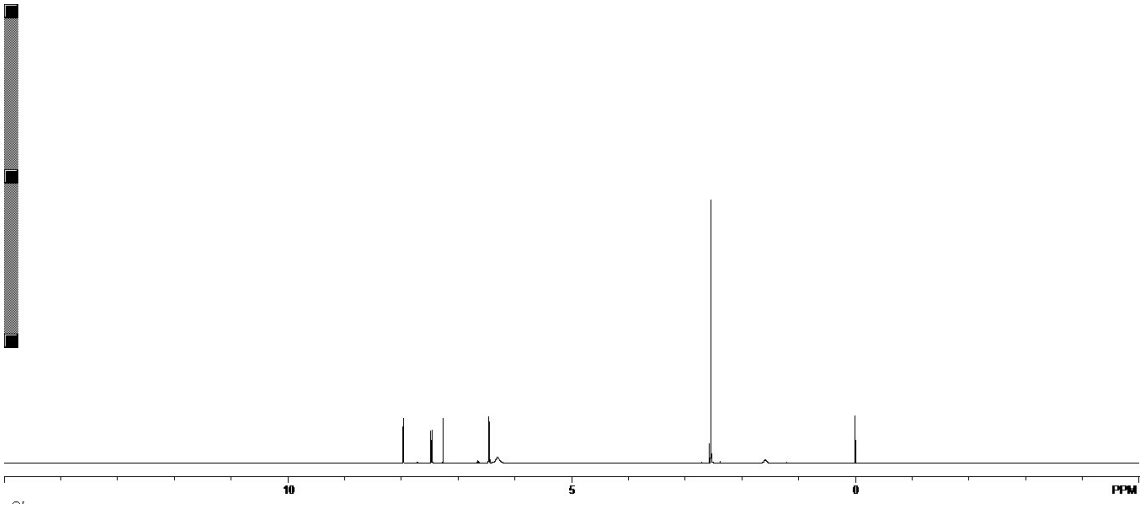

$^{13}$C NMR spectrum



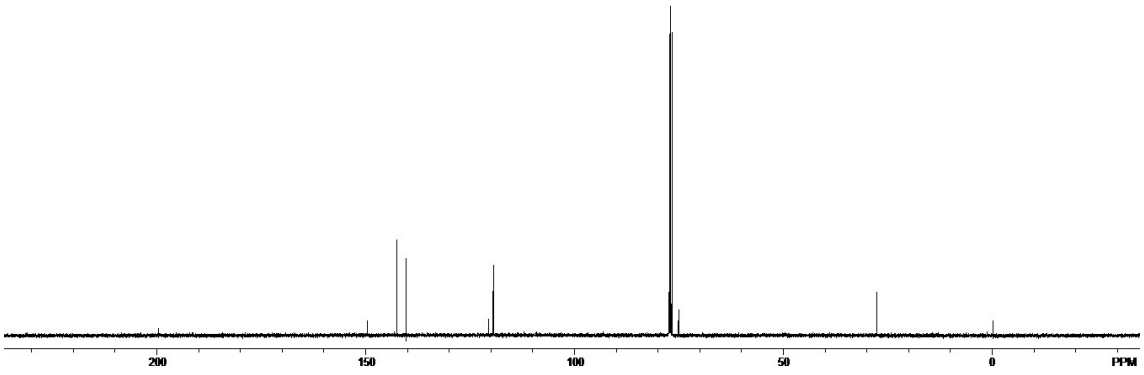
1-(2-amino-3-iodophenyl)ethanone **5k**



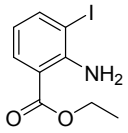

$^{1}$H NMR spectrum



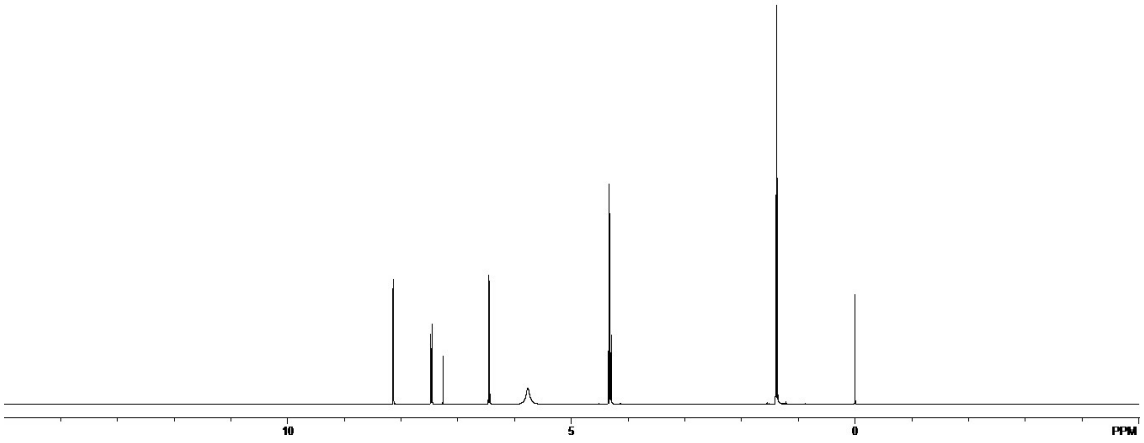

$^{13}$C NMR spectrum



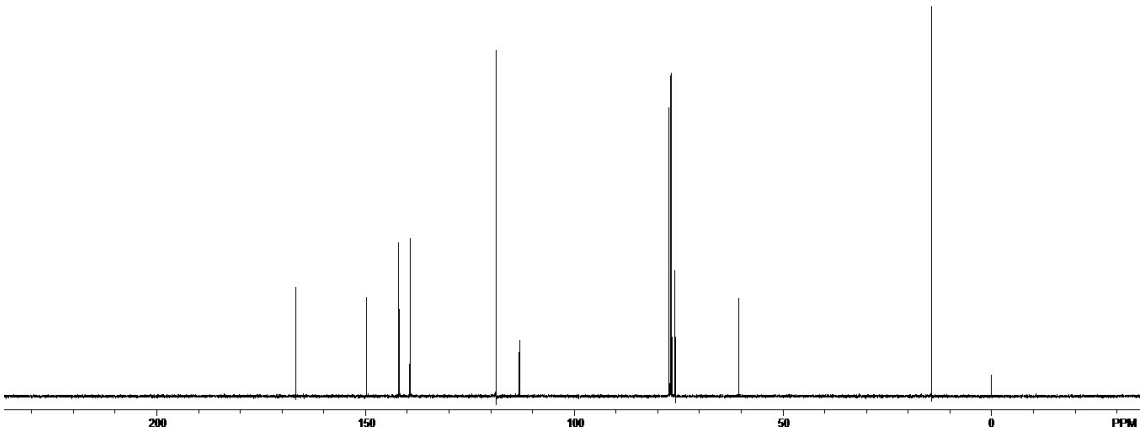
ethyl 2-amino-3-iodobenzoate **5l**



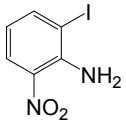

$^{1}$H NMR spectrum



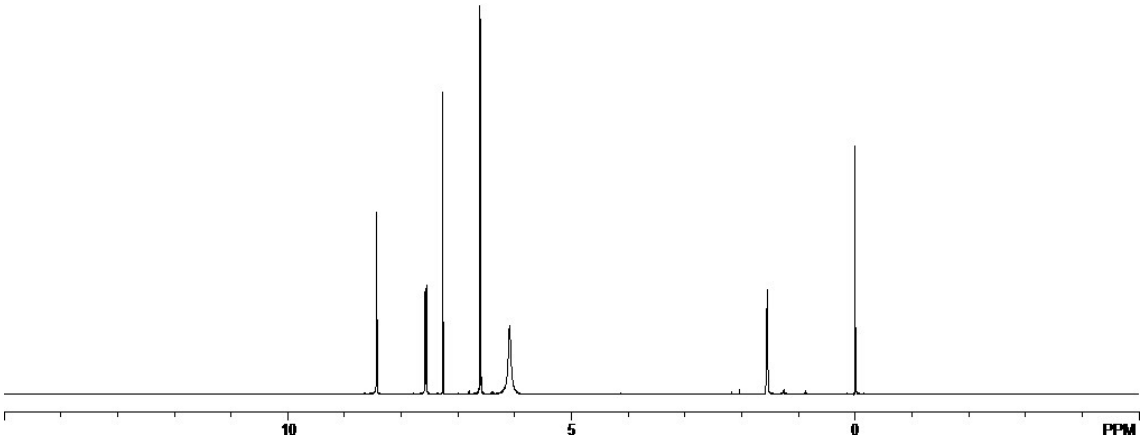

$^{13}$C NMR spectrum



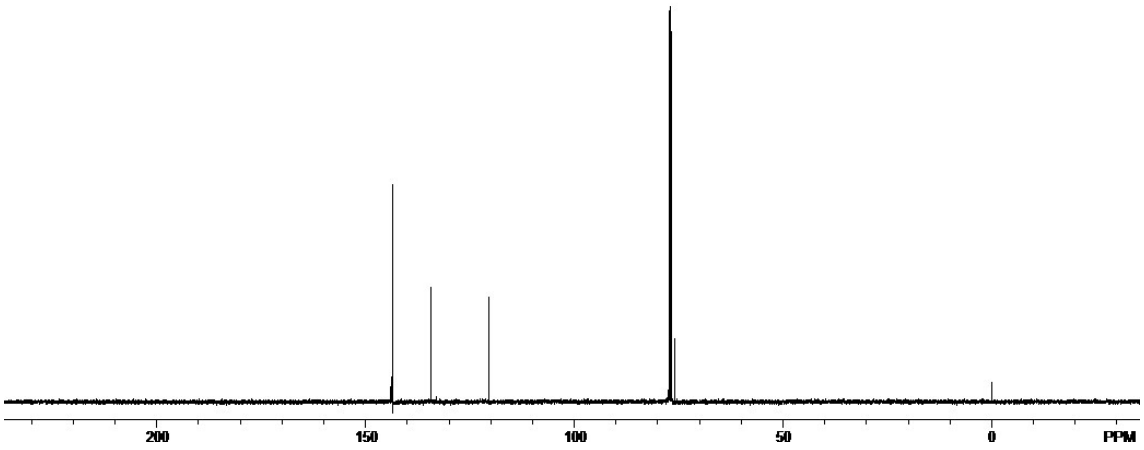
2-iodo-6-nitrobenzenamine **5m**



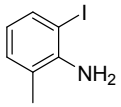

$^{1}$H NMR spectrum



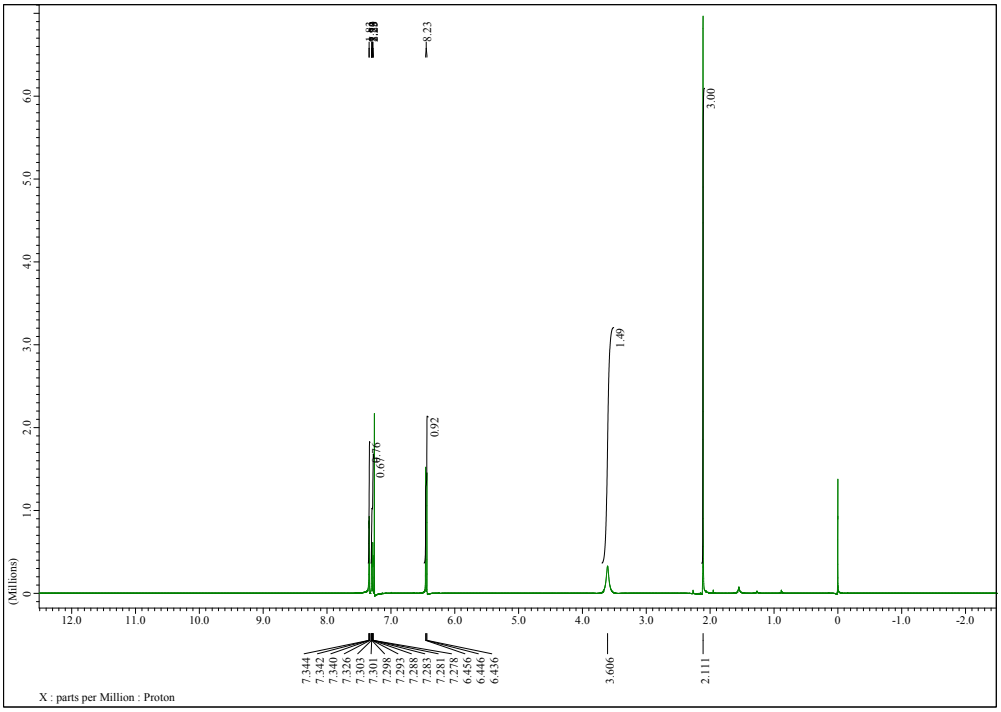

$^{13}$C NMR spectrum



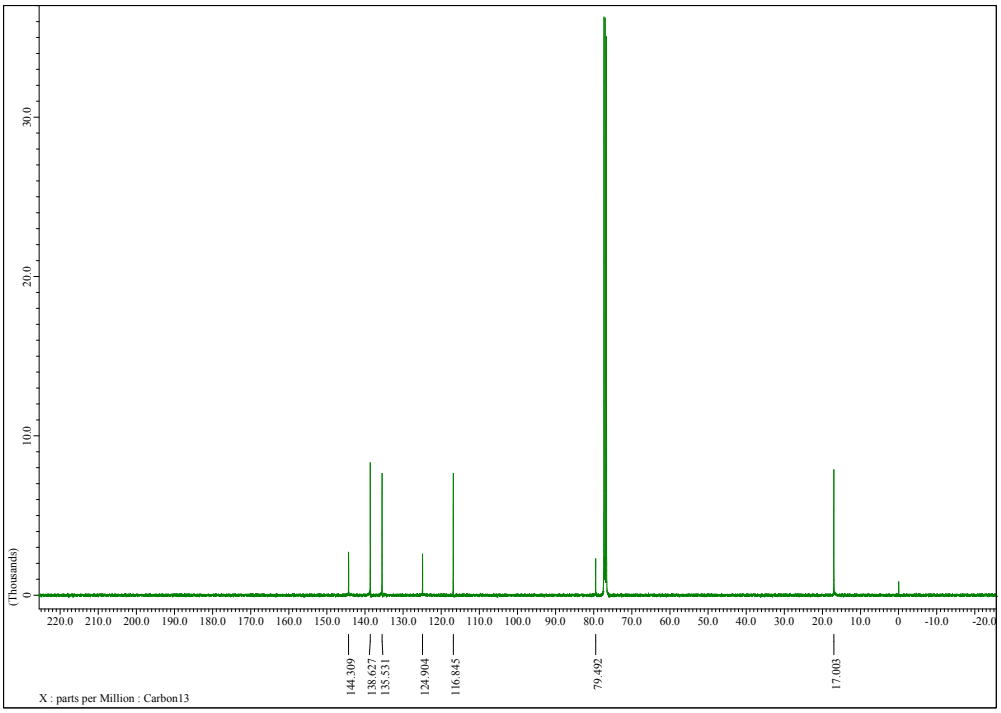
2-iodo-6-methylbenzenamine **5n**



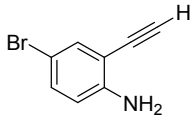

$^{1}$H NMR spectrum



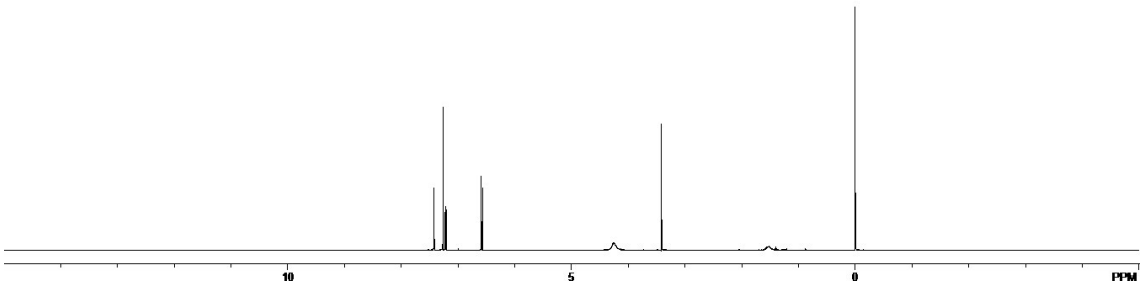

$^{13}$C NMR spectrum



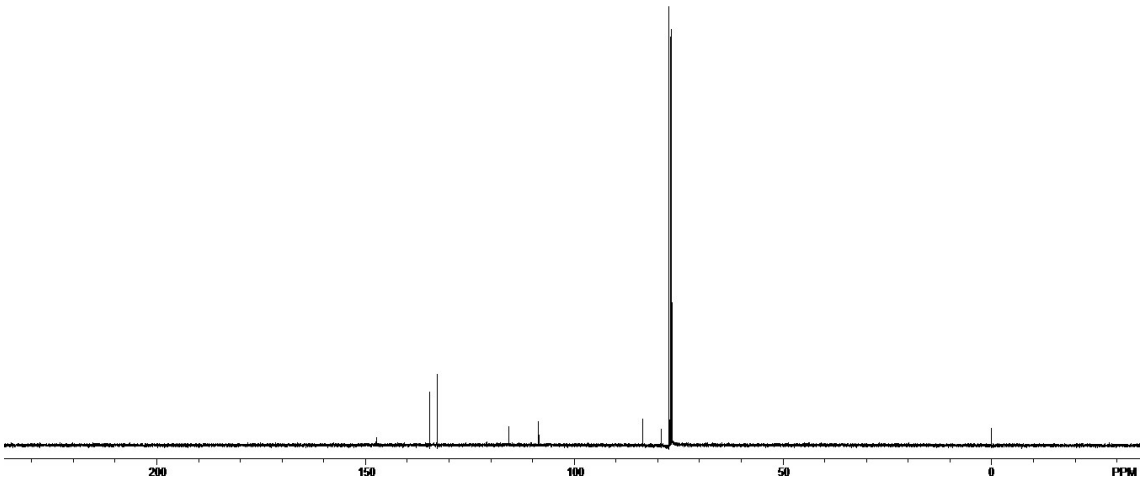

4-bromo-2-ethynylbenzenamine **2c**



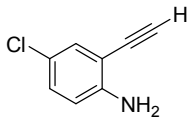

$^{1}$H NMR spectrum



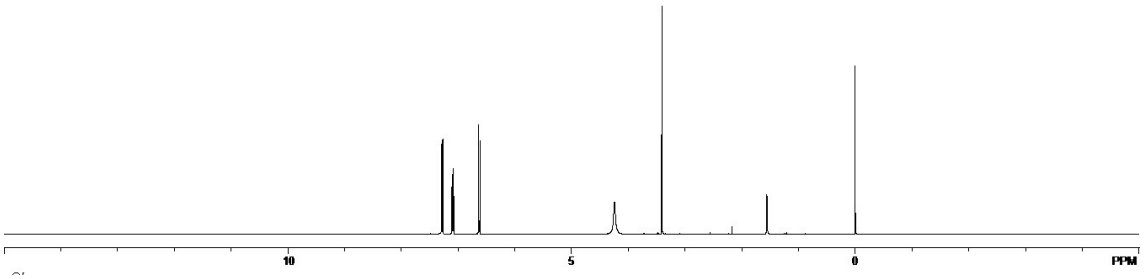

$^{13}$C NMR spectrum



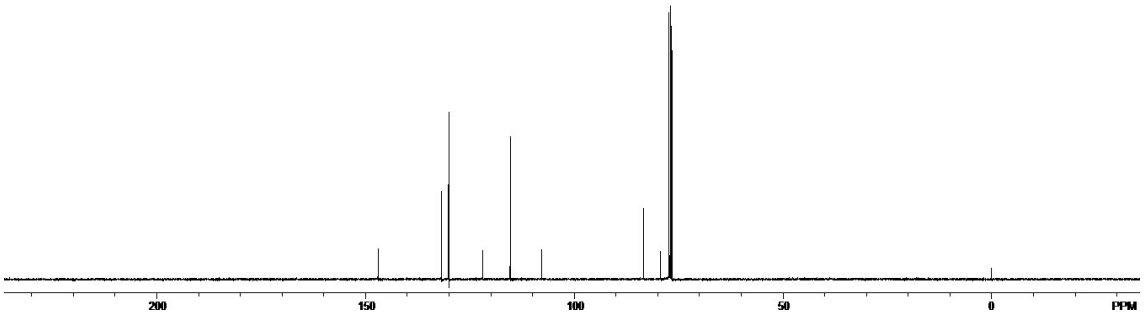

4-chloro-2-ethynylbenzenamine **2d**



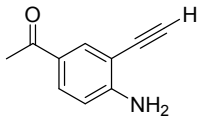

$^{1}$H NMR spectrum



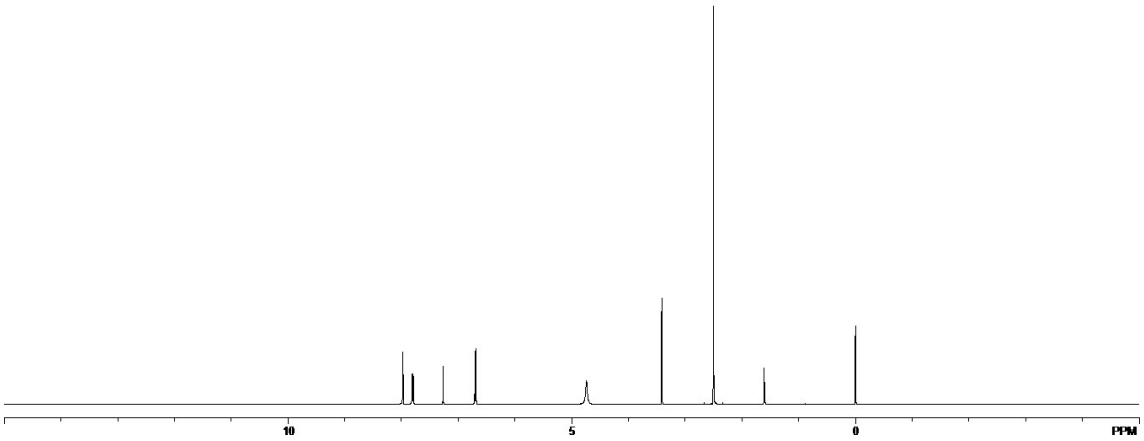

$^{13}$C NMR spectrum



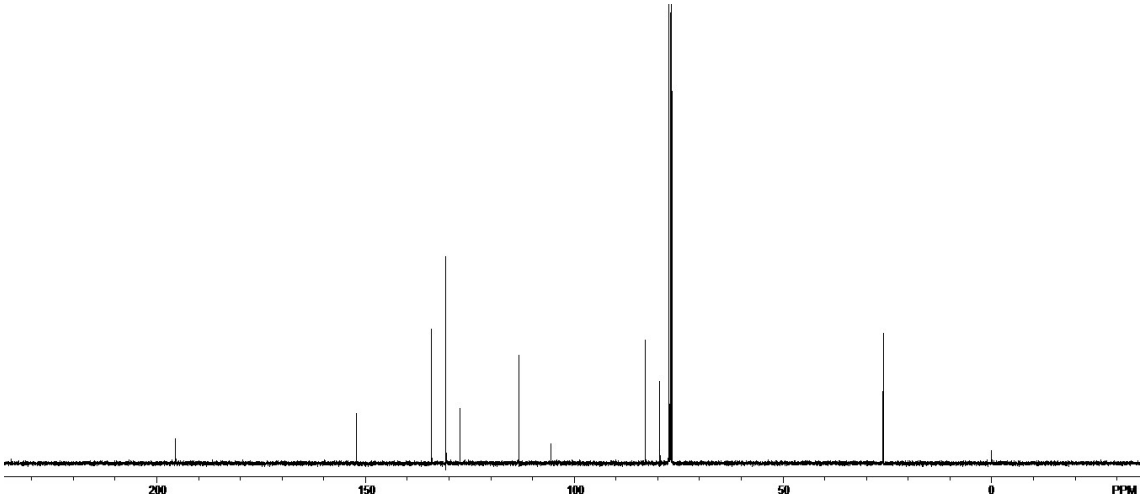

1-(4-amino-3-ethynylphenyl)ethanone **2e**



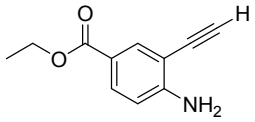

$^{1}$H NMR spectrum



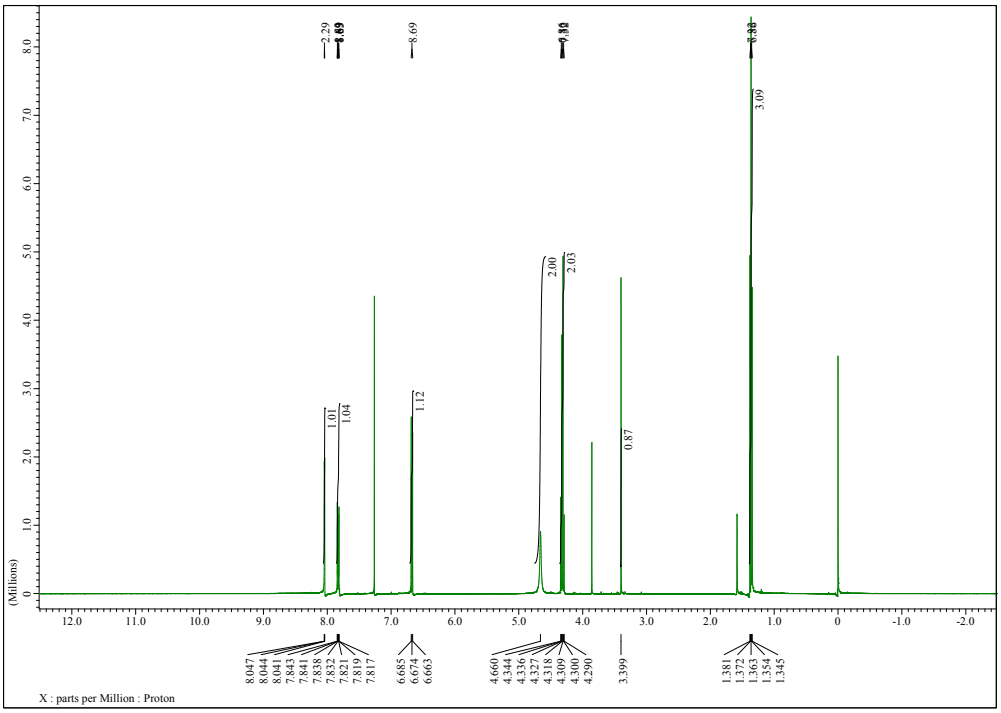

$^{13}$C NMR spectrum



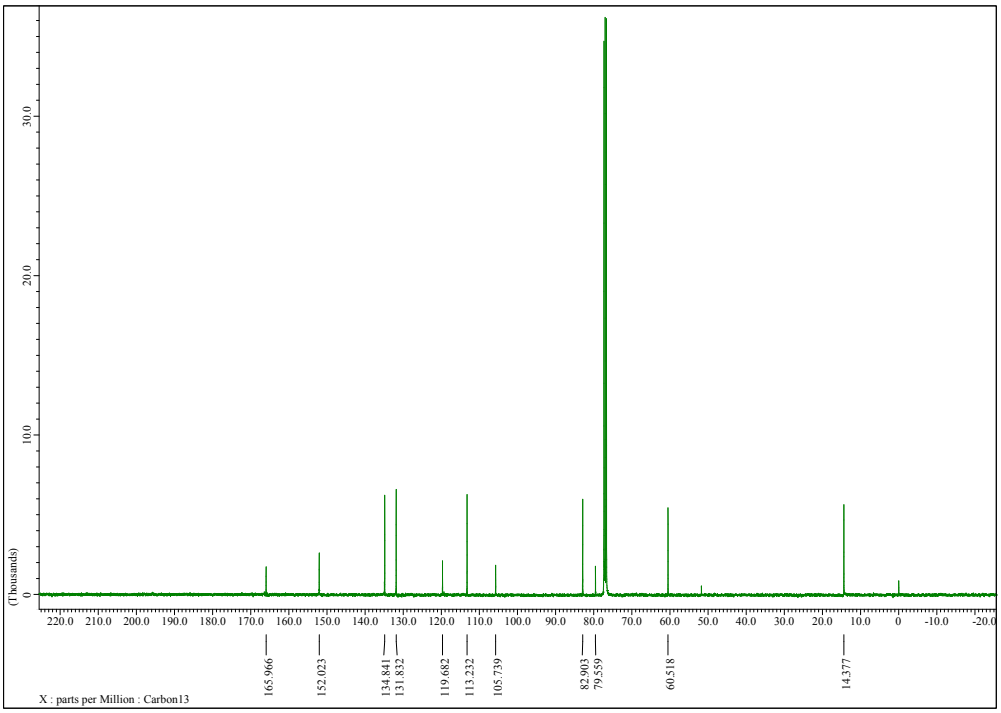

ethyl 4-amino-3-ethynylbenzoate **2f**



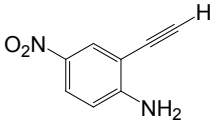

$^{1}$H NMR spectrum



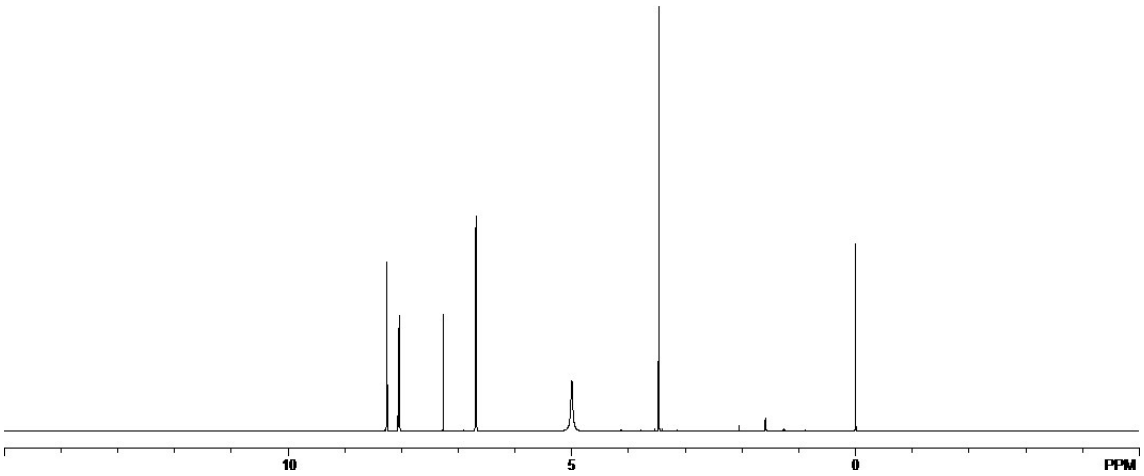

$^{13}$C NMR spectrum



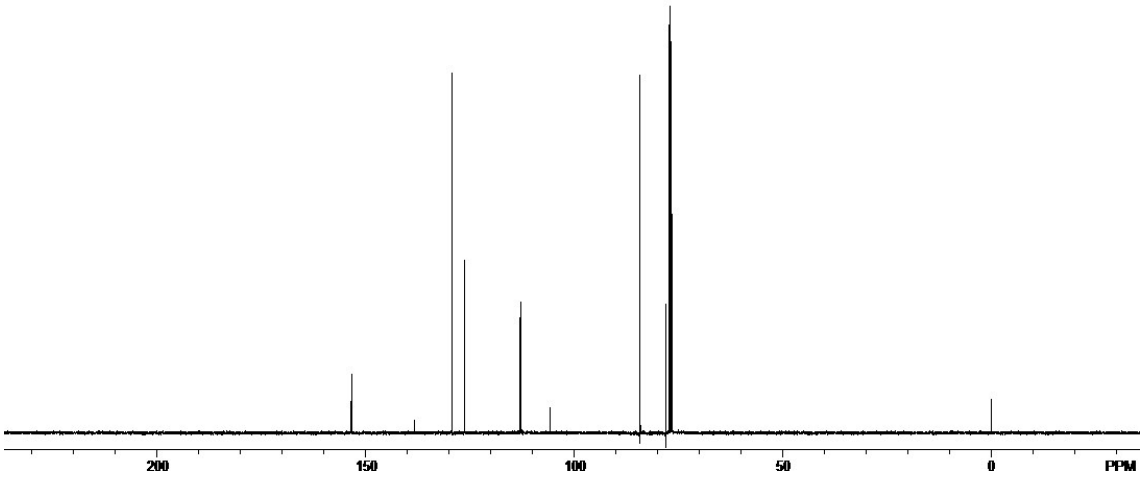

2-ethynyl-4-nitrobenzenamine **2g**



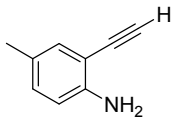

$^{1}$H NMR spectrum



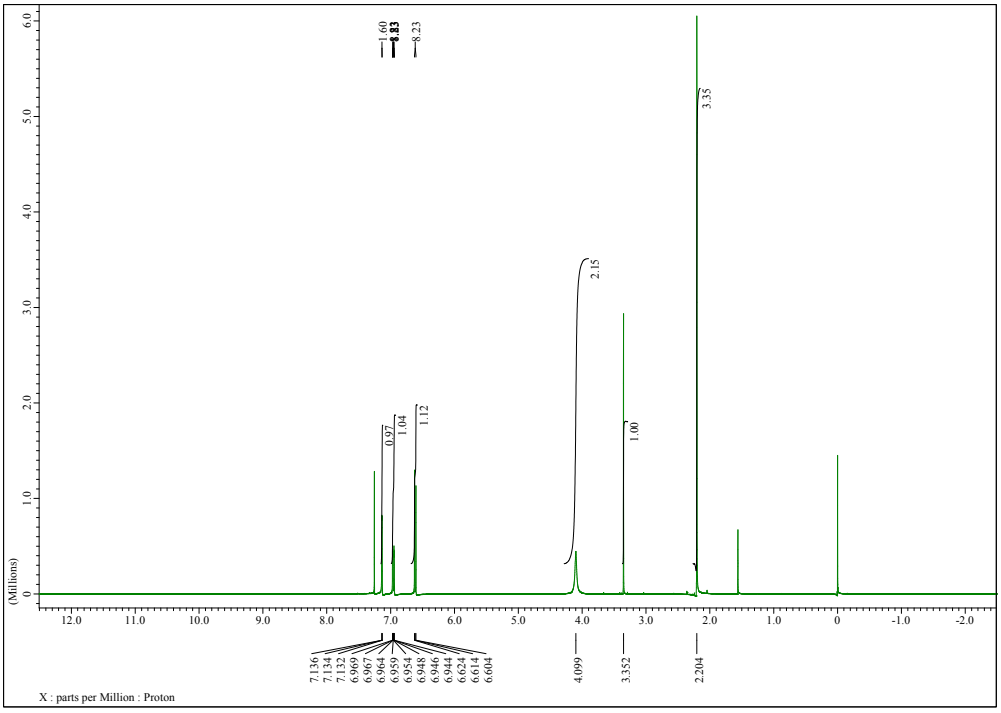

$^{13}$C NMR spectrum



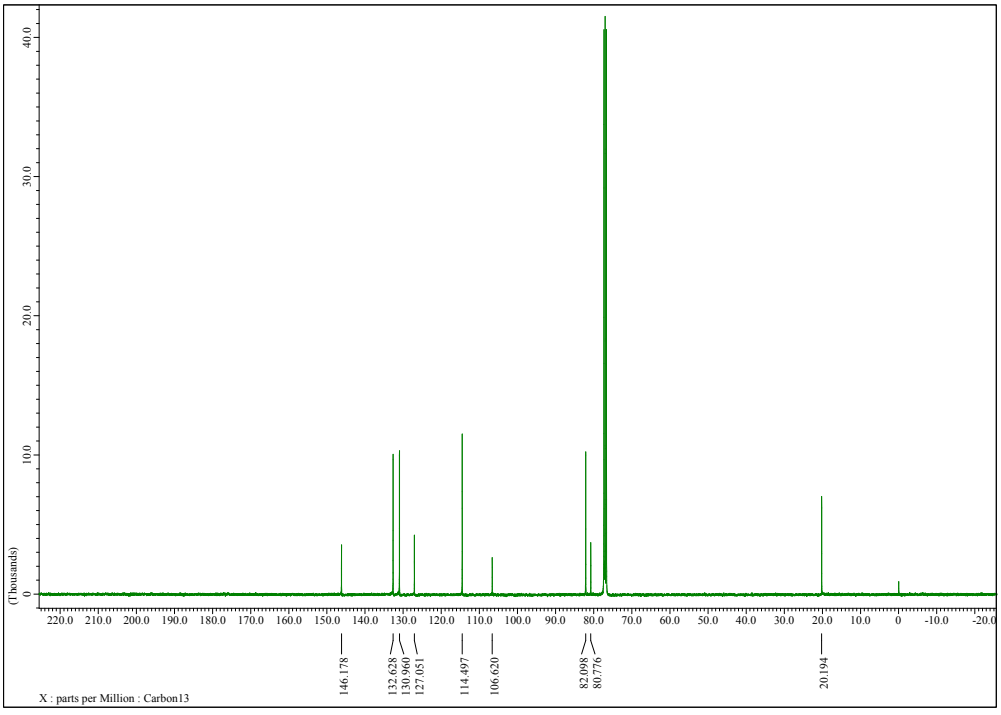

2-ethynyl-4-methylbenzenamine **2h**



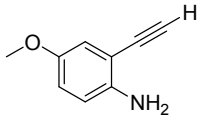
$^{1}$H NMR spectrum



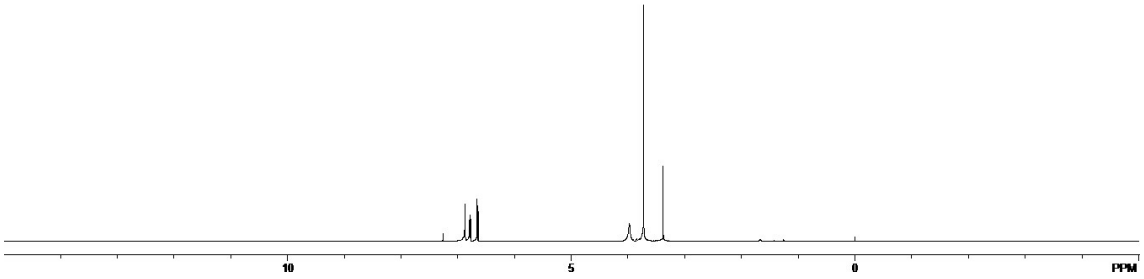

$^{13}$C NMR spectrum



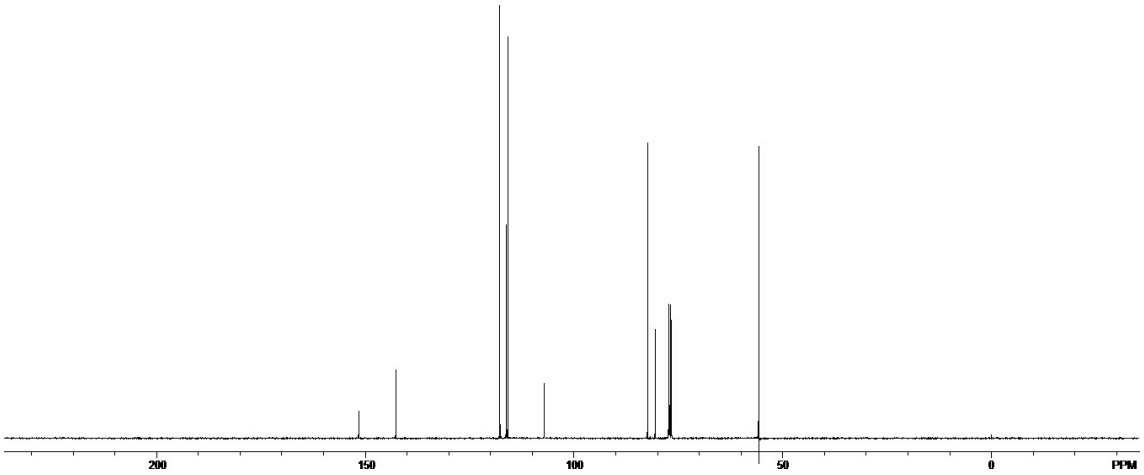

2-ethynyl-4-methoxybenzenamine **2i**



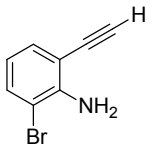
$^{1}$H NMR spectrum



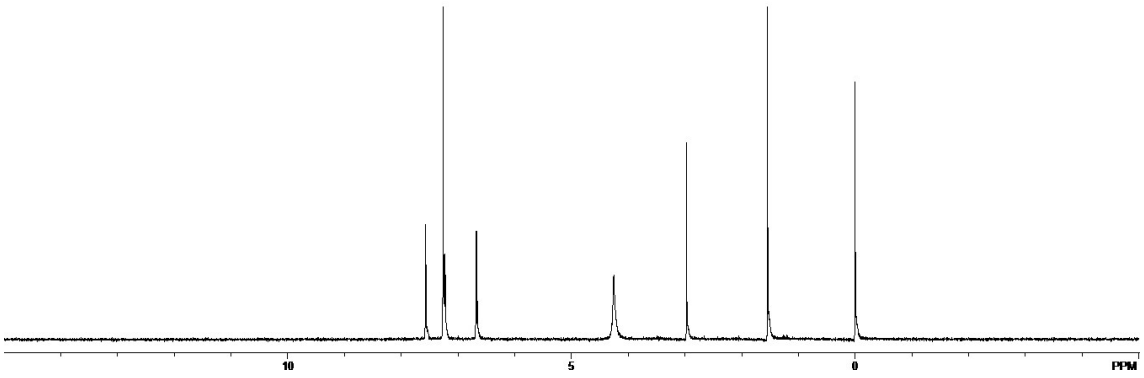

$^{13}$C NMR spectrum



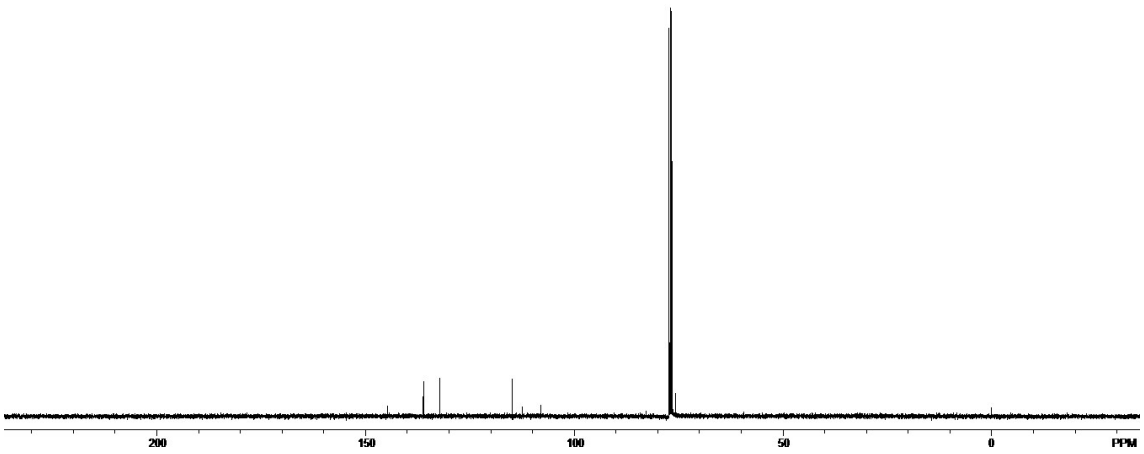

2-bromo-6-ethynylbenzenamine **2j**



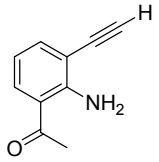
$^{1}$H NMR spectrum



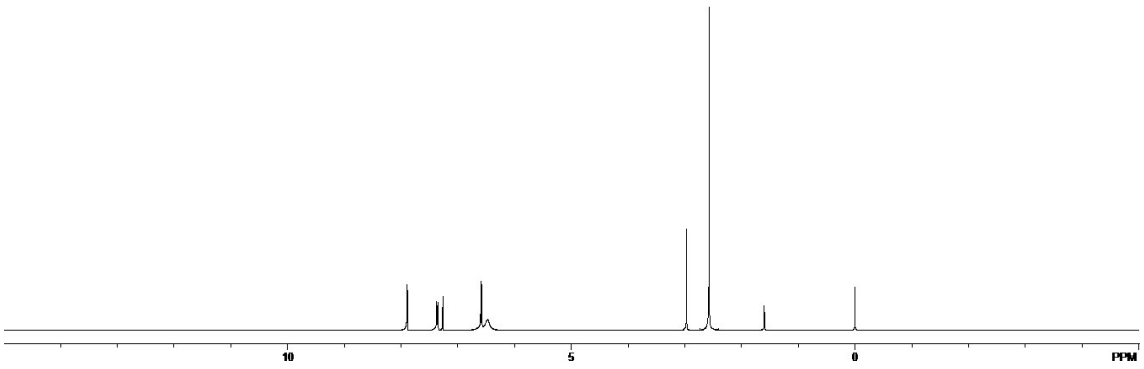

$^{13}$C NMR spectrum



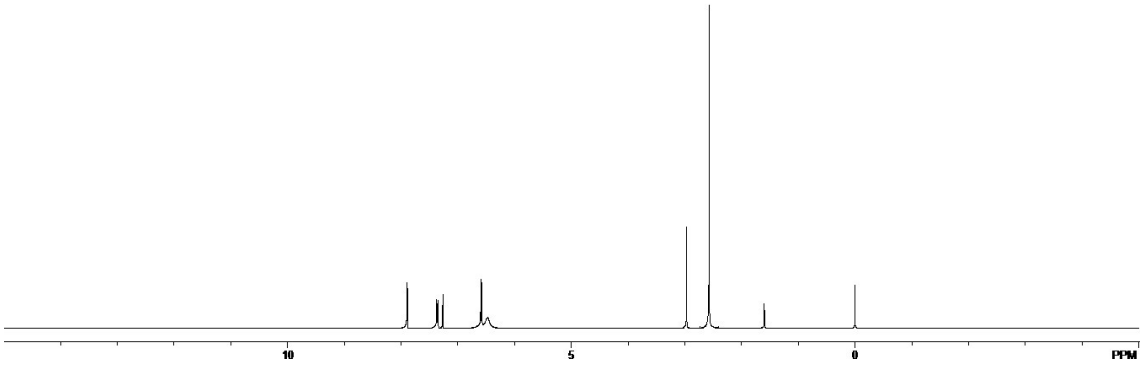

1-(2-amino-3-ethynylphenyl)ethanone **2k**



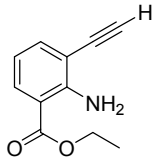
$^{1}$H NMR spectrum



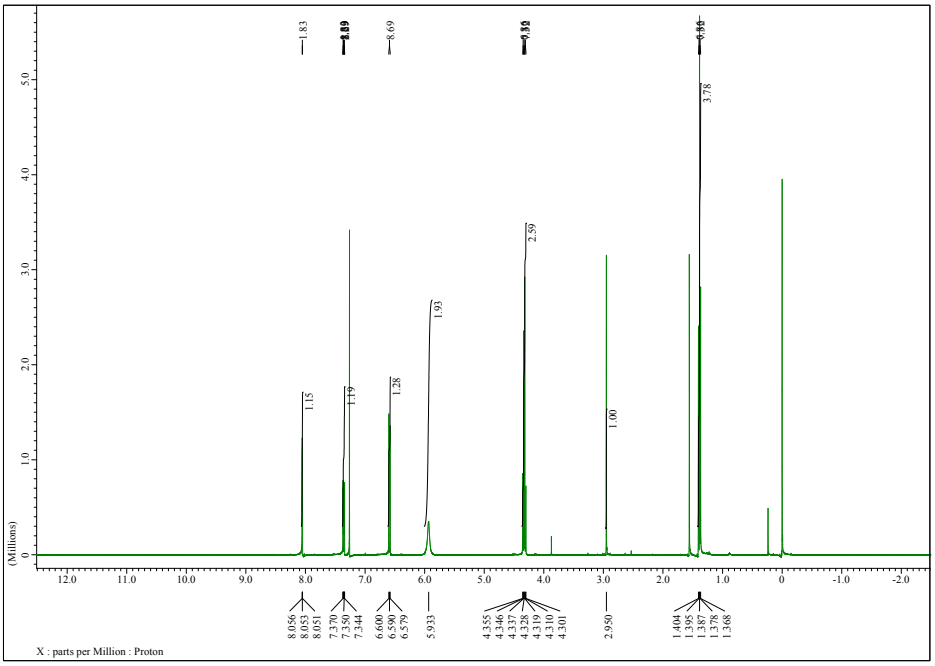

$^{13}$C NMR spectrum



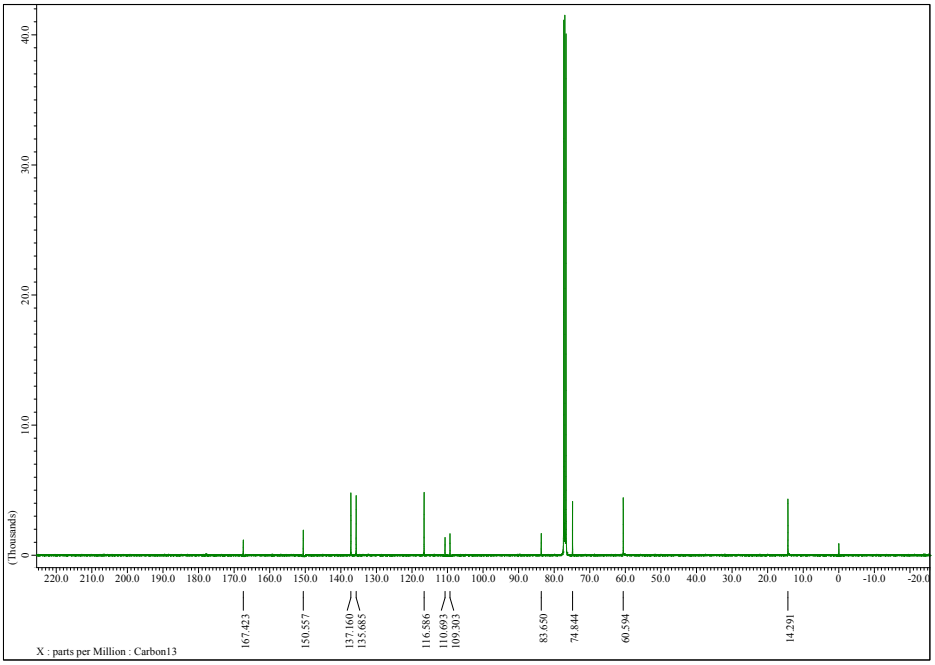

ethyl 2-amino-3-ethynylbenzoate **2l**



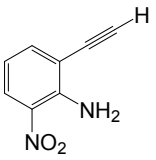
$^{1}$H NMR spectrum



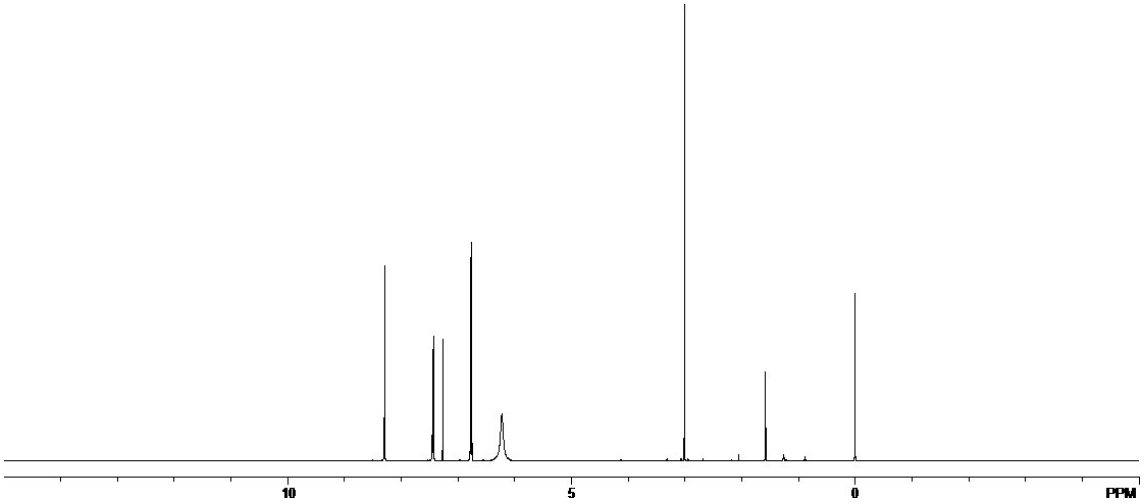

$^{13}$C NMR spectrum



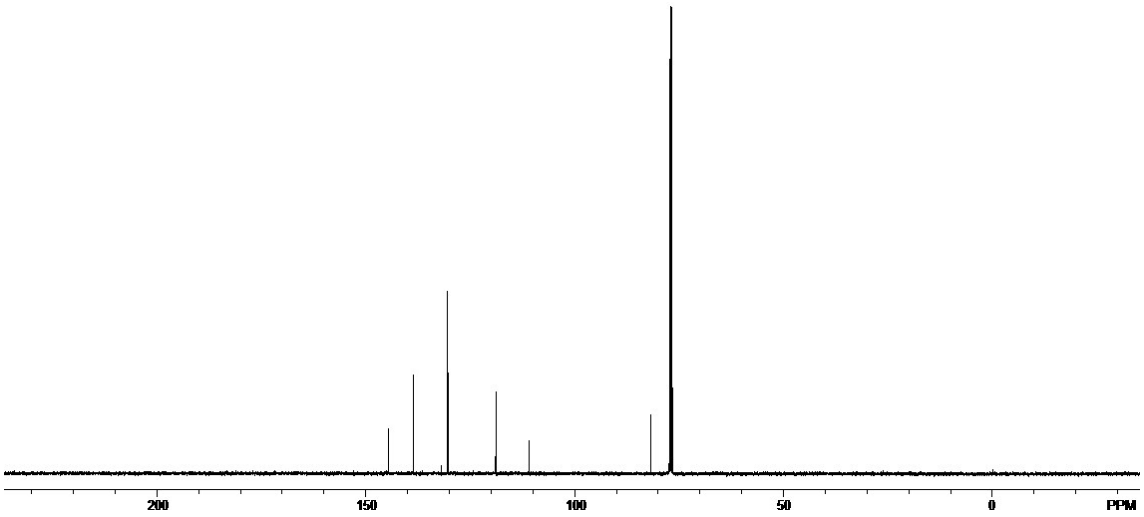

2-ethynyl-6-methylbenzenamine **2m**



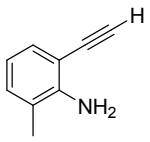
$^{1}$H NMR spectrum



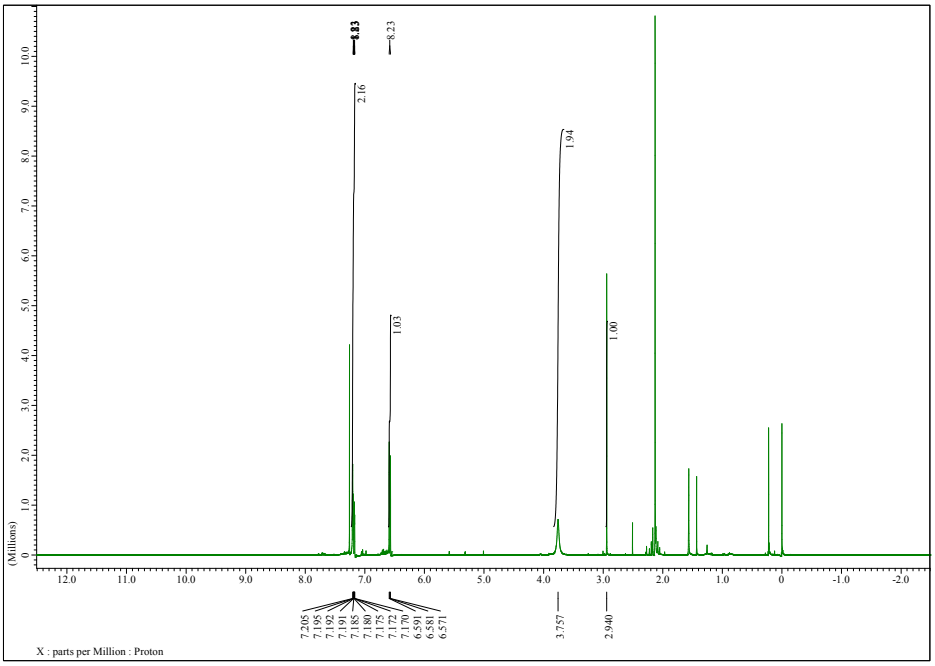

$^{13}$C NMR spectrum



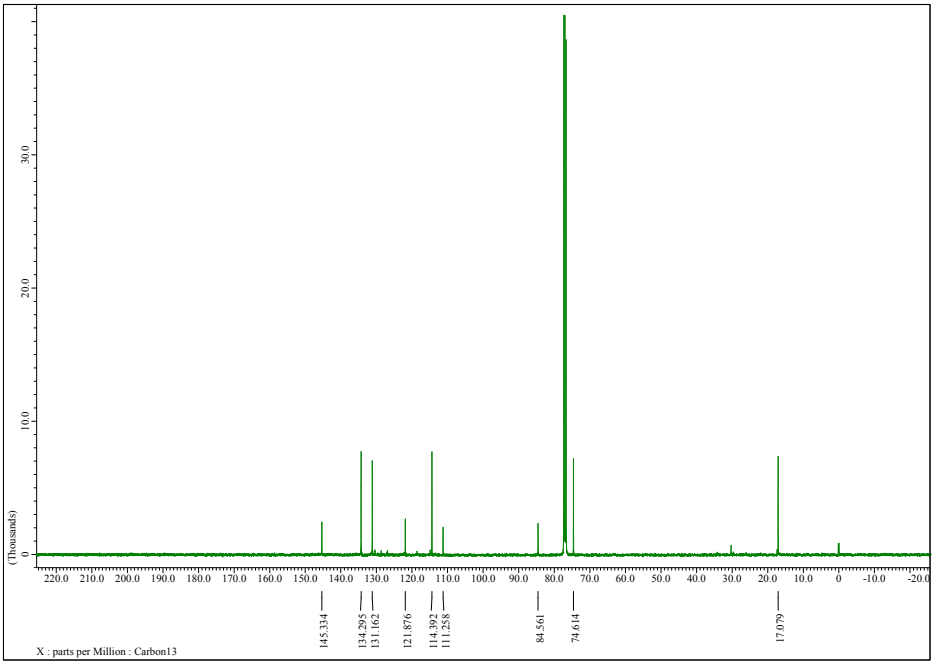

2-ethynyl-6-methylbenzenamine **2n**



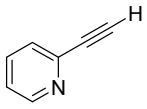
$^{1}$H NMR spectrum



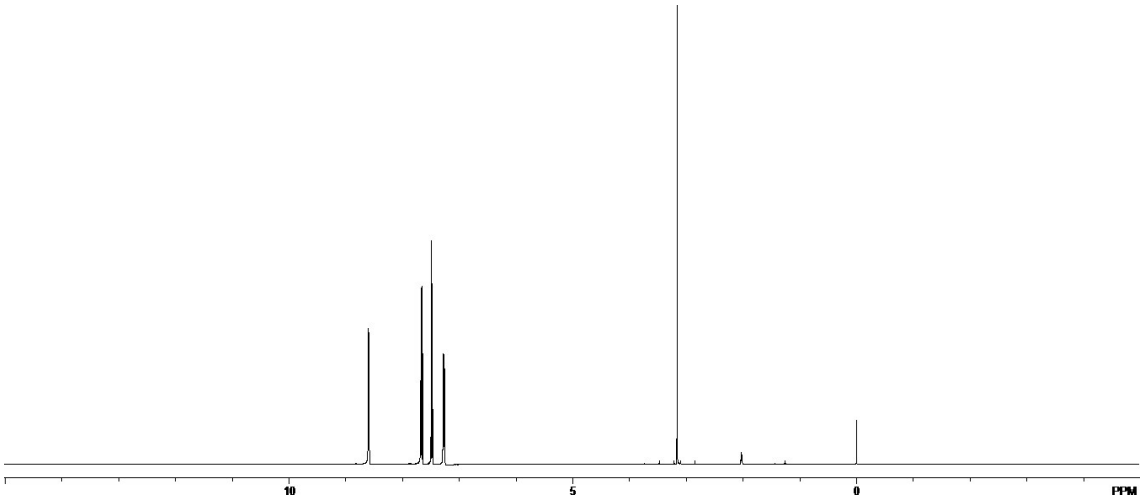

$^{13}$C NMR spectrum



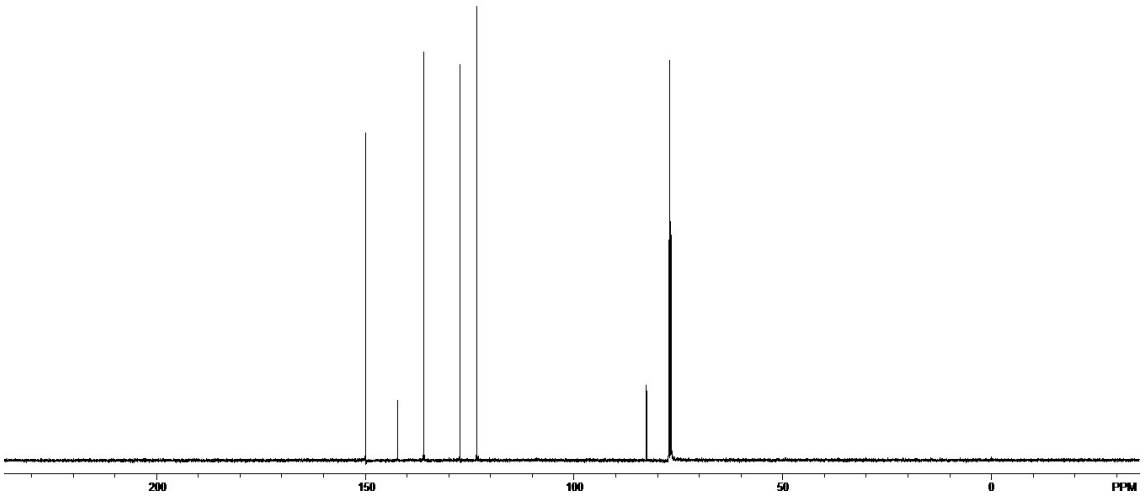

2-ethynylpyridine **2o**



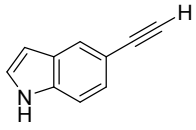
$^{1}$H NMR spectrum



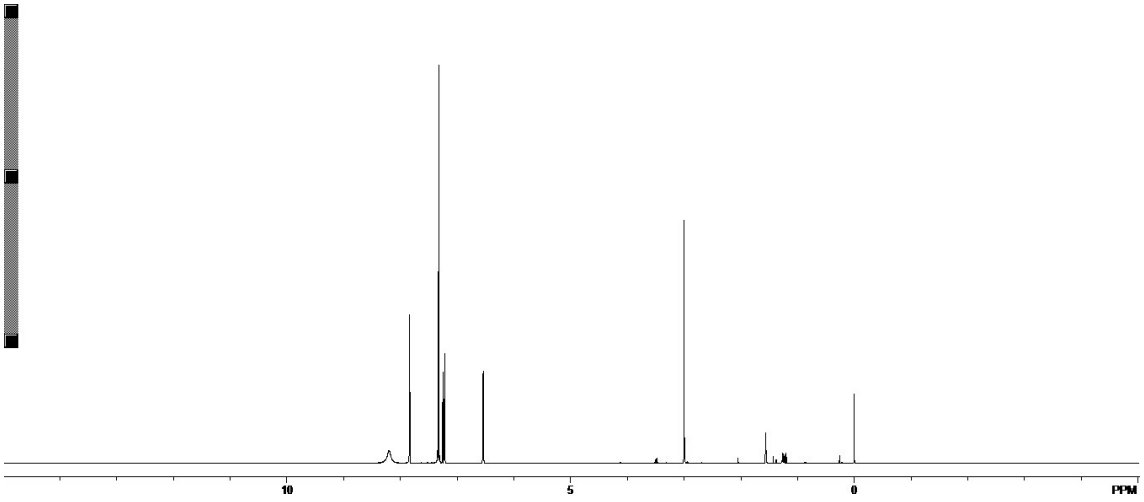

$^{13}$C NMR spectrum



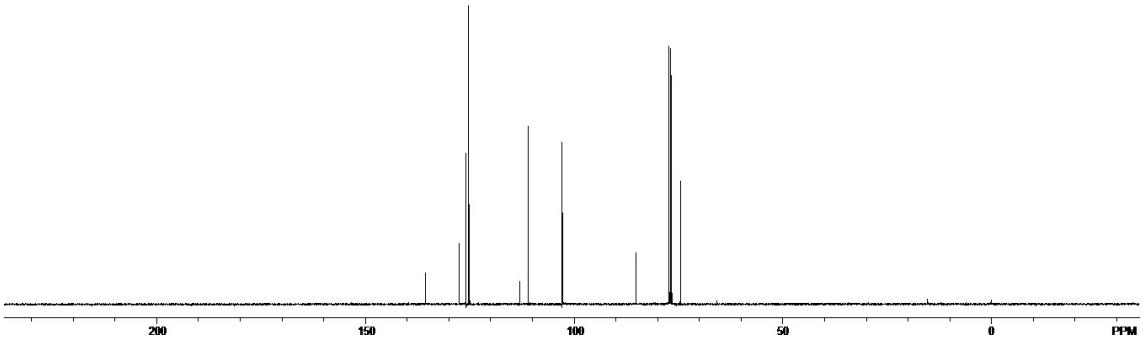

5-ethynyl-1*H*-indole **2p**



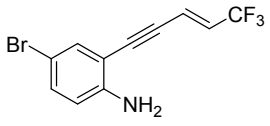
$^{1}$H NMR spectrum



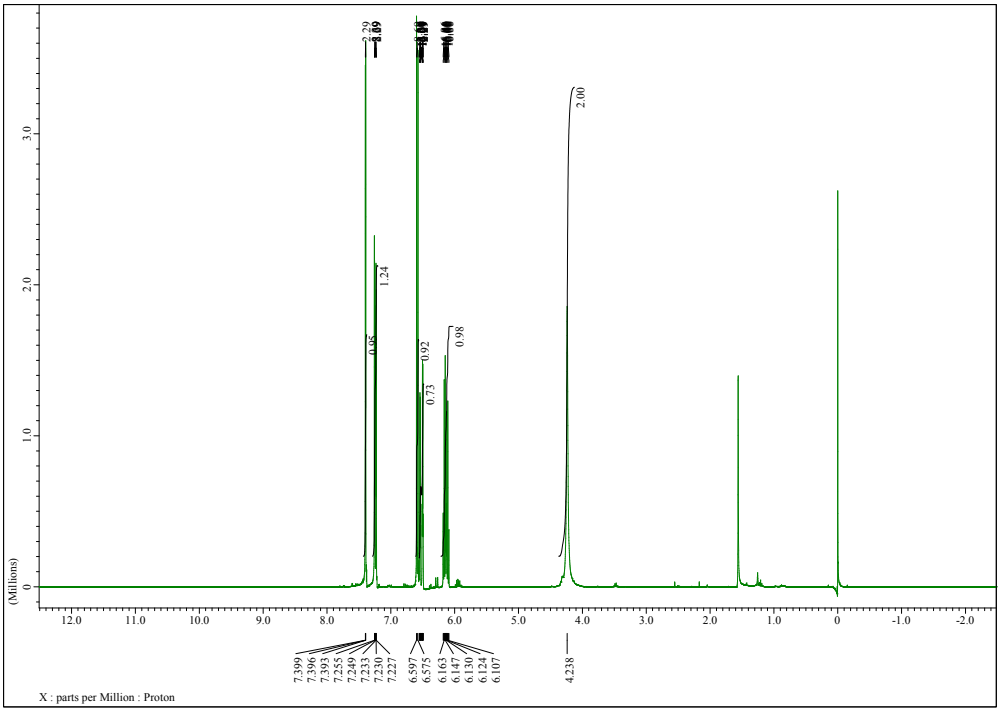

$^{13}$C NMR spectrum



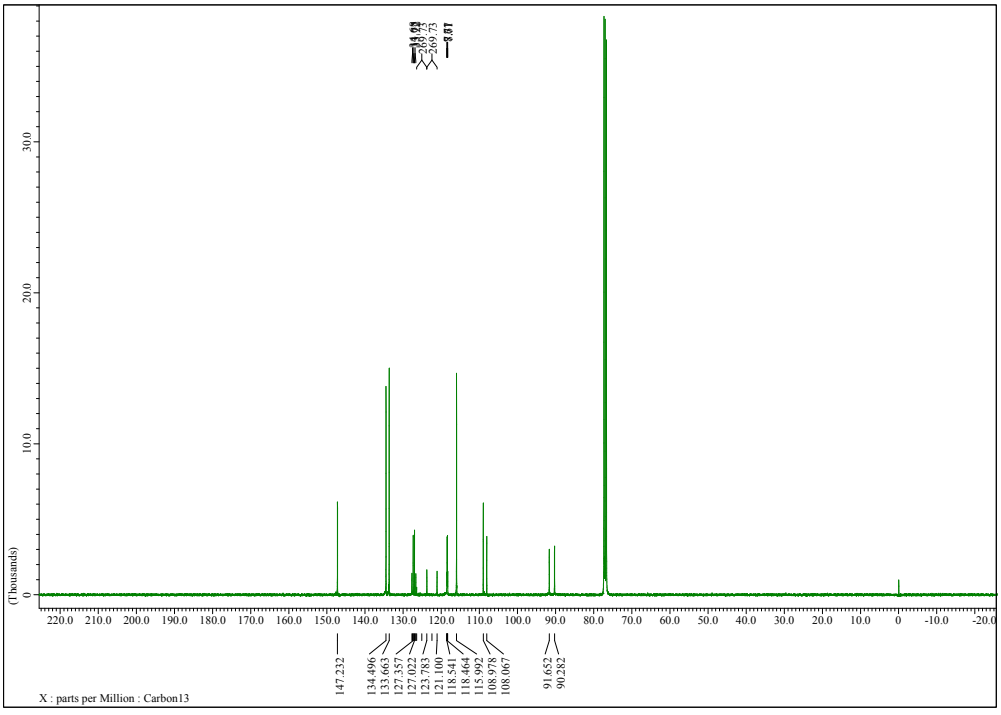

(*E*)-4-bromo-2-(5,5,5-trifluoropent-3-en-1-ynel)benzenamine **3c**



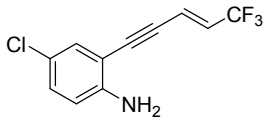
$^{1}$H NMR spectrum



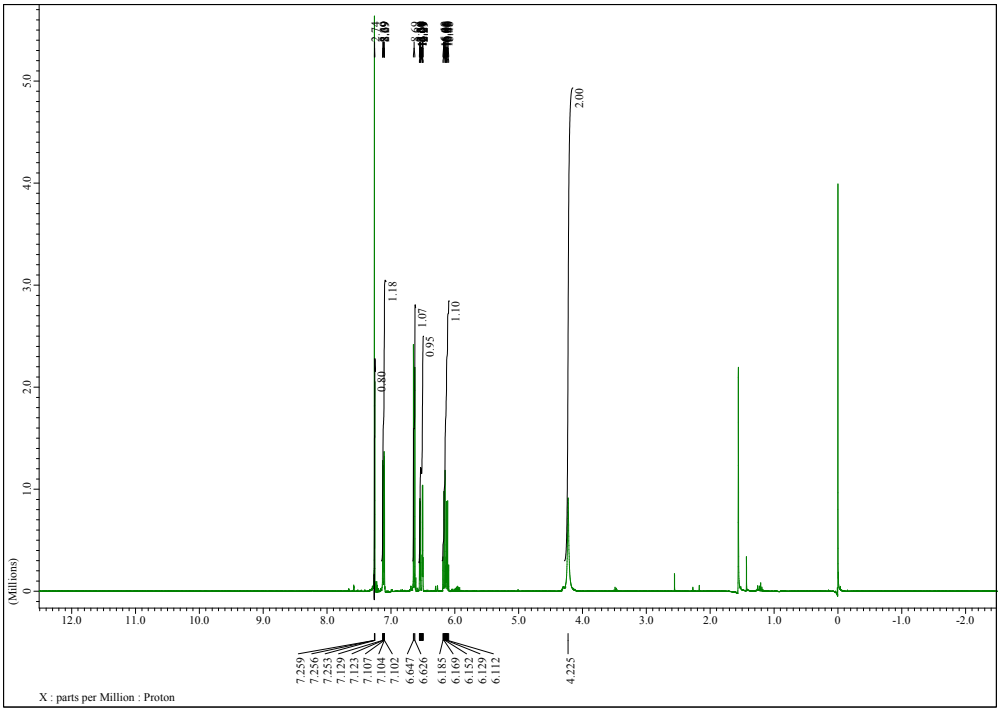

$^{13}$C NMR spectrum



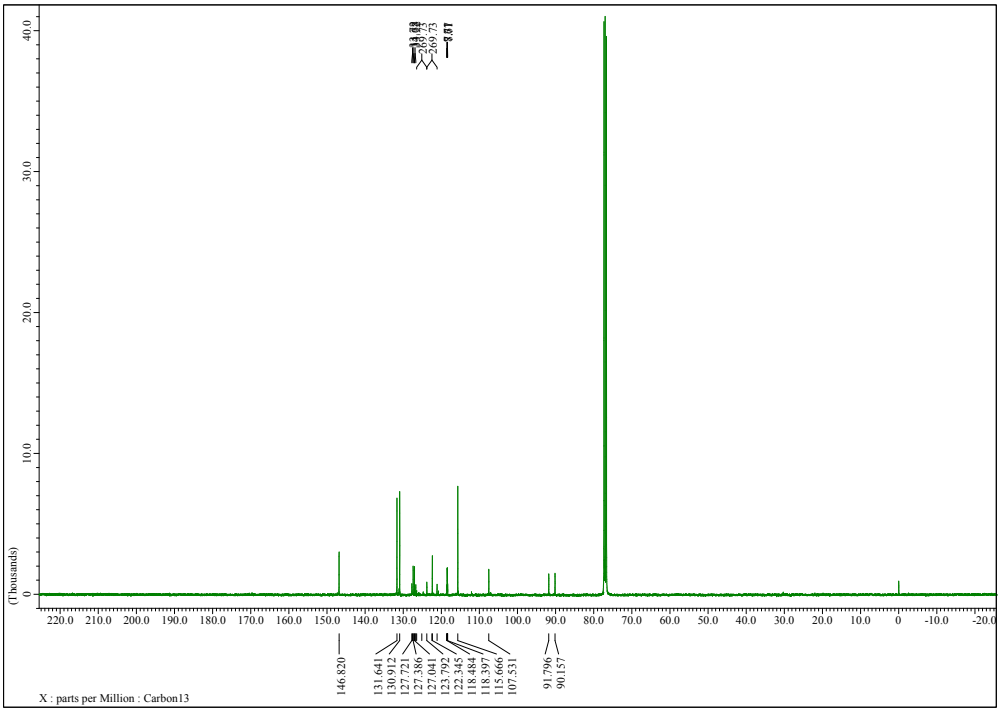

(*E*)-4-chloro-2-(5,5,5-trifluoropent-3-en-1-ynel)benzenamine **3d**



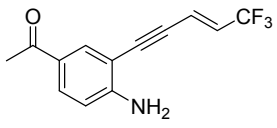
$^{1}$H NMR spectrum



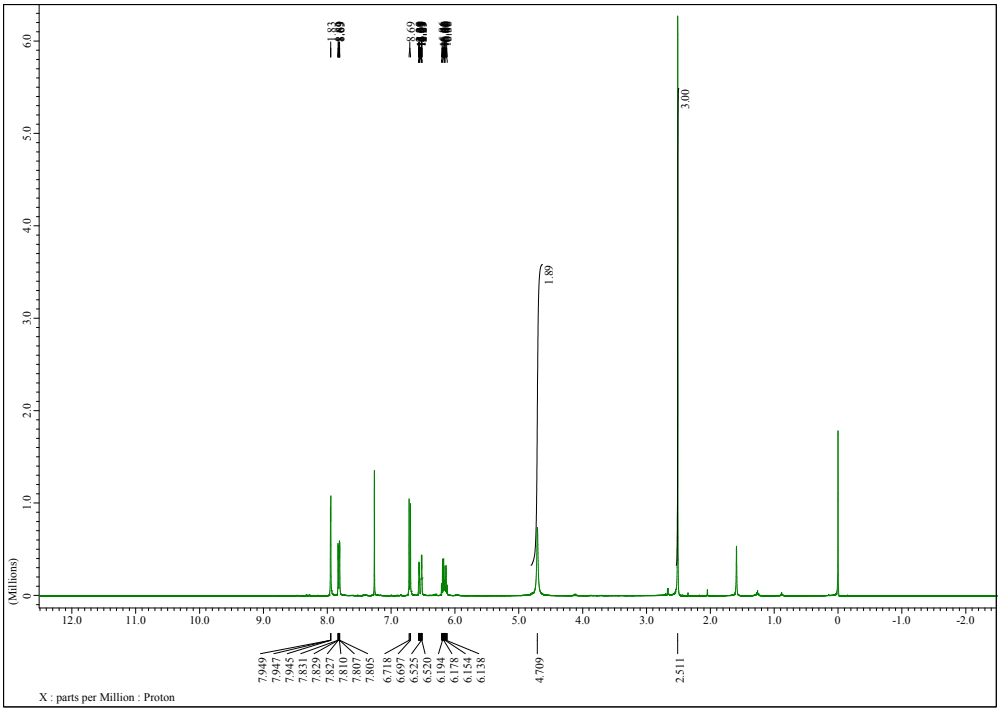

$^{13}$C NMR spectrum



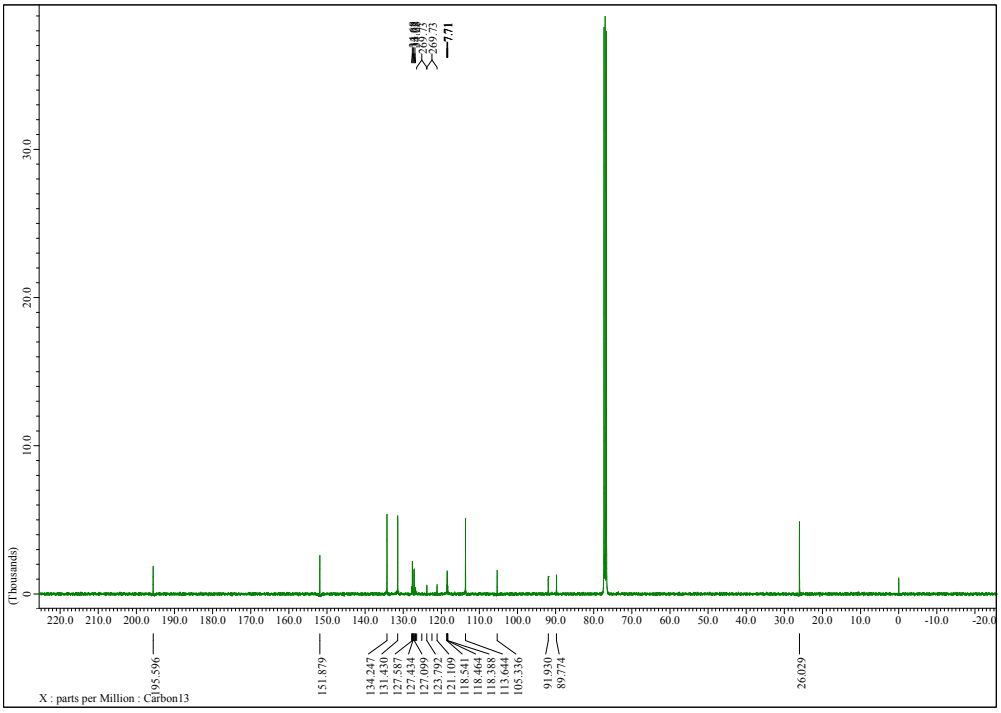

(*E*)-1-(4-amino-3-(5,5,5-trifluoropent-3-en-1-ynyl)phenyl)ethanone **3e**



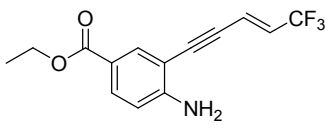
$^{1}$H NMR spectrum



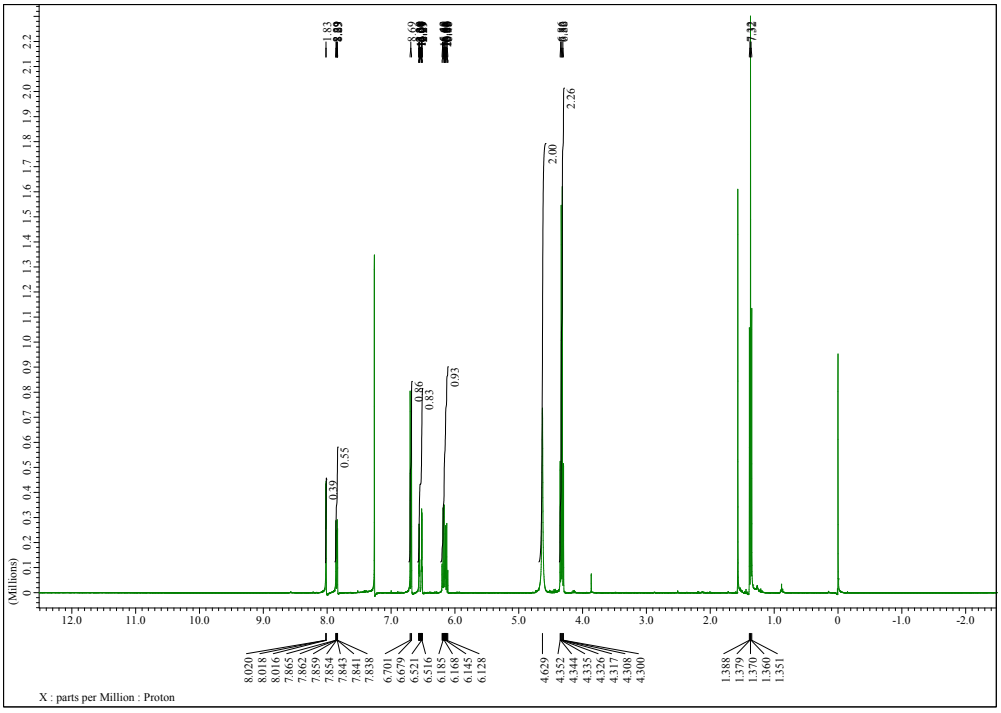

$^{13}$C NMR spectrum



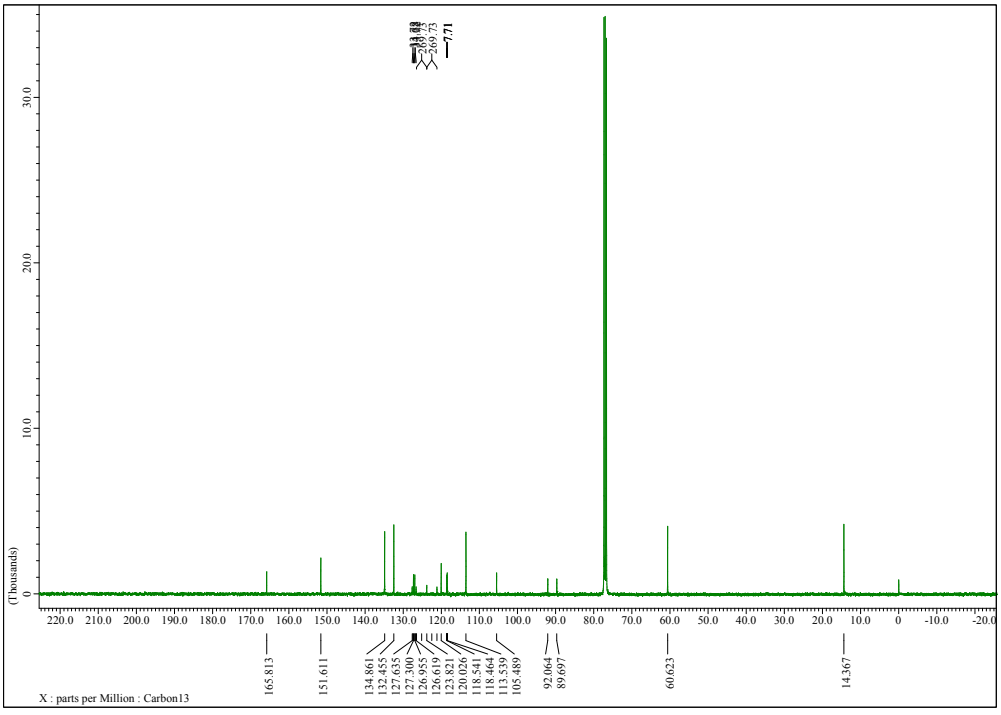

(*E*)-ethyl 4-amino-3-(5,5,5-trifluoropent-3-en-1-ynyl)benzoate **3f**



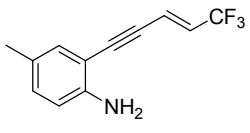
$^{1}$H NMR spectrum



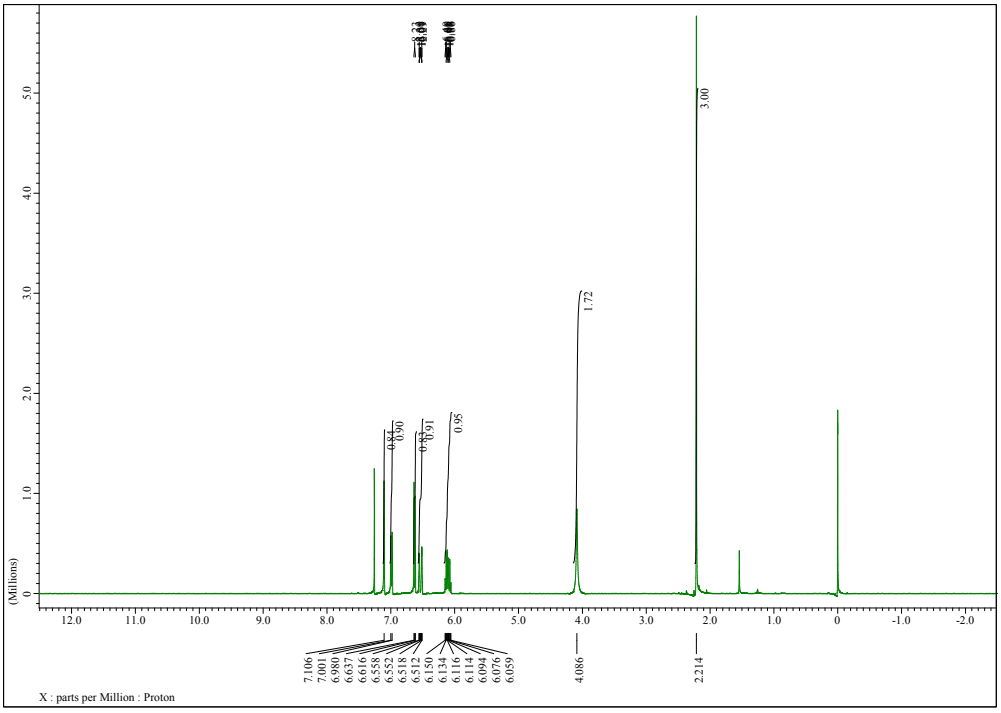

$^{13}$C NMR spectrum



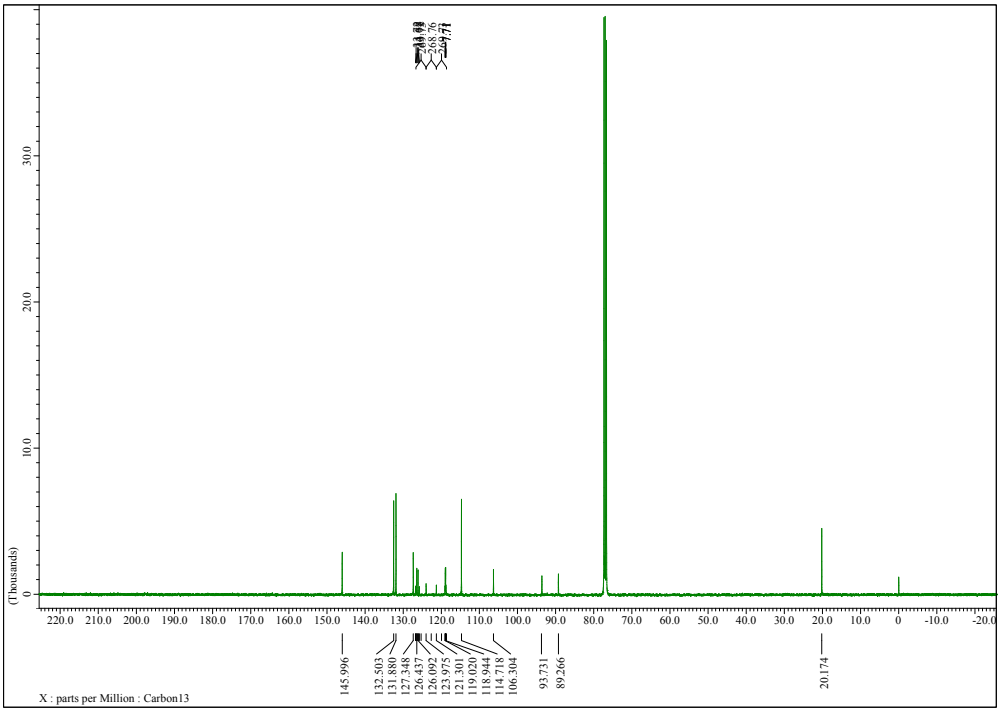

(*E*)-4-methyl-2-(5,5,5-trifluoropent-3-en-1-ynyl)benzenamine **3h**



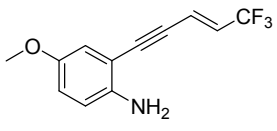
$^{1}$H NMR spectrum



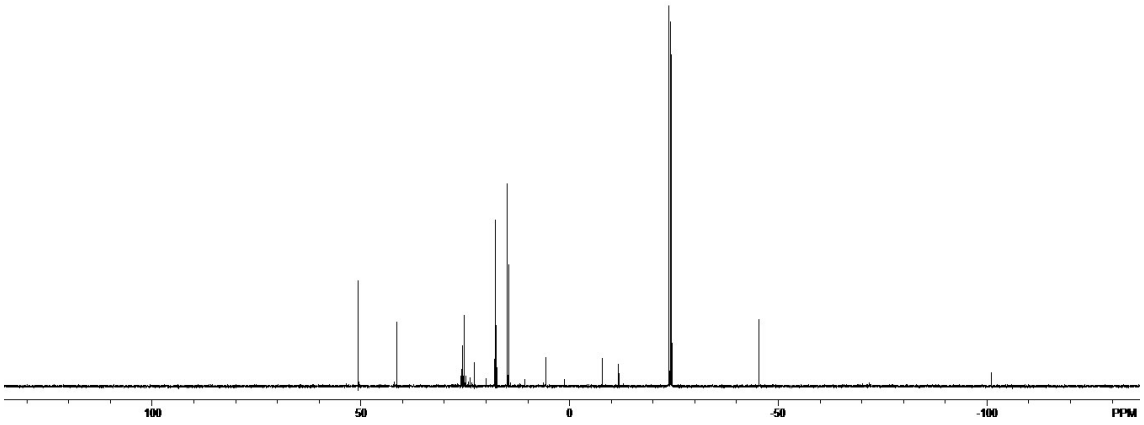

$^{13}$C NMR spectrum



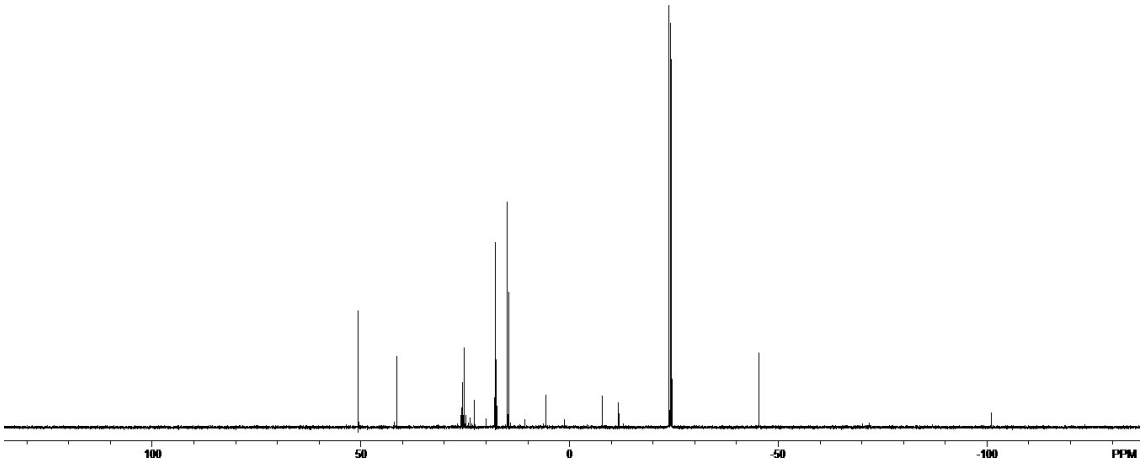

(*E*)-4-methoxy-2-(5,5,5-trifluoropent-3-en-1-ynyl)benzenamine **3i**



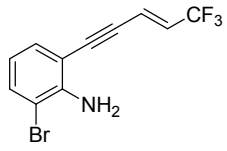
$^{1}$H NMR spectrum



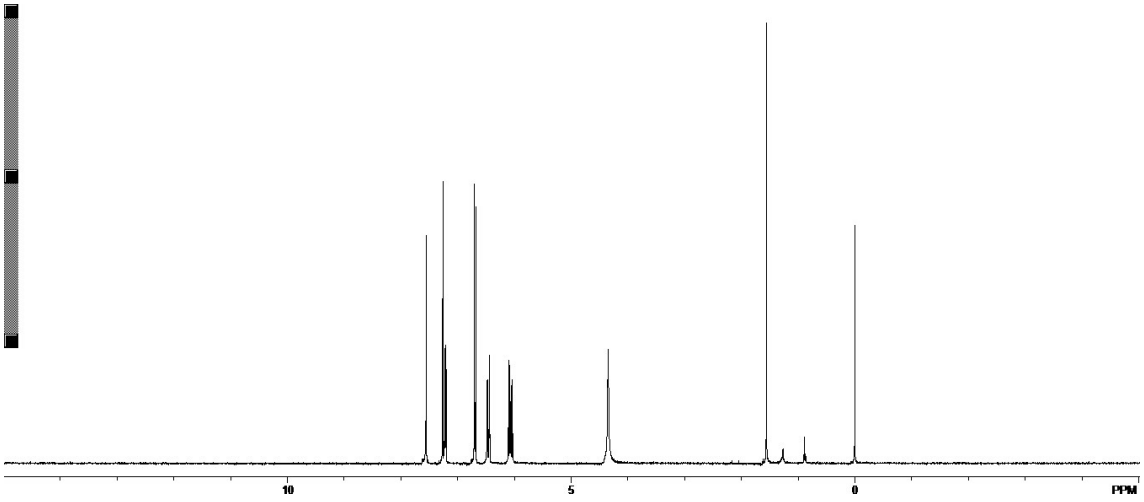

$^{13}$C NMR spectrum



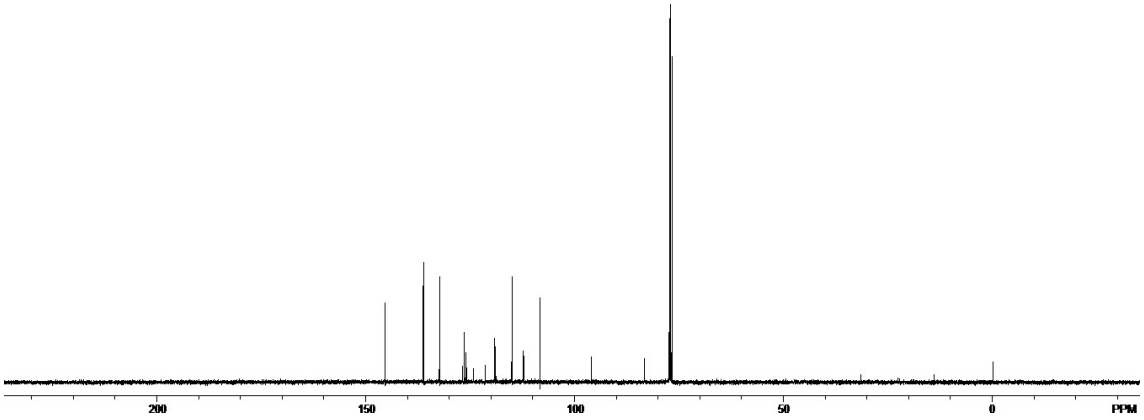

(*E*)-2-bromo-6-(5,5,5-trifluoropent-3-en-1-ynel)benzenamine **3j**



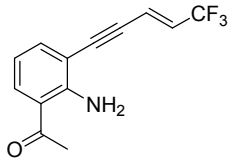
$^{1}$H NMR spectrum



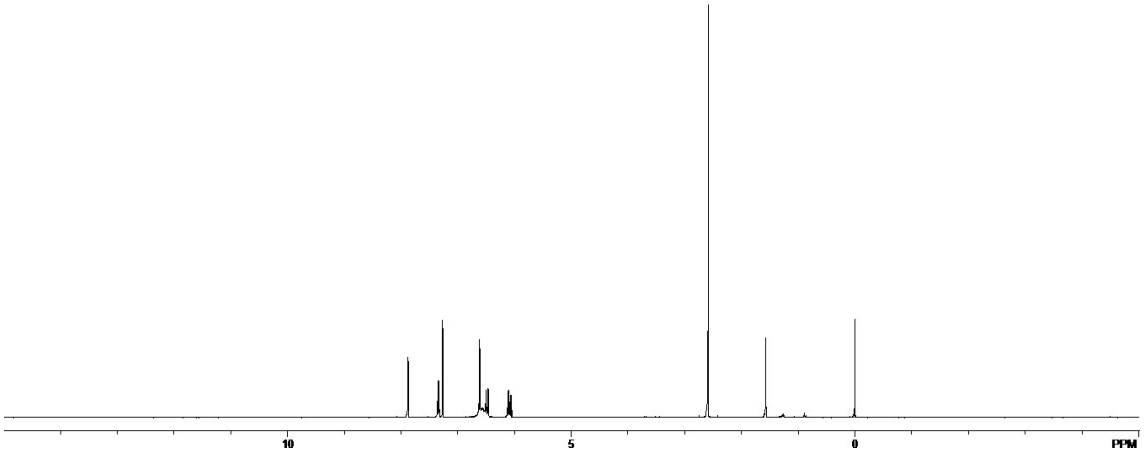

$^{13}$C NMR spectrum



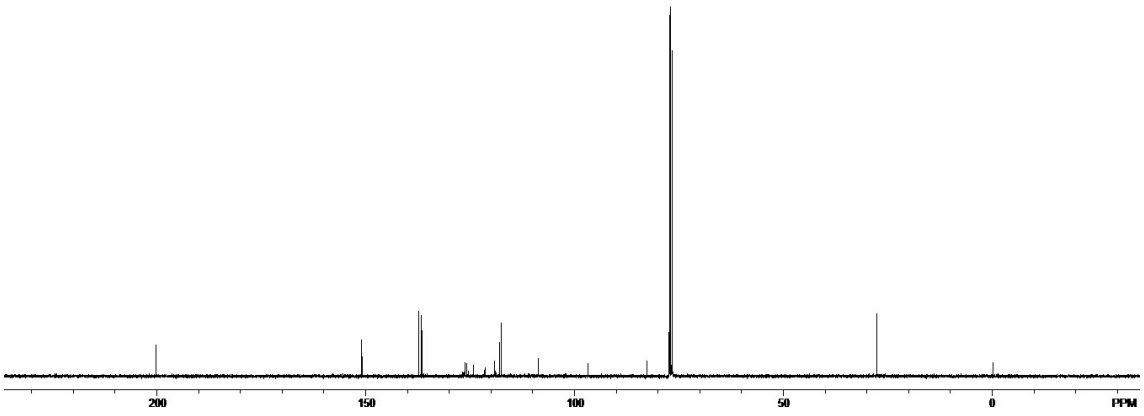

(*E*)-1-(2-amino-3-(5,5,5-trifluoropent-3-en-1-ynyl)phenyl)ethanone **3k**



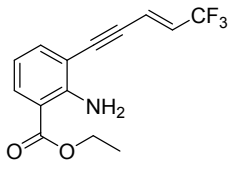
$^{1}$H NMR spectrum



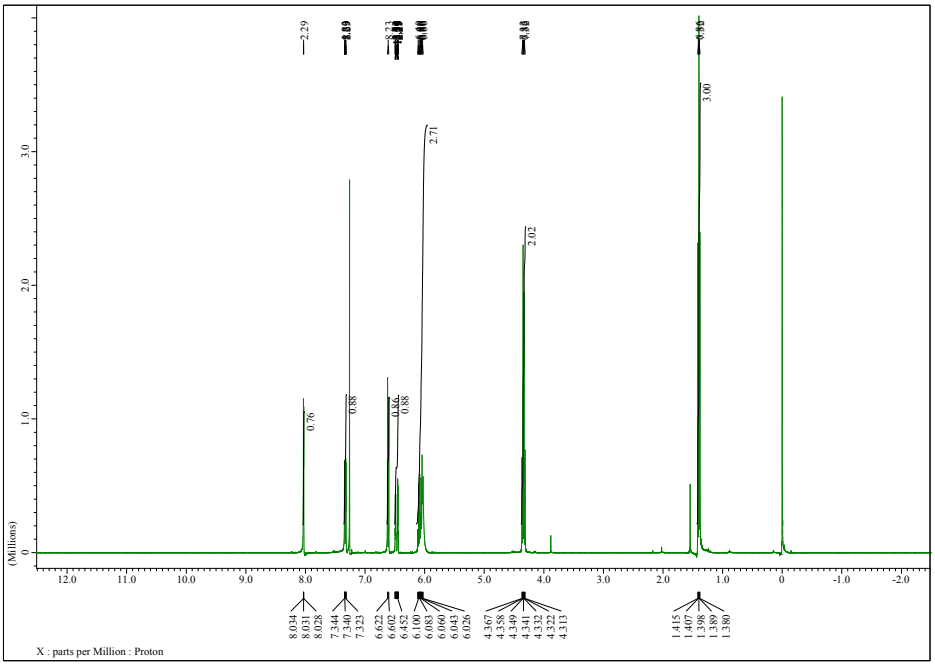

$^{13}$C NMR spectrum



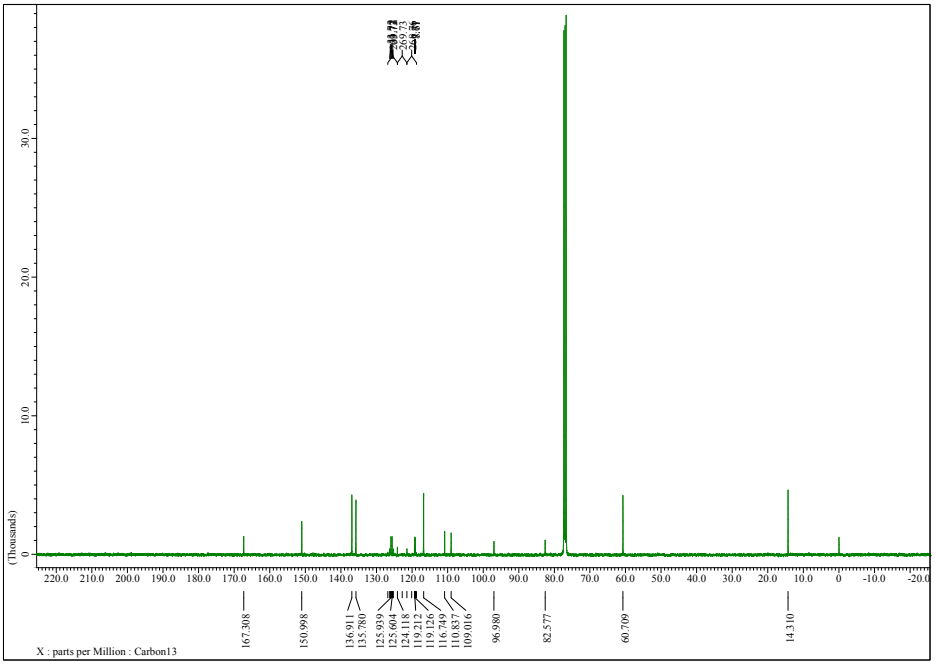

(*E*)-ethyl 2-amino-3-(5,5,5-trifluoropent-3-en-1-ynyl)benzoate **3l**



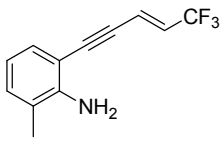
$^{1}$H NMR spectrum



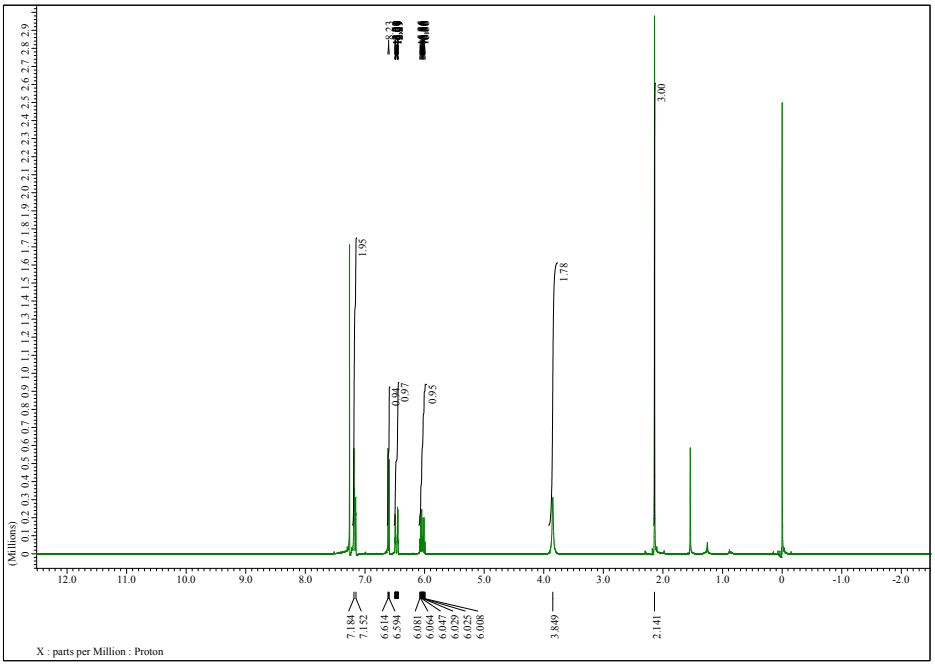

$^{13}$C NMR spectrum



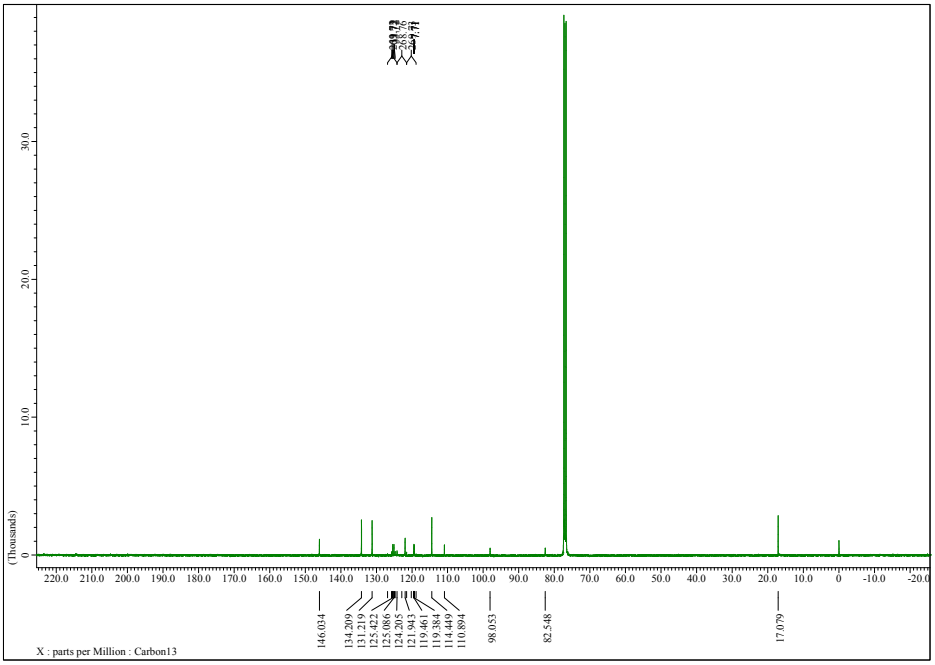

(*E*)-2-methyl-2-(5,5,5-trifluoropent-3-en-1-ynyl)benzenamine **3n**



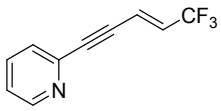
$^{1}$H NMR spectrum



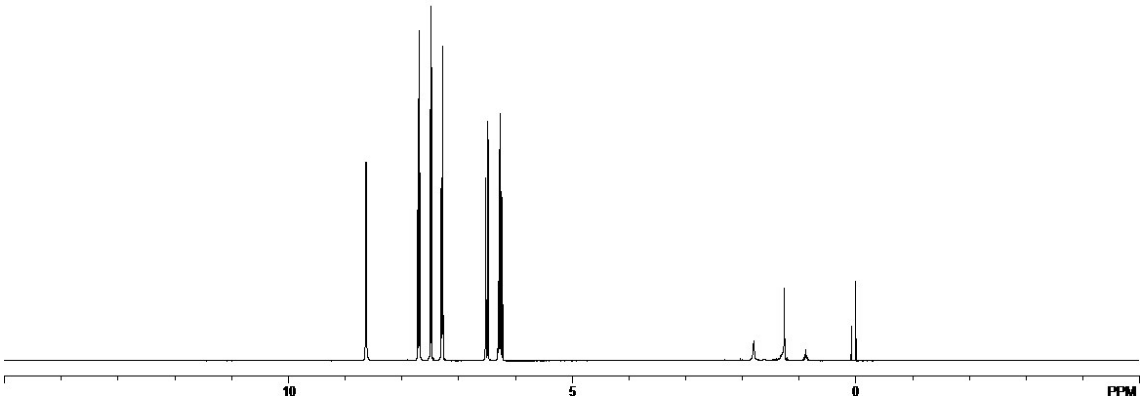

$^{13}$C NMR spectrum



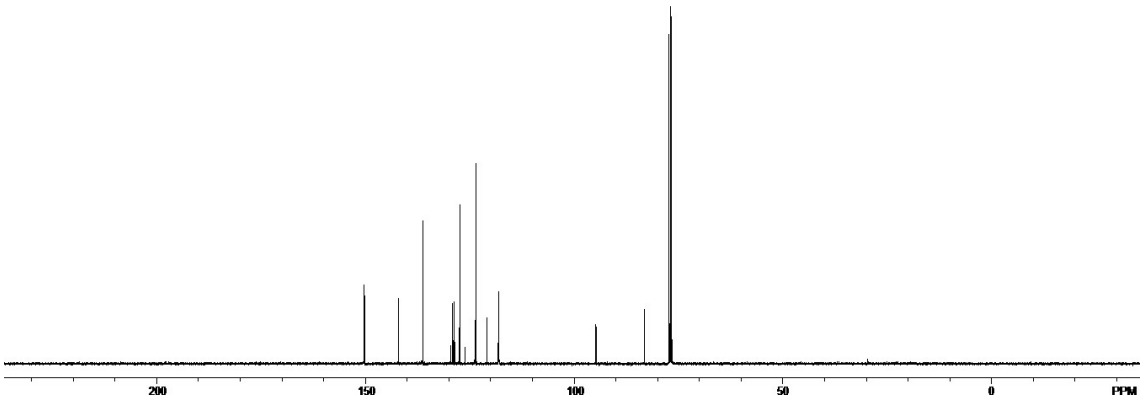

(*E*)-2-(5,5,5-trifluoropent-3-en-1-ynyl)pyridine **3o**



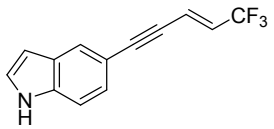
$^{1}$H NMR spectrum



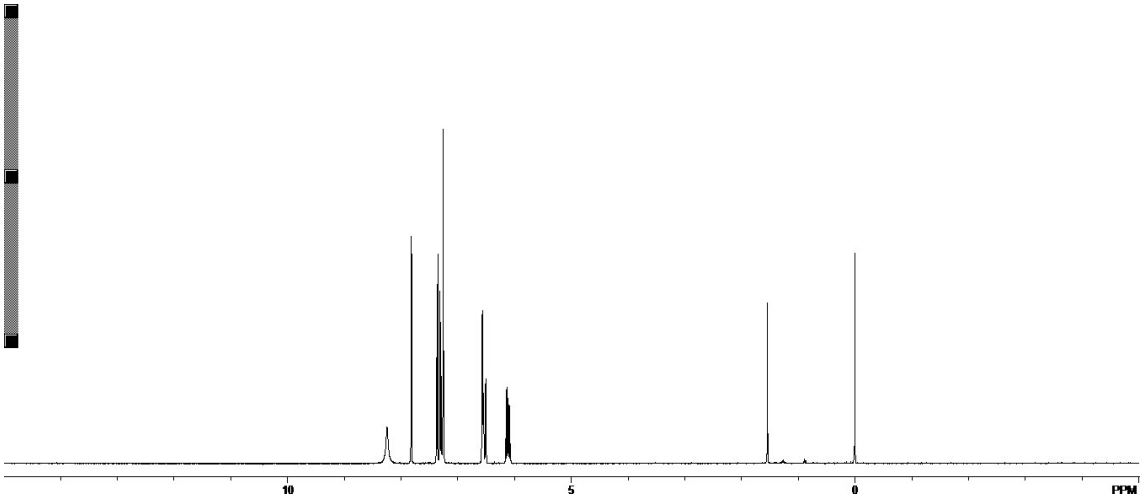

$^{13}$C NMR spectrum



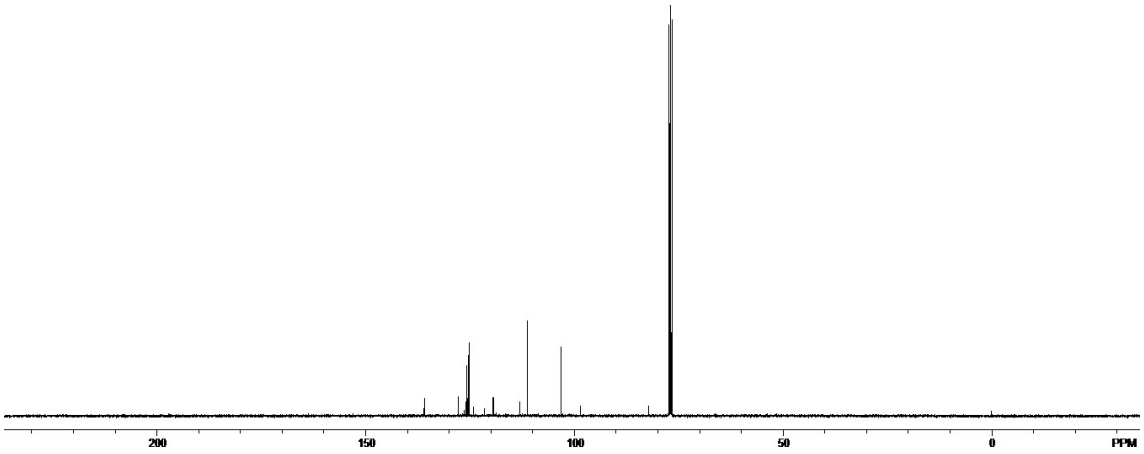

(*E*)-5-(5,5,5-trifluoropent-3-en-1-ynyl)-1*H*-indole **3p**



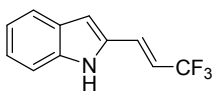
$^{1}$H NMR spectrum



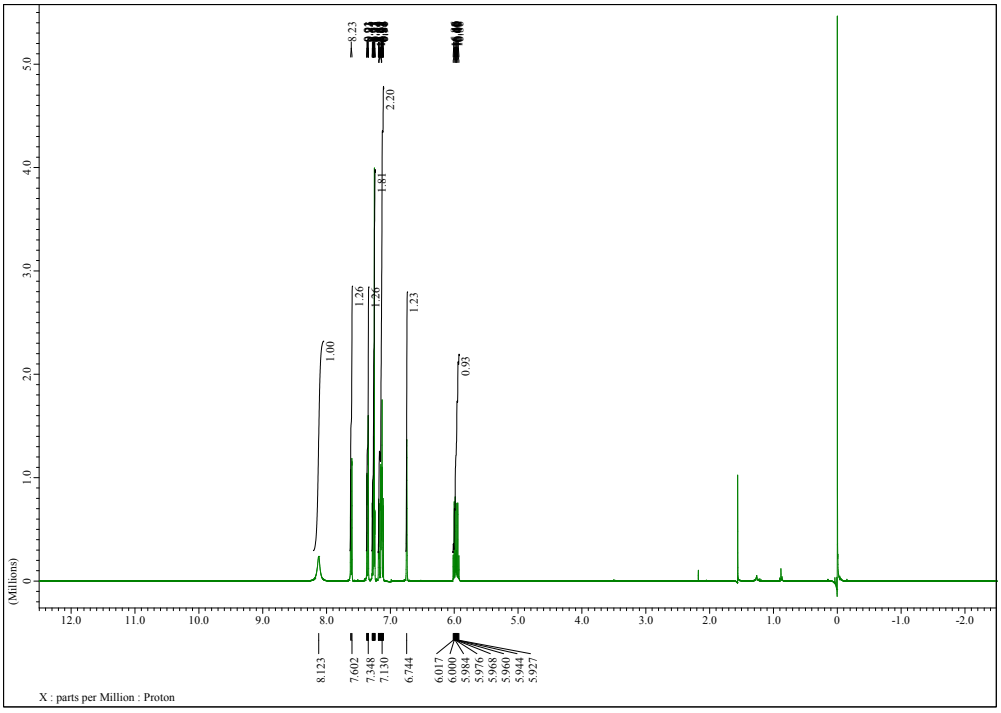

$^{13}$C NMR spectrum



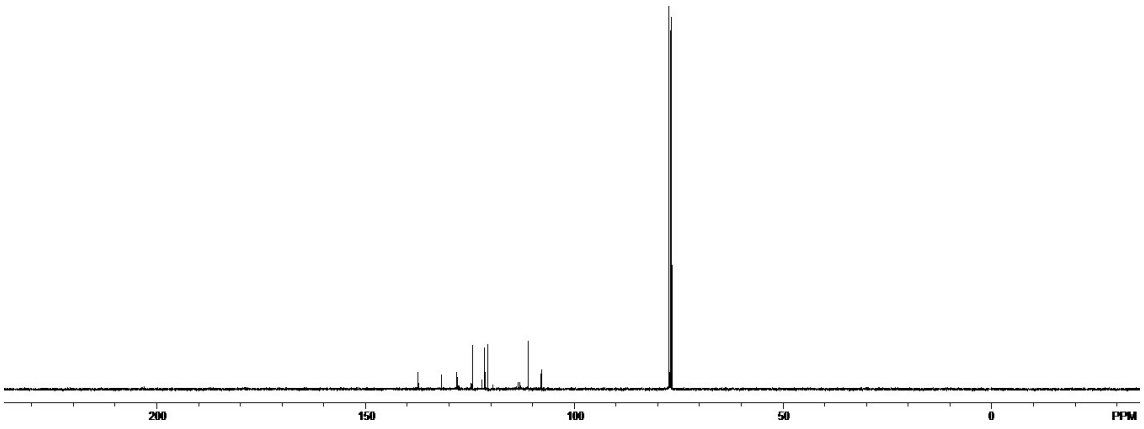

(*E*)-2-(3,3,3-trifluoroprop-1-enyl)-1*H*-indole **4b**



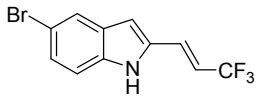
$^{1}$H NMR spectrum



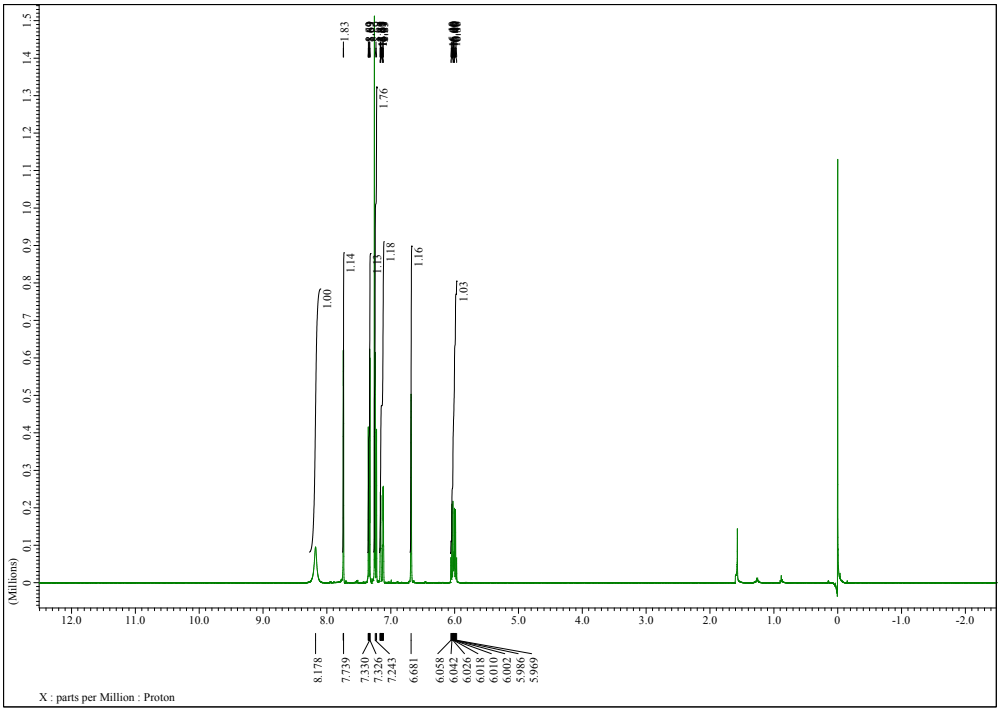

$^{13}$C NMR spectrum



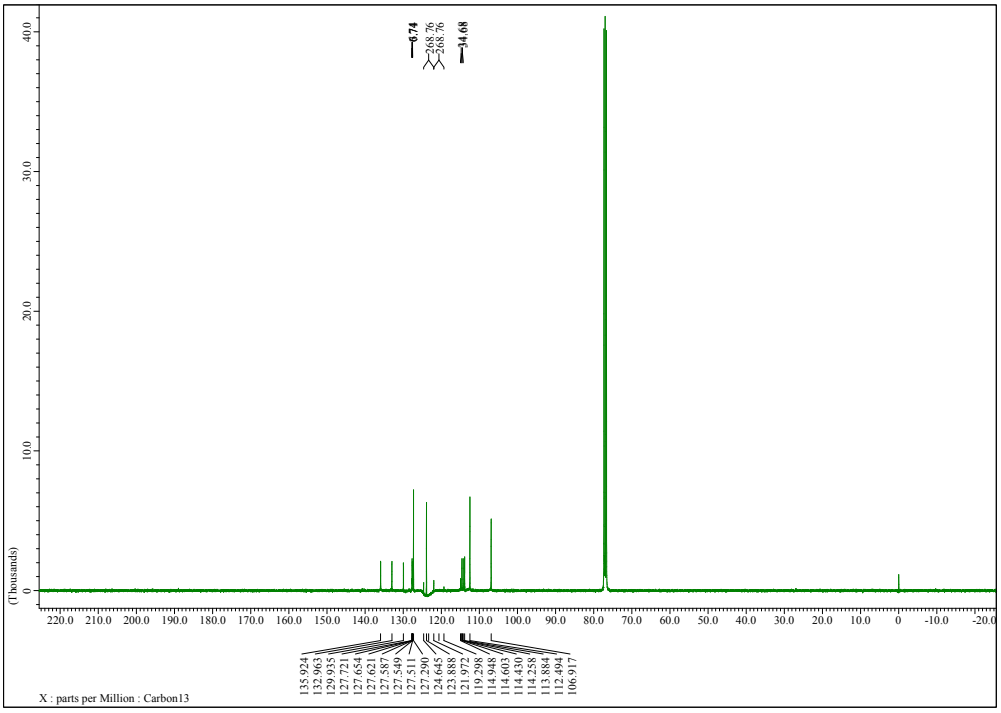

(*E*)-5-bromo-2-(3,3,3-trifluoroprop-1-enyl)-1*H*-indole **4c**



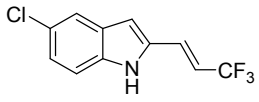
$^{1}$H NMR spectrum



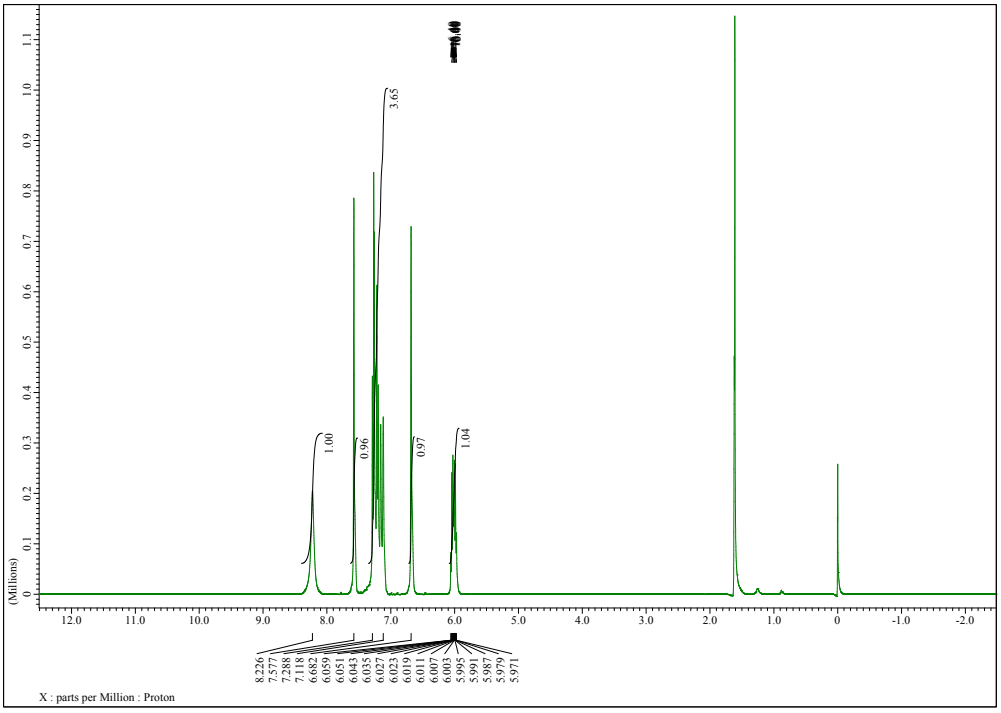

$^{13}$C NMR spectrum



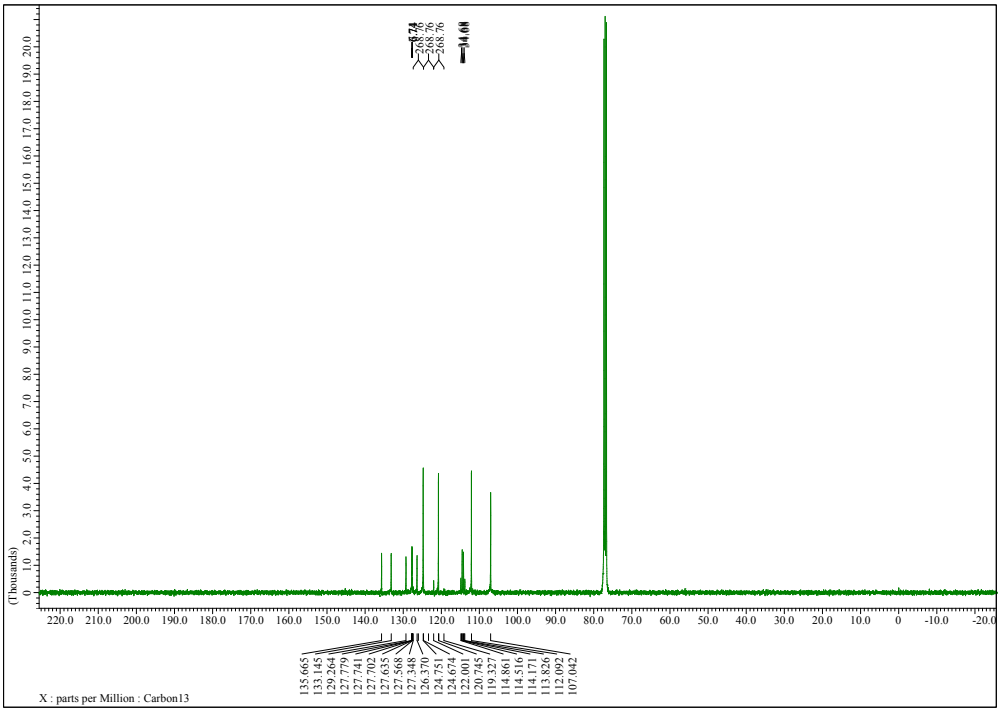

(*E*)-5-chloro-2-(3,3,3-trifluoroprop-1-enyl)-1*H*-indole **4d**



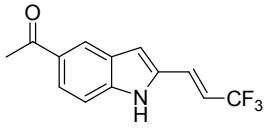
$^{1}$H NMR spectrum



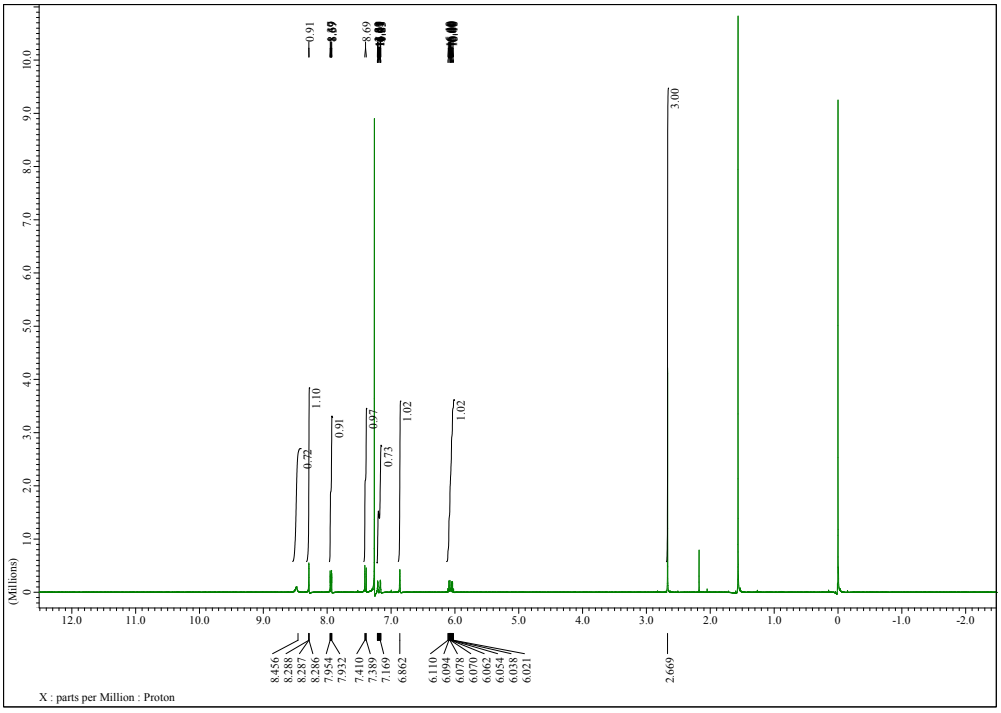

$^{13}$C NMR spectrum



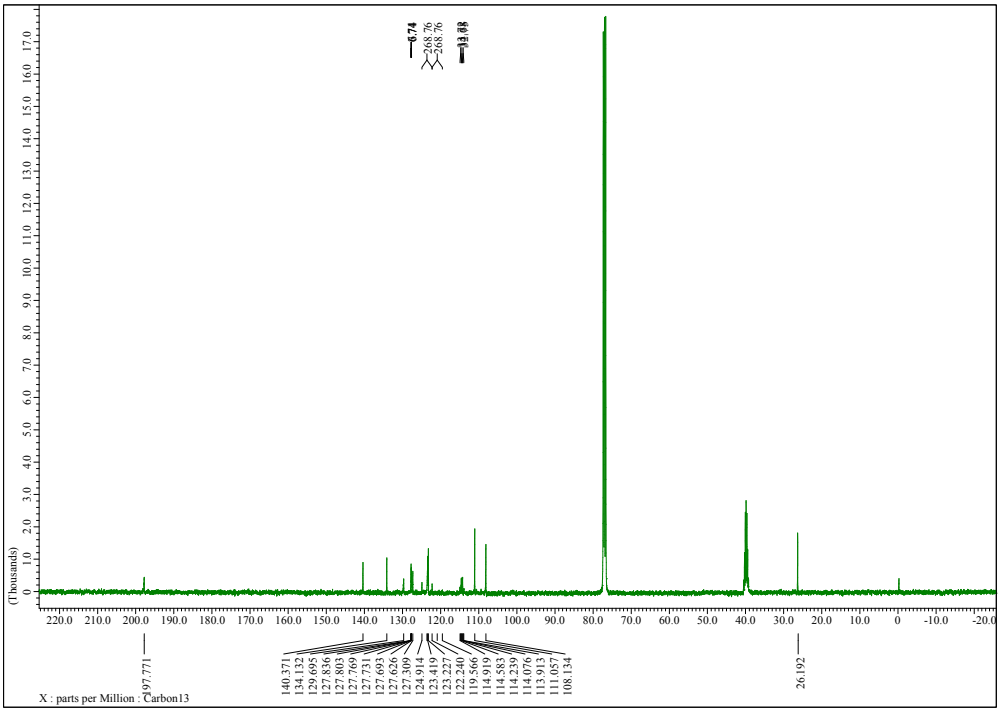

(*E*)-1-(2-(3,3,3-trifluoroprop-1-enyl)-1*H*-indol-5-yl)ethanone **4e**



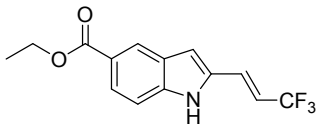
$^{1}$H NMR spectrum



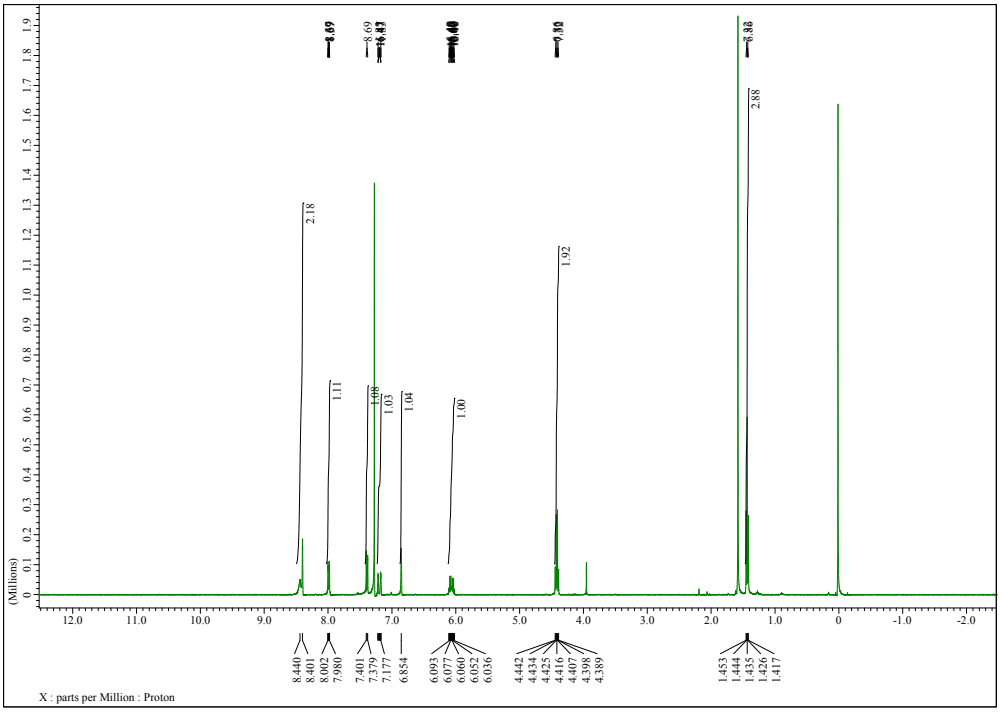

$^{13}$C NMR spectrum



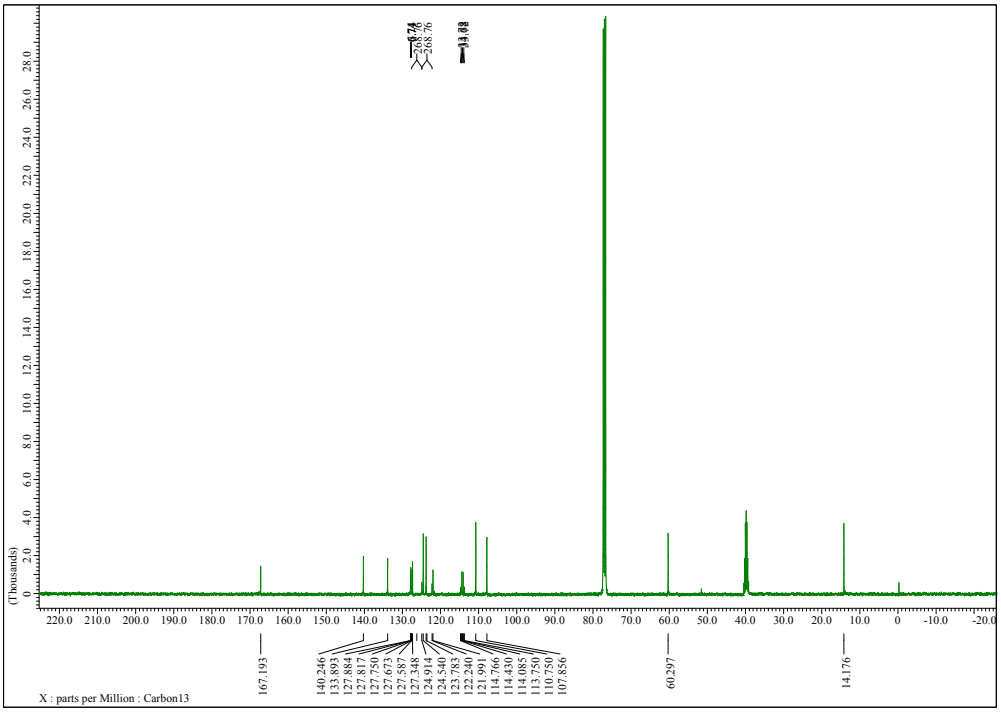

(*E*)-ethyl 2-(3,3,3-trifluoroprop-1-enyl)-1*H*-indol-5-carboxylate **4f**



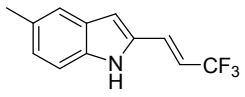
$^{1}$H NMR spectrum



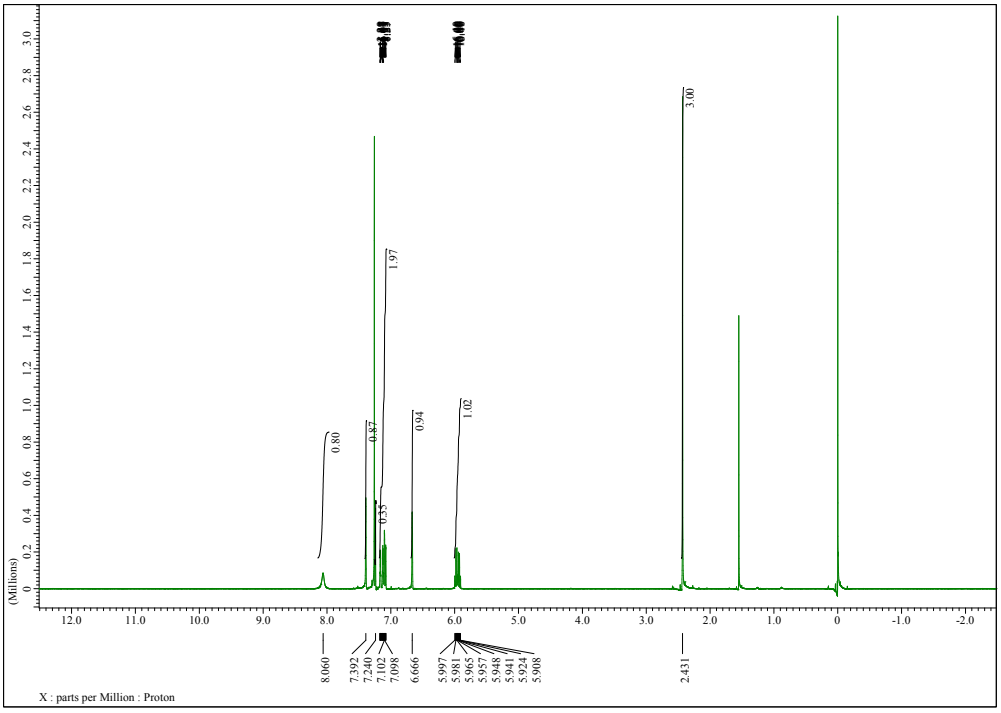

$^{13}$C NMR spectrum



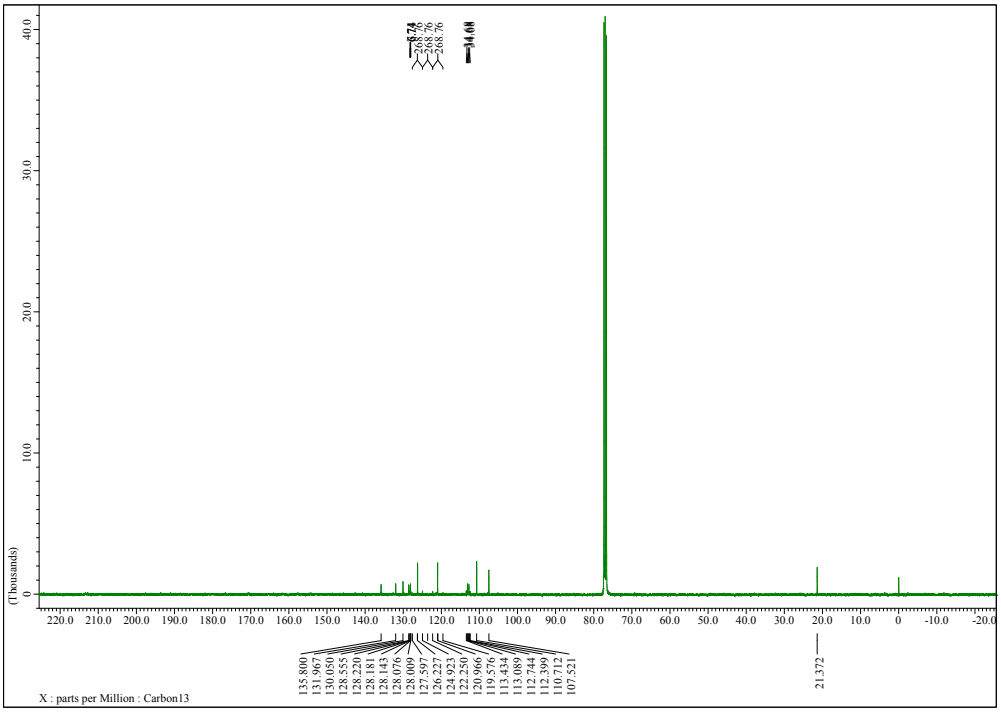

(*E*)-5-methyl-2-(3,3,3-trifluoroprop-1-enyl)-1*H*-indole **4h**



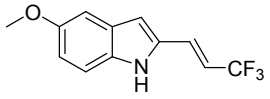
$^{1}$H NMR spectrum



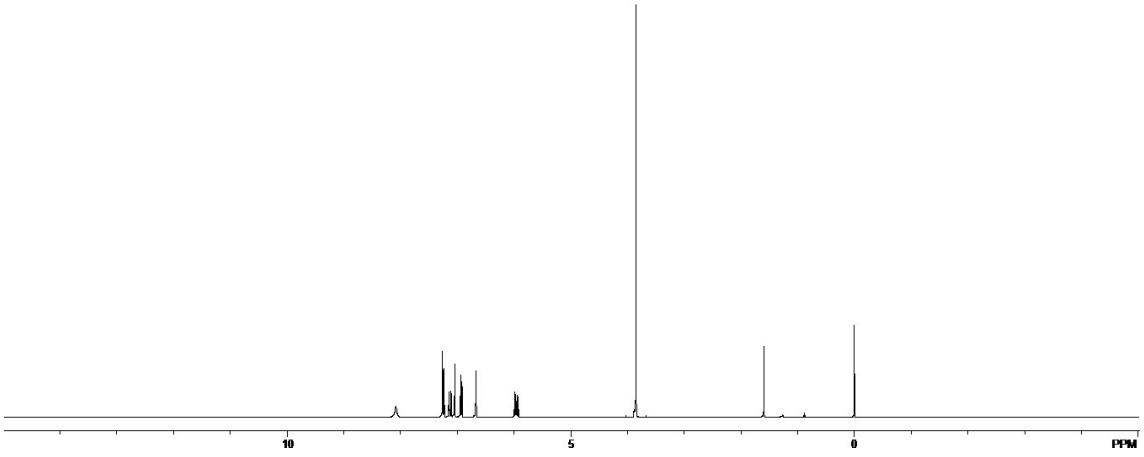

$^{13}$C NMR spectrum



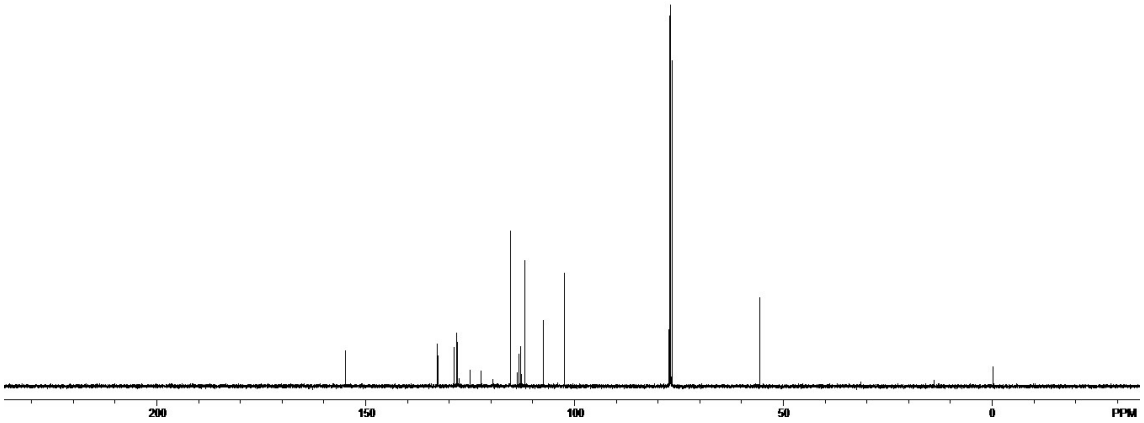

(*E*)-5-methoxy-2-(3,3,3-trifluoroprop-1-enyl)-1*H*-indole **4i**



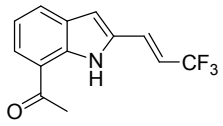
$^{1}$H NMR spectrum



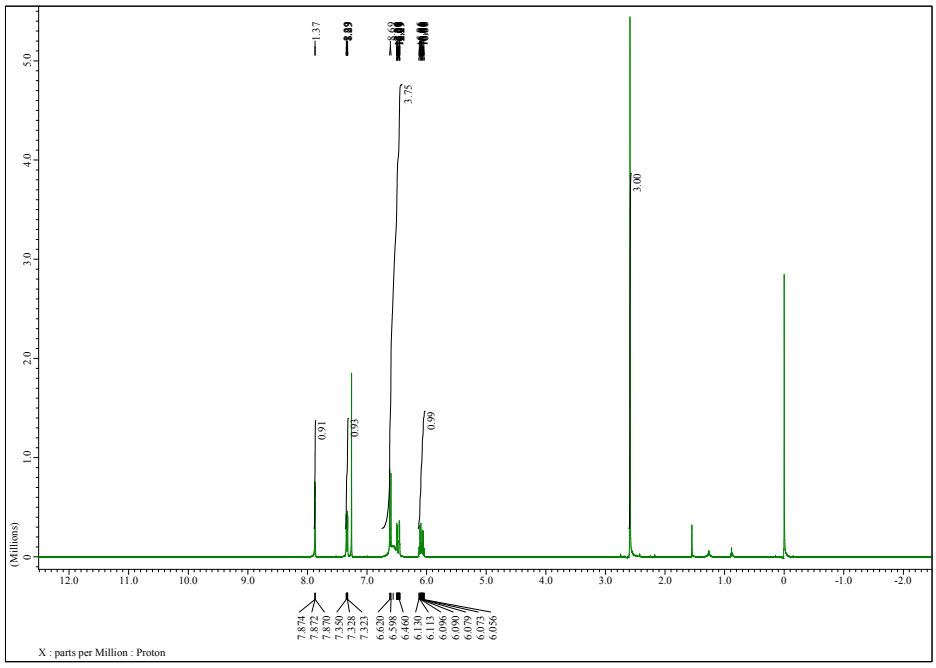

$^{13}$C NMR spectrum




(*E*)-1-(2-(3,3,3-trifluoroprop-1-enyl)-1*H*-indol-7-yl)ethanone **4k**



$^{1}$H NMR spectrum




$^{13}$C NMR spectrum