Supporting Information

Palladium Nanomaterials in Catalytic Intramolecular C-H Amination Reactions

Leng Leng Chng,[a] Jun Yang,[a] Yifeng Wei[a] and Jackie Y. Ying[a,*]

[a] Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos, Singapore 138669

Fax: (+65) 6478-9020; E-mail: jyying@ibn.a-star.edu.sg

Materials

All reagents were purchased from Aldrich, Fluka and Merck, and used as received. Silica gel 60 (230–400 mesh, Merck) was used for column chromatography. DMSO (anhydrous grade), DMF (anhydrous grade), DMA (anhydrous grade), toluene (anhydrous grade) and 1,4-dioxane (anhydrous grade) were used as received from Aldrich Chemical Company. 4 Å molecular sieves were activated by heating at 110°C under vacuum for 1 day prior to use. All other reagents were purchased from commercial sources, and used as received. Substrates **1a**-**1q** were prepared according to literature procedure.[1]

Characterization

TEM was performed on a FEI Tecnai G^2 F20 electron microscope operated at 200 kV with the software package for automated electron tomography. For TEM studies, a drop of the nanoparticle solution was dispensed onto a 3-mm carbon-coated copper grid. Excess solution was removed by an absorbent paper, and the sample was dried under vacuum at room temperature (RT). XPS analysis was conducted on a VG ESCALAB MKII spectrometer. ICP-MS analyses were performed on a Perkin-Elmer Elan DRC II. XPS analysis was conducted on a VG ESCALAB MKII spectrometer. ^{1}H and ^{13}C NMR spectra were collected in $CDCl_3$ using a Bruker AV-400 spectrometer at 25°C. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP2010.

Synthesis of Supported Palladium Nanoparticles

Ag-Pd on carbon (Ag-Pd/C). Synthesis of Ag-Pd alloy nanoparticles was achieved using an established solution method with some modifications. A mixture of $AgNO_3$ (0.042 g) and palladium(II) acetylacetonate (0.152 g) in 20 mL of oleylamine was heated at 160°C for 2 h under an argon flow. The reaction mixture was cooled to RT, and methanol (30 mL) was added to precipitate the Ag-Pd alloy nanoparticles. The precipitated nanoparticles were collected *via* centrifugation, and washed twice with methanol (15 mL). The Ag-Pd alloy nanoparticles were re-dispersed in toluene (20 mL), Vulcan XC-72 carbon (1.25 g) was added, and the mixture was stirred at RT overnight. The supported Ag-Pd alloy nanoparticles on carbon were collected *via* centrifugation, washed twice with methanol (15 mL), and dried at RT under vacuum overnight. A mixture of the nanoparticles and acetic acid (10 mL) was refluxed at 120°C for 3 h. The mixture was then cooled to RT, and the supported Ag-Pd alloy nanoparticles on carbon were collected *via* centrifugation, washed twice with methanol (15 mL), and dried at RT under vacuum overnight.

Core-shell Ag@Pd on carbon (Ag@Pd/C). Synthesis of core-shell Ag@Pd nanoparticles was achieved using an established solution method with some modifications. A mixture of $AgNO_3$ (0.085 g) and oleylamine (20 mL) was heated at 150°C for 2 h under an argon flow. $PdCl_2$ (0.177 g) was added, and the mixture was heated at 160°C for 2 h. The reaction mixture was cooled to RT, and methanol (30 mL) was added to precipitate the core-shell Ag@Pd nanoparticles. The precipitated nanoparticles were collected *via* centrifugation, and washed twice with methanol (15 mL). The Ag@Pd nanoparticles were re-dispersed in toluene (20 mL), Vulcan XC-72 carbon (2.50 g) was added, and the mixture was stirred at RT overnight. The supported Ag@Pd nanoparticles on carbon were collected *via* centrifugation, washed twice with methanol (15 mL), and dried at RT under vacuum overnight. A mixture of the nanoparticles and acetic acid (10 mL) was refluxed at 120°C for 3 h. The mixture was then cooled to RT, and the supported Ag@Pd nanoparticles on carbon were collected *via* centrifugation, washed twice with methanol (15 mL), and dried at RT under vacuum overnight.

Core-shell Ag_2S@Pd on carbon (Ag_2S@Pd/C). Synthesis of core-shell Ag_2S@Pd nanoparticles was achieved using an established solution method with some modifications. For the synthesis of the Ag_2S seed nanocrystals, 120 mg of bis(p-sulfonatophenyl)phenylphosphane dihydrate dipotassium salt (BSPP) was added to 60 mL of 1 mM aqueous $AgNO_3$ solution in a 250 mL beaker. The mixture was stirred for 1 h, followed by the prompt addition of 2 mL of 50 mM aqueous Na_2S solution. A brown-colored hydrosol was obtained after 4 h of stirring of the reaction mixture at RT, indicating the formation of Ag_2S nanocrystals. Next, the Ag_2S hydrosol prepared above was refluxed at

110°C for 3 min in a 250-mL three-necked flask equipped with a condenser and a Teflon-coated magnetic stirring bar, followed by the addition of 6 mL of 100 mM aqueous sodium citrate solution. The mixture was refluxed at 110°C for 1 min, and then 2.4 mL of 50 mM aqueous Na_2PdCl_4 solution was added swiftly. The reaction mixture was continuously refluxed for 120 min at 110°C to form the hydrosol of core-shell Ag_2S@Pd nanocomposites.

To load the core-shell Ag_2S@Pd nanocrystals on Vulcan XC-72 carbon support, the Ag_2S@Pd nanoparticles were transferred into toluene using the approach for the transfer of metal nanoparticles and metal ions.[2] The phase transfer of Ag_2S@Pd nanocrystals from aqueous phase to a non-polar organic medium was conducted since we experimentally found that the loading efficiency of the particles on XC-72C carbon support from organic medium (~99%) was much higher than that from aqueous phase (~37%). Typically, Ag_2S@Pd hydrosol was mixed with an equal volume of ethanolic solution of dodecylamine (DDA, 90 mM). After 3 min of stirring, an equal volume of toluene were added and stirred for another minute. Phase transfer of the Ag_2S@Pd nanocrystals from water to toluene would then occur quickly and completely, leaving a clear colorless solution in the aqueous phase. ICP-AES analysis showed that the phase transfer efficiency was ~ 100%. Next, 540 mg of XC-72C carbon powder was introduced into the Ag_2S@Pd organosol. After 24 h of stirring of the mixtures, the Ag_2S@Pd/C was collected *via* centrifugation, and washed 3 times with methanol. They were then dried at room temperature in vacuum. A mixture of the nanoparticles and acetic acid (10 mL) was refluxed at 120°C for 3 h. The mixture was then cooled to RT, and the supported Ag_2S@Pd nanoparticles on carbon were collected *via* centrifugation, washed twice with methanol (15 mL), and dried at RT under vacuum overnight.

Pd nanoparticles on carbon (Pd/C). A solution of $Pd(OAc)_2$ (0.124 g) in dry dichloromethane (2 mL) was added to a mixture of Vulcan XC-72 carbon (1.00 g) in dry toluene (20 mL) at RT under argon. 2 mL of dry methanol was then added dropwise at RT, and the reaction mixture was heated at 60°C under argon for 24 h. The Pd/C nanoparticles were collected *via* centrifugation, washed four times with methanol (15 mL), and dried at RT under vacuum overnight.

Pd nanoparticles on ceria (Pd/CeO_2). A solution of $Pd(OAc)_2$ (0.124 g) in dry dichloromethane (2 mL) was added to a mixture of ceria nanopowder (Aldrich 520764, 1.00 g) in dry toluene (20 mL) at RT under argon. 2 mL of dry methanol was then added dropwise at RT, and the reaction mixture was heated at 60°C under argon for 24 h. The Pd/C nanoparticles were collected *via* centrifugation, washed four times with methanol (15 mL), and dried at RT under vacuum overnight.

Pd nanoparticles on titania (Pd/TiO_2). A solution of $Pd(OAc)_2$ (0.124 g) in dry dichloromethane (2 mL) was added to a mixture of titania (Degussa Aeroxide P25, 1.00 g) in dry toluene (20 mL) at RT under argon. 2 mL of dry methanol was then added dropwise at RT, and the reaction mixture was heated at 60°C under argon for 24 h. The Pd/C nanoparticles were collected *via* centrifugation, washed four times with methanol (15 mL), and dried at RT under vacuum overnight.

Pd nanoparticles on alumina (Pd/Al_2O_3). A solution of $Pd(OAc)_2$ (0.124 g) in dry dichloromethane (2 mL) was added to a mixture of alumina (Aldrich 19997-4, 1.00 g) in dry toluene (20 mL) at RT under argon. 2 mL of dry methanol was then added dropwise at RT, and the reaction mixture was heated at 60°C under argon for 24 h. The Pd/C nanoparticles were collected *via* centrifugation, washed four times with methanol (15 mL), and dried at RT under vacuum overnight.

Pd nanoparticles on silica (Pd/SiO_2). A solution of $Pd(OAc)_2$ (0.124 g) in dry dichloromethane (2 mL) was added to a mixture of silica (Aldrich 28859, 1.00 g) in dry toluene (20 mL) at RT under argon. 2 mL of dry methanol was then added dropwise at RT, and the reaction mixture was heated at 60°C under argon for 24 h. The Pd/C nanoparticles were collected *via* centrifugation, washed four times with methanol (15 mL), and dried at RT under vacuum overnight.

Preparation of Heteroaryl Amide Substrates

***N*-(2-(Furan-2-yl)phenyl)acetamide**, **(1r).** A mixture of $Pd(OAc)_2$ (0.0045 g, 0.02 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos, 0.016 g, 0.039 mmol), 2'-bromoacetanilide (0.21 g, 0.98 mmol), furan-2-boronic acid (0.17 g, 1.52 mmol) and K_3PO_4 (0.43 g, 2.03 mmol) in dry toluene (1.5 mL) was heated at 90°C under argon for 4 h. The reaction mixture was filtered through a Celite pad, which was rinsed with EtOAc (3 x 5 mL). The solvent was removed by rotary evaporation. Purification by column chromatography (silica gel, 3/2 hexanes/ethyl acetate) provided **1r** as an off-white solid (0.12 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.44 (s, 1H), 8.32 (d, J = 8.45 Hz, 1H), 7.59–7.53 (m, 2H), 7.36–7.32 (m, 1H), 7.15 (t, J = 7.46 Hz, 1H), 6.64–6.56 (m, 2H), 2.22 (s, 3H). GC-MS: 201 (M^+), 130 (base).

***N*-(2-(Furan-3-yl)phenyl)acetamide**, **(1s).** A mixture of $Pd(OAc)_2$ (0.0045 g, 0.02 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos, 0.016 g, 0.039 mmol), 2'-bromoacetanilide (0.21 g, 0.98 mmol), furan-3-boronic acid (0.17 g, 1.52 mmol) and K_3PO_4 (0.43 g, 2.03 mmol) in dry toluene (1.5 mL) was heated at 90°C under argon for 30 min. The reaction mixture was filtered through a Celite pad, which was rinsed with EtOAc

(3 x 5 mL). The solvent was removed by rotary evaporation. Purification by column chromatography (silica gel, 3/2 hexanes/ethyl acetate) provided **1s** as a light yellow solid (0.19 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.24 (d, *J* = 8.21 Hz, 1H), 7.59 (s, 2H), 7.38–7.29 (m, 3H), 7.16 (t, *J* = 7.48 Hz, 1H), 6.57 (s, 1H), 2.14 (s, 3H). GC-MS: 201 (M^+), 130 (base).

***N*-(2-(Thiophen-2-yl)phenyl)acetamide**, **(1t).** A mixture of $Pd(OAc)_2$ (0.0045 g, 0.02 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos, 0.016 g, 0.039 mmol), 2'-bromoacetanilide (0.21 g, 0.98 mmol), thiophene-2-boronic acid (0.19 g, 1.48 mmol) and K_3PO_4 (0.43 g, 2.03 mmol) in dry toluene (1.5 mL) was heated at 90°C under argon for 30 min. The reaction mixture was filtered through a Celite pad, which was rinsed with EtOAc (3 x 5 mL). The solvent was removed by rotary evaporation. Purification by column chromatography (silica gel, 3/2 hexanes/ethyl acetate) provided **1t** as a yellow solid (0.21 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.27 (d, *J* = 8.04 Hz, 1H), 7.49 (s, 1H), 7.46 (dd, *J* = 5.00 and 1.16 Hz, 1H), 7.40–7.36 (m, 2H), 7.19–7.15 (m, 3H), 2.13 (s, 3H). GC-MS: 217 (M^+), 175 (base).

***N*-(2-(Thiophen-3-yl)phenyl)acetamide**, **(1u).** A mixture of $Pd(OAc)_2$ (0.0045 g, 0.02 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos, 0.016 g, 0.039 mmol), 2'-bromoacetanilide (0.21 g, 0.98 mmol), thiophene-3-boronic acid (0.19 g, 1.48 mmol) and K_3PO_4 (0.43 g, 2.03 mmol) in dry toluene (1.5 mL) was heated at 90°C under argon for 30 min. The reaction mixture was filtered through a Celite pad, which was rinsed with EtOAc (3 x 5 mL). The solvent was removed by rotary evaporation. Purification by column chromatography (silica gel, 3/2 hexanes/ethyl acetate) provided **1u** as a yellow solid (0.21 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.28 (d, *J* = 8.13 Hz, 1H), 7.51 (dd, *J* = 4.84 and 2.96 Hz, 1H), 7.39–7.34 (m, 2H), 7.32–7.28 (m, 2H), 7.19–7.15 (m, 2H), 2.10 (s, 1H). GC-MS: 217 (M^+), 175 (base).

Synthesis of Substituted Carbazoles by Cyclization of Biaryl or Heteroaryl Amides

General procedure for the cyclization of biaryl or heteroaryl amides (Table 4, **2b-2u**): A mixture of the Pd/C nanomaterial (5 mol% Pd), substrate (0.2 mmol), 4 Å molecular sieves (0.040 g) and dry DMSO (1 mL, purged with O_2 for 5 min) were added to a 8-mL glass vial equipped with a screw cap. The headspace in the glass vial was purged with O_2. The reaction mixture was heated at 120°C under O_2 for 24 h. The mixture was centrifuged at 6500 rpm for 10 min. The organic layer containing the product was separated, and the solids were washed with dichloromethane (3 x 3 mL). More dichloromethane (20 mL) was added, and the organic layer was washed with water (3 x 10 mL). The organic layer was separated, dried over

Na_2SO_4, and the solvent was removed by rotary evaporation, followed by purification by column chromatography (silica gel, 2/1 dichloromethane/hexanes, unless noted otherwise).

For the recycling experiments, the solid catalyst recovered *via* centrifugation was dried at RT under vacuum for 1 day, and at 120°C under vacuum for 3 h before it was used in the next run.

1-(9*H*-carbazol-9-yl)ethanone (Table 3, Entry 11, **2a**). Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.24 (d, *J* = 8.37 Hz, 2H), 8.03 (ddd, *J* = 7.67, 1.39 and 0.67 Hz, 2H), 7.51 (ddd, *J* = 8.47, 7.22 and 1.32 Hz, 2H), 7.41 (td, *J* = 7.48 and 0.95 Hz, 2H), 2.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 170.17, 138.64, 127.38, 126.44, 123.72, 119.87, 116.28, 27.82. GC-MS: 209 (M^+), 167 (base).

1-(2-Methyl-9*H*-carbazol-9-yl)ethanone (Table 4, **2b**). Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.18 (d, *J* = 8.32 Hz, 1H), 8.08 (s, 1H), 7.97 (ddd, *J* = 7.61, 1.41 and 0.63 Hz, 1H), 7.89 (d, *J* = 7.88 Hz, 1H), 7.46 (ddd, *J* = 8.44, 7.22 and 1.32 Hz, 1H), 7.39 (td, *J* = 7.47 and 1.00 Hz, 1H), 7.23 (ddd, *J* = 7.93, 1.37 and 0.67 Hz, 1H), 2.90 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 170.23, 139.06, 138.58, 137.65, 126.79, 126.59, 124.93, 124.02, 123.64, 119.58, 119.45, 116.75, 116.16, 27.86, 22.39. GC-MS: 223 (M^+), 181 (base).

1-(2-Methoxy-9*H*-carbazol-9-yl)ethanone (Table 4, **2c**). Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.06 (d, *J* = 8.04 Hz, 1H), 7.94–7.90 (m, 2H), 7.87 (d, *J* = 8.53 Hz, 1H), 7.43–7.35 (m, 2H), 7.00 (dd, *J* = 8.53 and 2.28 Hz, 1H), 3.94 (s, 3H), 2.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.73, 159.22, 139.54, 137.86, 126.15, 125.36, 123.15, 119.67, 119.19, 118.65, 115.20, 110.85, 101.43, 55.24, 27.24. GC-MS: 239 (M^+), 197 (base).

1-(2-(Trifluoromethyl)-9*H*-carbazol-9-yl)ethanone (Table 4, **2d**). Yield: 34%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.69 (s, 1H), 8.14–8.07 (m, 3H), 7.67 (ddd, *J* = 8.14, 1.42 and 0.56 Hz, 1H), 7.58 (ddd, *J* = 8.51, 7.25 and 1.33 Hz, 1H), 7.46 (td, *J* = 7.52 and 0.80 Hz, 1H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.42, 138.64, 137.66, 128.83, 128.51, 128.40, 127.98, 125.23, 124.80, 123.45, 122.53, 120.17, 120.14, 120.11, 120.07, 119.39, 119.37, 115.32, 113.59, 113.56, 113.52, 113.47, 27.21. GC-MS: 277 (M^+), 235 (base).

1-(2-Fluoro-9*H*-carbazol-9-yl)ethanone (Table 4, **2e**). Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.12–8.01 (m, 2H), 7.97 (d, *J* = 7.16 Hz, 1H), 7.93 (dd, *J* = 8.53 and 5.60 Hz, 1H), 7.48 (td, *J* = 7.83 and 1.24 Hz, 1H), 7.41 (t, *J* = 7.48 Hz, 1H), 7.14 (td, *J* = 8.69 and 2.28 Hz, 1H), 2.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.43, 163.02,

160.61, 138.78, 138.65, 138.19, 126.28, 125.41, 123.31, 121.87, 119.89, 119.79, 119.14, 115.22, 111.13, 110.90, 104.12, 103.83, 27.10. GC-MS: 227 (M^+), 185 (base).

1-(2-*tert*-Butyl-9*H*-carbazol-9-yl)ethanone (Table 4, **2f**). Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.34 (d, *J* = 1.16 Hz, 1H), 8.17 (d, *J* = 8.33 Hz, 1H), 7.98 (ddd, *J* = 7.60, 1.40 and 0.62 Hz, 1H), 7.93 (dd, *J* = 8.27 and 0.38 Hz, 1H), 7.49–7.44 (m, 2H), 7.38 (td, *J* = 7.47 and 0.97 Hz, 1H), 2.92 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 170.24, 151.14, 139.06, 138.81, 126.81, 126.52, 123.96, 123.63, 121.44, 119.68, 119.20, 116.10, 113.27, 35.45, 31.72, 27.86. GC-MS: 265 (M^+), 208 (base).

1-(4-Methyl-9*H*-carbazol-9-yl)ethanone (Table 4, **2g**). Yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.31 (d, *J* = 8.37 Hz, 1H), 8.15 (dd, *J* = 7.80 and 0.80 Hz, 1H), 8.09 (d, *J* = 8.49 Hz, 1H), 7.50 (ddd, *J* = 8.46, 7.23 and 1.31 Hz, 1H), 7.44–7.37 (m, 2H), 7.19 (dt, *J* = 7.44 and 0.79 Hz, 1H), 2.91 (s, 3H), 2.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.61, 138.12, 138.05, 132.51, 126.45, 126.16, 125.95, 124.96, 123.96, 122.92, 121.89, 115.35, 112.92, 27.35, 20.55. GC-MS: 223 (M^+), 181 (base).

1-(4-Methoxy-9*H*-carbazol-9-yl)ethanone (Table 4, **2h**). Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.36 (ddd, *J* = 7.63, 1.47 and 0.53 Hz, 1H), 8.23 (d, *J* = 8.29 Hz, 1H), 7.82 (d, *J* = 8.45 Hz, 1H), 7.48–7.37 (m, 3H), 6.89 (d, *J* = 8.12 Hz, 1H), 4.09 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.70, 155.10, 139.21, 137.26, 127.29, 125.69, 125.04, 123.09, 122.61, 114.94, 114.68, 108.08, 104.31, 54.94, 27.21. GC-MS: 239 (M^+), 197 (base).

1-(4-(Trifluoromethyl)-9*H*-carbazol-9-yl)ethanone (Table 4, **2i**). Yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.67 (d, *J* = 8.53 Hz, 1H), 8.35–8.33 (m, 1H), 8.13 (d, *J* = 8.58 Hz, 1H), 7.74 (d, *J* = 7.69 Hz, 1H), 7.60–7.55 (m, 2H), 7.46 (ddd, *J* = 8.13, 7.23 and 0.95 Hz, 1H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.50, 139.21, 138.20, 126.27, 125.10, 124.22, 123.39, 123.23, 123.17, 123.12, 123.06, 122.77, 122.44, 122.39, 122.29, 122.11, 120.77, 120.71, 120.64, 120.58, 119.65, 119.52, 114.69, 110.11, 27.45. GC-MS: 277 (M^+), 235 (base).

1-(4-Fluoro-9*H*-carbazol-9-yl)ethanone (Table 4, **2j**). Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.20 (d, *J* = 8.53 Hz, 2H), 8.06 (d, *J* = 8.41 Hz, 1H), 7.53 (ddd, *J* = 8.48, 7.32 and 1.28 Hz, 1H), 7.46–7.41 (m, 2H), 7.13–7.08 (m, 1H), 2.91 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.54, 158.59, 156.11, 139.90, 139.82, 137.54, 127.42, 127.34, 126.86, 123.54, 123.13, 122.50, 122.45, 115.22, 114.32, 114.12, 111.59, 111.55, 109.51, 109.32, 27.19. GC-MS: 227 (M^+), 185 (base).

1-(3-Methyl-9H-carbazol-9-yl)ethanone (Table 4, **2k**). Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.23 (d, *J* = 8.37 Hz, 1H), 8.08 (d, *J* = 8.53 Hz, 1H), 7.98 (dt, *J* = 7.72 and 0.64 Hz, 1H), 7.80 (s, 1H), 7.48 (ddd, *J* = 8.43, 7.23 and 1.29 Hz, 1H), 7.39 (td, *J* = 7.47 and 0.76 Hz, 1H), 7.30 (dd, *J* = 8.57 and 1.72 Hz, 1H), 2.88 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.48, 138.34, 136.19, 132.83, 127.90, 126.69, 126.04, 125.88, 123.11, 119.47, 119.19, 115.81, 115.38, 27.22, 20.72. GC-MS: 223 (M^+), 181 (base).

1-(1,3-Dimethyl-9*H*-carbazol-9-yl)ethanone (Table 4, **2l**). Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.96–7.93 (m, 2H), 7.64 (s, 1H), 7.45 (td, *J* = 7.78 and 1.26 Hz, 1H), 7.35 (t, *J* = 7.52 Hz, 1H), 7.13 (s, 1H), 2.70 (s, 3H), 2.49 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 170.23, 139.48, 136.59, 133.31, 130.73, 127.42, 126.38, 126.13, 125.47, 122.75, 119.37, 116.96, 114.00, 26.47, 20.69, 20.62. GC-MS: 237 (M^+), 195 (base).

1-(1-Methyl-9*H*-carbazol-9-yl)ethanone (Table 4, **2m**). Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.99–7.95 (m, 2H), 7.85 (d, *J* = 7.22 Hz, 1H), 7.47 (td, *J* = 7.79 and 1.28 Hz, 1H), 7.39–7.30 (m, 3H), 2.73 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 170.30, 139.12, 138.37, 129.53, 127.18, 126.50, 126.06, 125.76, 123.57, 122.77, 119.48, 116.75, 113.82, 26.51, 20.77. GC-MS: 223 (M^+), 181 (base).

1-(3-Methyl-9*H*-carbazol-9-yl)ethanone (Table 4, **2n**). Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.23 (d, *J* = 8.37 Hz, 1H), 8.08 (d, *J* = 8.53 Hz, 1H), 7.98 (dt, *J* = 7.72 and 0.64 Hz, 1H), 7.80 (s, 1H), 7.48 (ddd, *J* = 8.43, 7.23 and 1.29 Hz, 1H), 7.39 (td, *J* = 7.47 and 0.76 Hz, 1H), 7.30 (dd, *J* = 8.57 and 1.72 Hz, 1H), 2.88 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.48, 138.34, 136.19, 132.83, 127.90, 126.69, 126.04, 125.88, 123.11, 119.47, 119.19, 115.81, 115.38, 27.22, 20.72. GC-MS: 223 (M^+), 181 (base).

1-(3-Fluoro-9*H*-carbazol-9-yl)ethanone (Table 4, **2o**). Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.31 (dd, *J* = 9.11 and 4.46 Hz, 1H), 8.11 (d, *J* = 8.45 Hz, 1H), 7.97 (d, *J* = 7.69 Hz, 1H), 7.65 (dd, *J* = 8.16 and 2.68 Hz, 1H), 7.53 (ddd, *J* = 8.47, 7.28 and 1.26 Hz, 1H), 7.41 (t, *J* = 7.50 Hz, 1H), 7.20 (td, *J* = 9.00 and 2.72 Hz, 1H), 2.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.26, 160.26, 157.86, 138.57, 134.45, 127.38, 127.12, 127.03, 125.37, 125.33, 123.16, 119.72, 117.31, 117.23, 115.45, 114.21, 113.97, 105.42, 105.18, 27.15. GC-MS: 227 (M^+), 185 (base).

1-(3-(Trifluoromethyl)-9*H*-carbazol-9-yl)ethanone (Table 4, **2p**). Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.44 (d, *J* = 8.81 Hz, 1H), 8.27–8.26 (m, 1H), 8.15 (d, *J* = 8.41 Hz, 1H), 8.07 (ddd, *J* = 7.72, 1.30 and 0.64 Hz, 1H), 7.74 (ddd, *J* = 8.79, 1.86 and 0.52 Hz, 1H), 7.57 (ddd, *J* = 8.50, 7.26 and 1.30 Hz, 1H), 7.46 (td, *J* = 7.51 and 0.85 Hz, 1H), 2.93

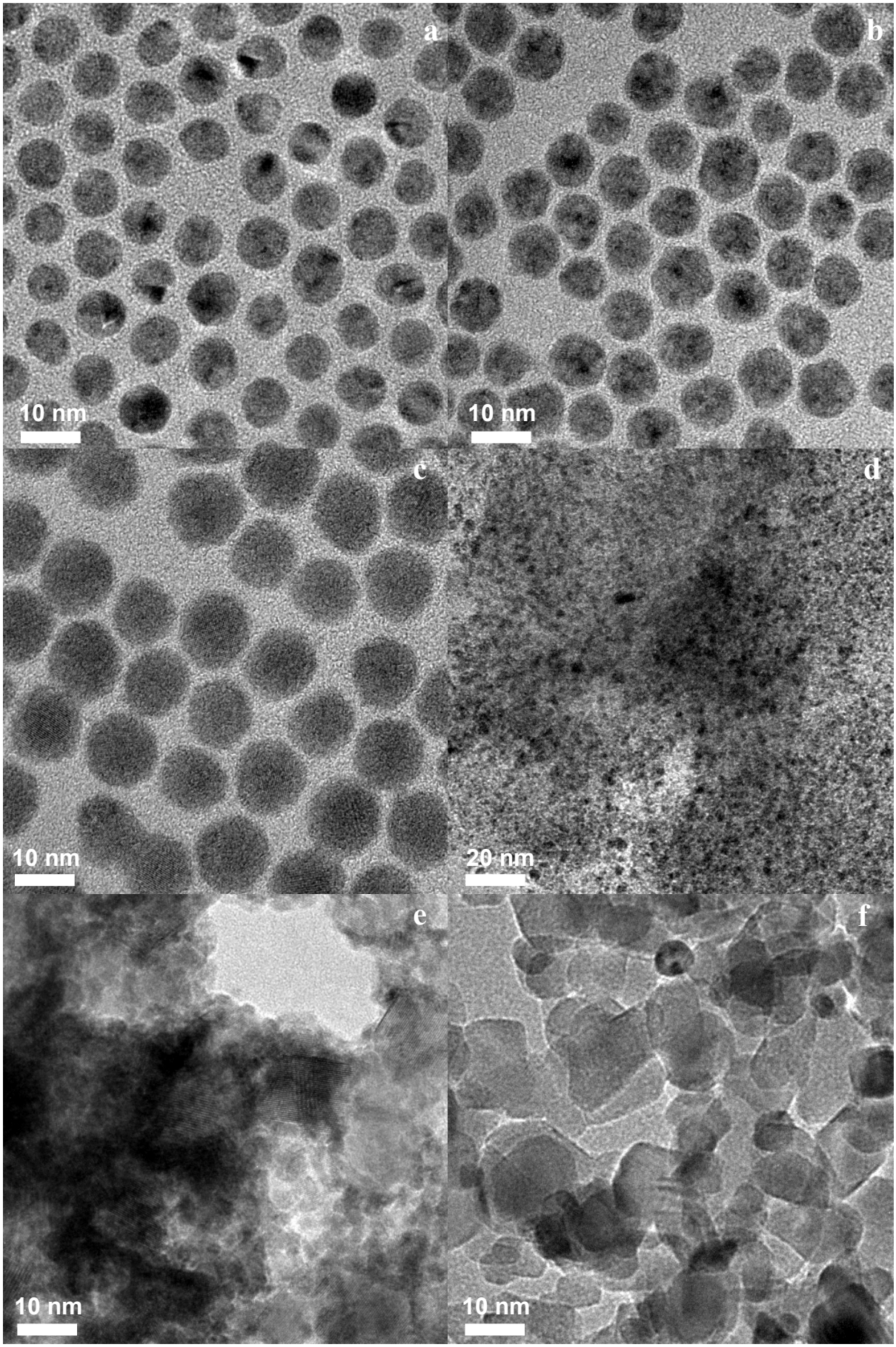
(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.53, 139.88, 138.37, 127.69, 125.76, 125.56, 125.23, 124.98, 124.92, 123.71, 123.68, 123.64, 123.61, 123.52, 122.53, 119.79, 116.53, 116.49, 116.45, 116.41, 116.20, 115.40, 27.23. GC-MS: 277 (M^+), 235 (base).

1-(1,3-Difluoro-9*H*-carbazol-9-yl)ethanone (Table 4, **2q**). Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.38 (d, *J* = 8.45 Hz, 1H), 7.92 (d, *J* = 7.58 Hz, 1H), 7.57–7.50 (m, 2H), 7.41 (td, *J* = 7.53 and 0.85 Hz, 1H), 7.01 (ddd, *J* = 12.17, 8.95 and 2.40 Hz, 1H), 2.71 (d, *J* = 6.72 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 170.06, 159.93, 159.83, 157.50, 157.40, 150.39, 150.25, 147.89, 147.76, 140.08, 130.29, 130.24, 130.17, 130.13, 128.39, 121.53, 121.50, 121.43, 121.40, 119.35, 115.57, 102.61, 102.35, 102.33, 102.08, 101.94, 101.90, 101.71, 101.67, 25.75, 25.59. GC-MS: 245 (M^+), 203 (base).

References

(1) W. C. P. Tsang, N. Zhang and S. Buchwald, *J. Am. Chem Soc.*, 2005, **127**, 14560-14561.

(2) (*a*) J. Yang, J. Y. Lee, T. C. Deivaraj and H. P. Too, *J. Colloid Interface Sci.*, 2004, **277**, 95; (*b*) J. Yang, E. H. Sargent, S. O. Kelley and J. Y. Ying, *Nat. Mater.*, 2009, **8**, 683.


a
10 nm
b
10 nm
c
10 nm
d
20 nm
e
10 nm
f
10 nm

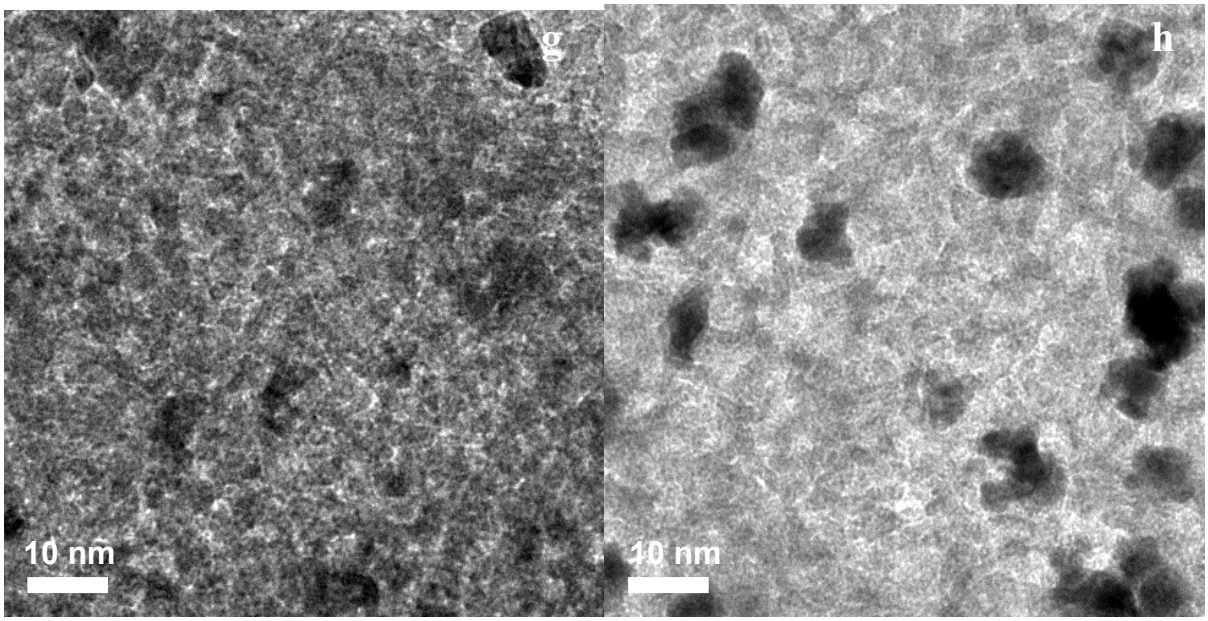


Figure S1. TEM images of Pd nanomaterials. (a) Ag-Pd, (b) Ag@Pd, (c) Ag_2S@Pd, (d) Pd/C, (e) Pd/CeO_2, (f) Pd/TiO_2, (g) Pd/ Al_2O_3, and (h) Pd/SiO_2.

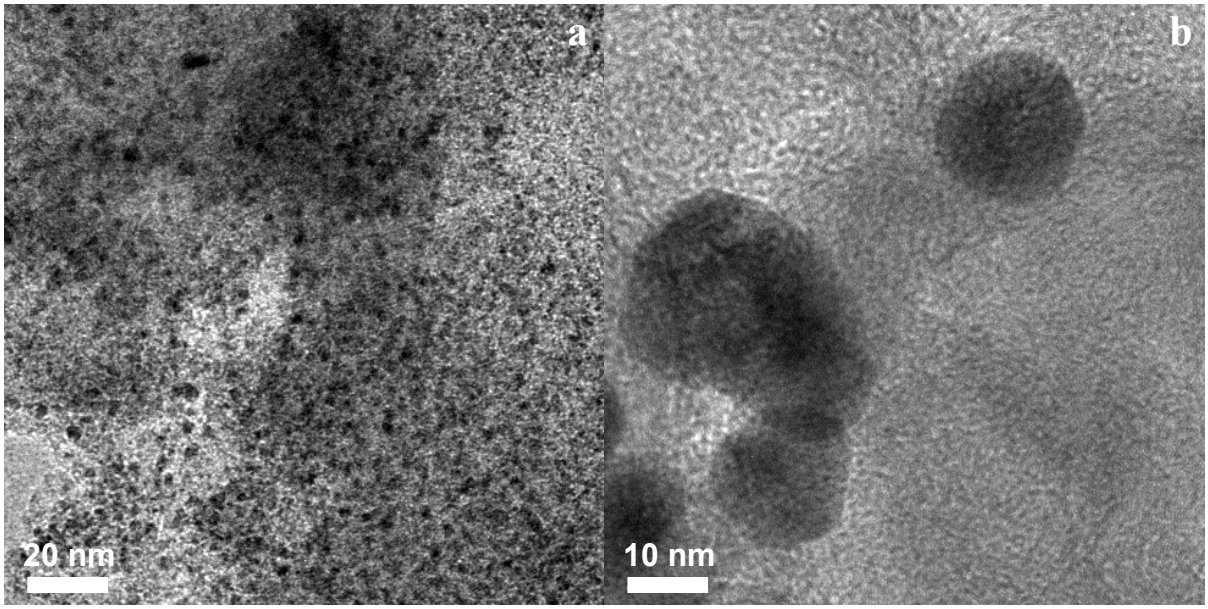


Figure S2. TEM images of supported Pd/C nanoparticles before (a) and after (b) reaction.

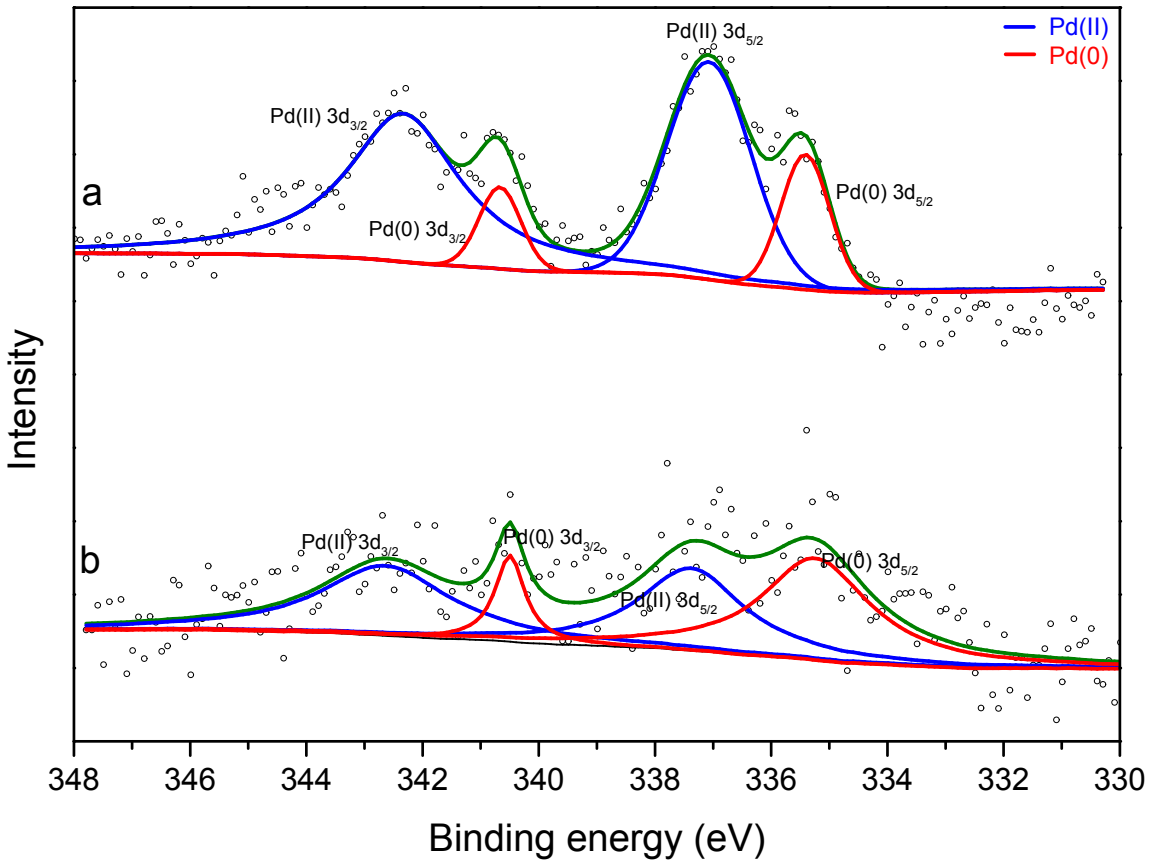


Figure S3. Pd 3d XPS spectra of Pd/C (a) before and (b) after the amination reaction. Approximately 88% and 78% of the Pd in (a) and (b) are in the Pd(II) oxidation state, respectively.

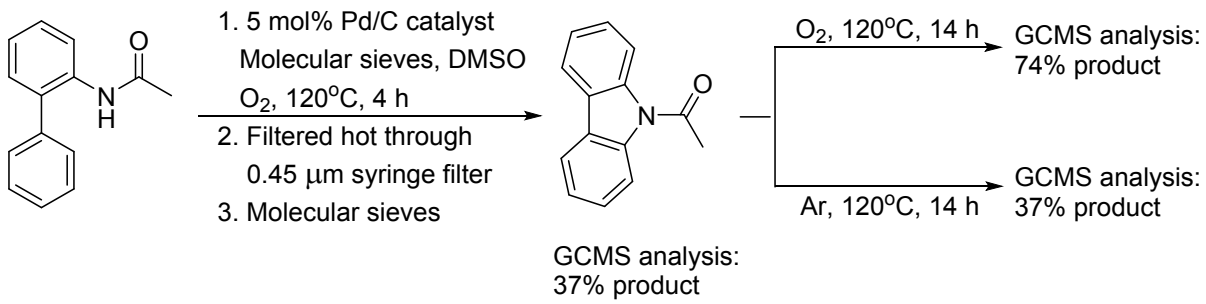


Figure S4. Heating of 2-acetaminobiphenyl with Pd/C and molecular sieves in DMSO at 120°C under O_2 for 4 h, followed by hot filtration through two 0.45-μm Teflon syringe filters. Next, molecular sieves were added to the filtrate, and the mixture was heated at 120°C for 14 h under O_2 or Ar.

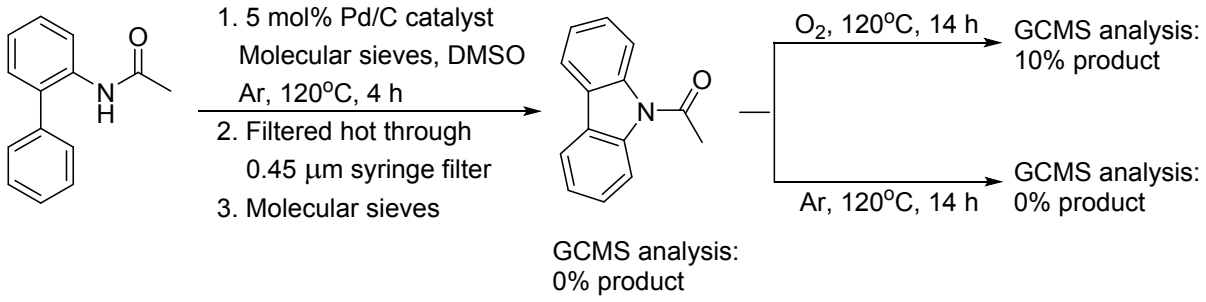


Figure S5. Heating of 2-acetaminobiphenyl with Pd/C and molecular sieves in DMSO at 120°C under Ar for 4 h, followed by hot filtration through two 0.45-μm Teflon syringe filters. Next, molecular sieves were added to the filtrate, and the mixture was heated at 120°C for 14 h under O_2 or Ar.

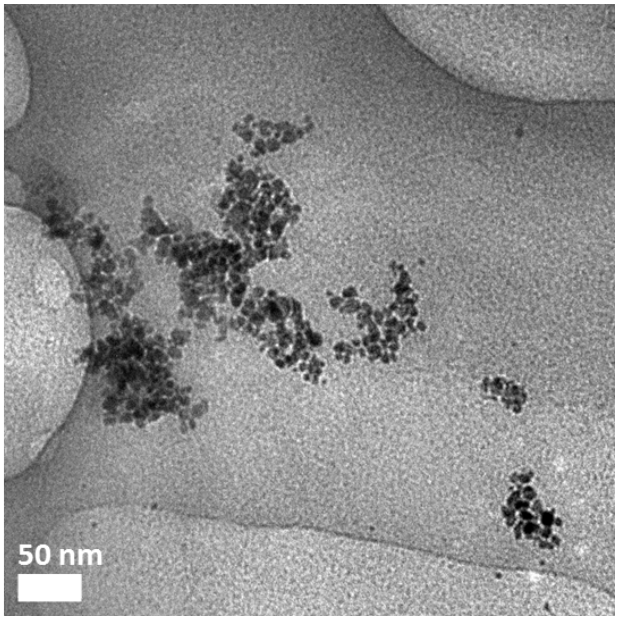


Figure S6. TEM image of leached Pd nanoparticles from filtrate obtained from heating of Pd/C in DMSO at 120°C under argon for 4 h, followed by hot filtration through two 0.45-μm Teflon syringe filters.

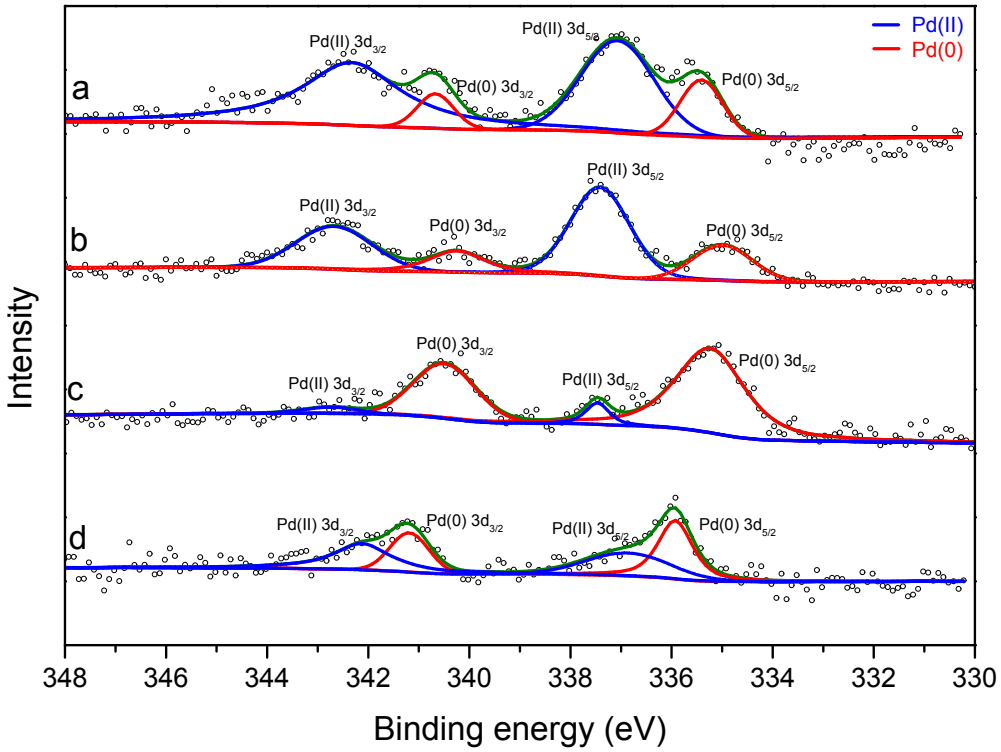
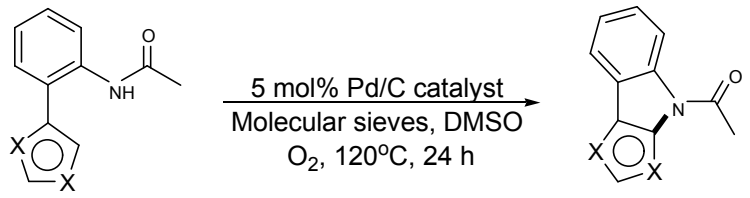
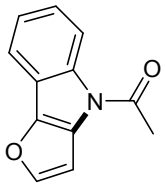


Figure S7. Pd 3d XPS spectra of (a) Pd/C, (b) Pd/CeO_2, (c) Ag-Pd/C and (d) Ag_2S@Pd/C. Approximately 88%, 69%, 9% and 60% of the Pd species in (a), (b), (c) and (d) are in the Pd(II) oxidation state, respectively.

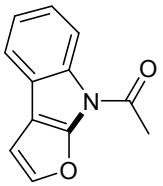
Table S1. Scope of C-N bond formation *via* C-H functionalization catalyzed by Pd/C.[a]



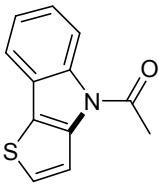
1 **2**



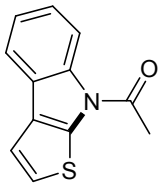
2r, 0%



2s, 0%



2t, 0%



2u, 0%

---

[a] Reaction conditions: Pd catalyst (5 mol%), 2-acetaminobiphenyl (0.2 mmol), 4 Å molecular sieves (0.040 g), DMSO (1.0 mL, purged with O_2 for 5 min), 120°C, under O_2, 24 h. [b] Isolated yield.

Heteroaromatic substrates (**1r-1u**) could not be coupled to produce the desired product. This could be due to the furan or thiophene moiety competing with the acetamide or DMSO ligand for binding to the active homogeneous Pd species. Alternatively, the presence of partial negative charges (due to resonance structures) on the furan or thiophene moiety could deter the attack of the nucleophilic N of the acetamide moiety on the furan or thiophene ring, hence inhibiting the ring closure reaction needed to produce the desired product.

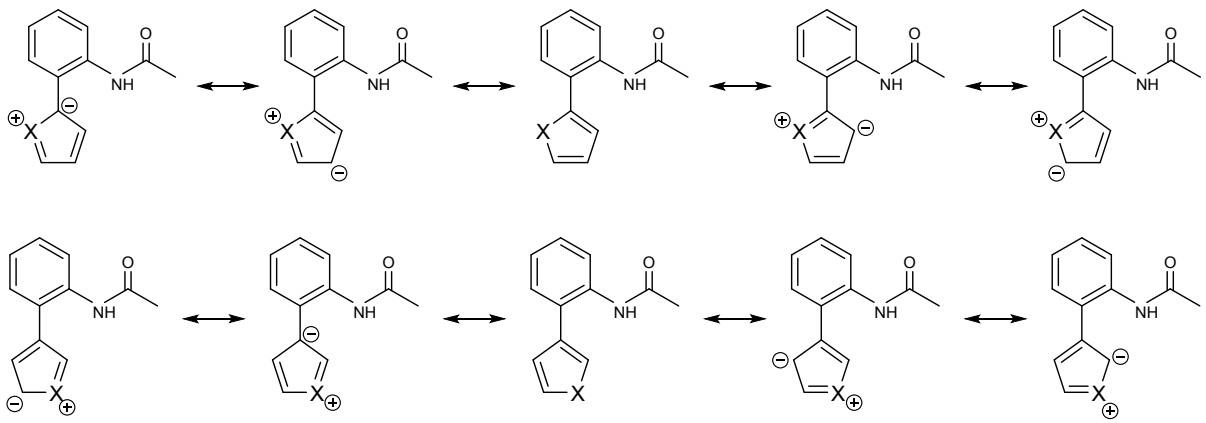
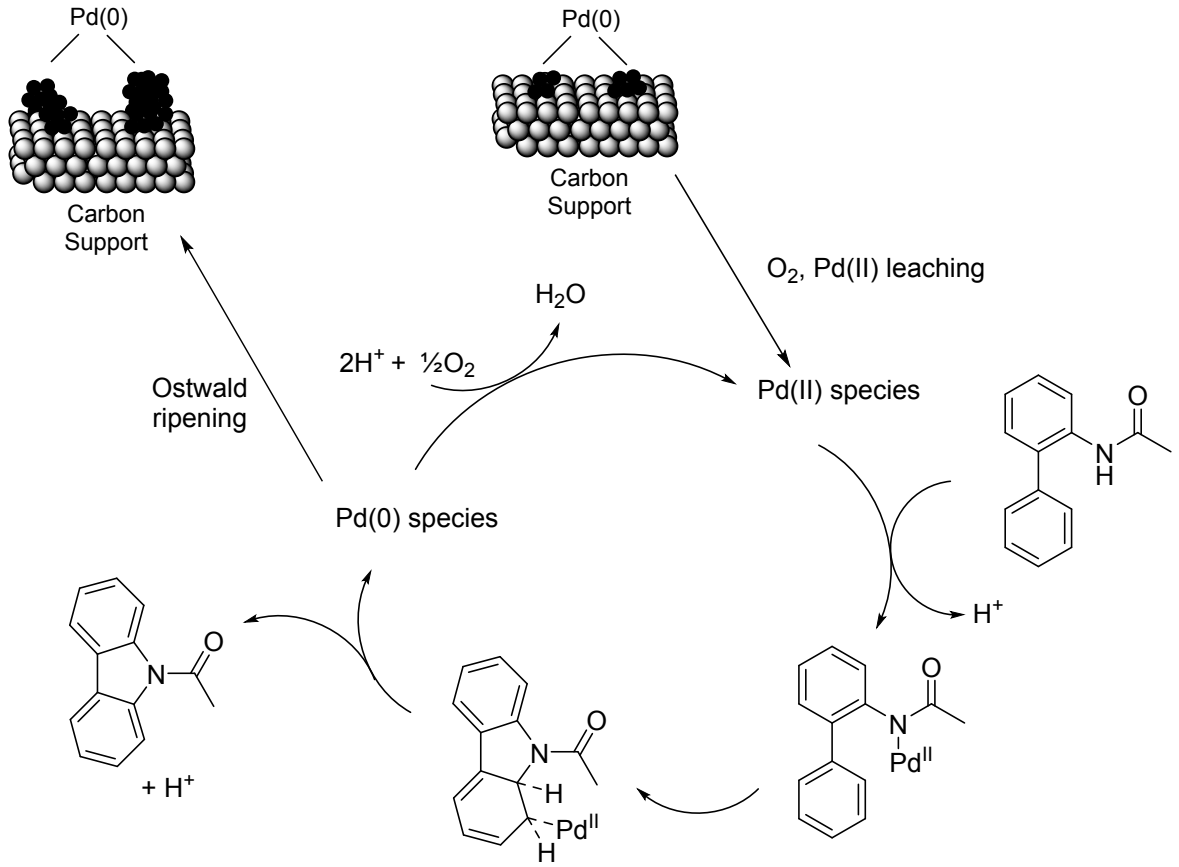


Table S2. ICP-MS analysis of the filtrate attained from the heating of Pd-based nanomaterials in the specified solvent at 120°C under O_2 for 4 h, followed by hot filtration through two 0.45-μm Teflon syringe filters.[a]

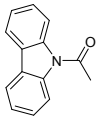
Entry	Pd nanomaterial	Solvent	% of Pd leached
1	Pd/C	DMSO	42
2	Pd/C	DMF	5
3	Pd/C	DMA	5
4	Pd/C	1,4-Dioxane	< 1
5	Pd/C	Toluene	< 1
6[b]	Pd/C	DMSO	8
7	Ag-Pd/C	DMSO	< 1
8	Ag@Pd/C	DMSO	1
9	Ag_2S@Pd/C	DMSO	2
10	Pd/CeO_2	DMSO	25
11	Pd/TiO_2	DMSO	22
12	Pd/Al_2O_3	DMSO	23
13	Pd/SiO_2	DMSO	12

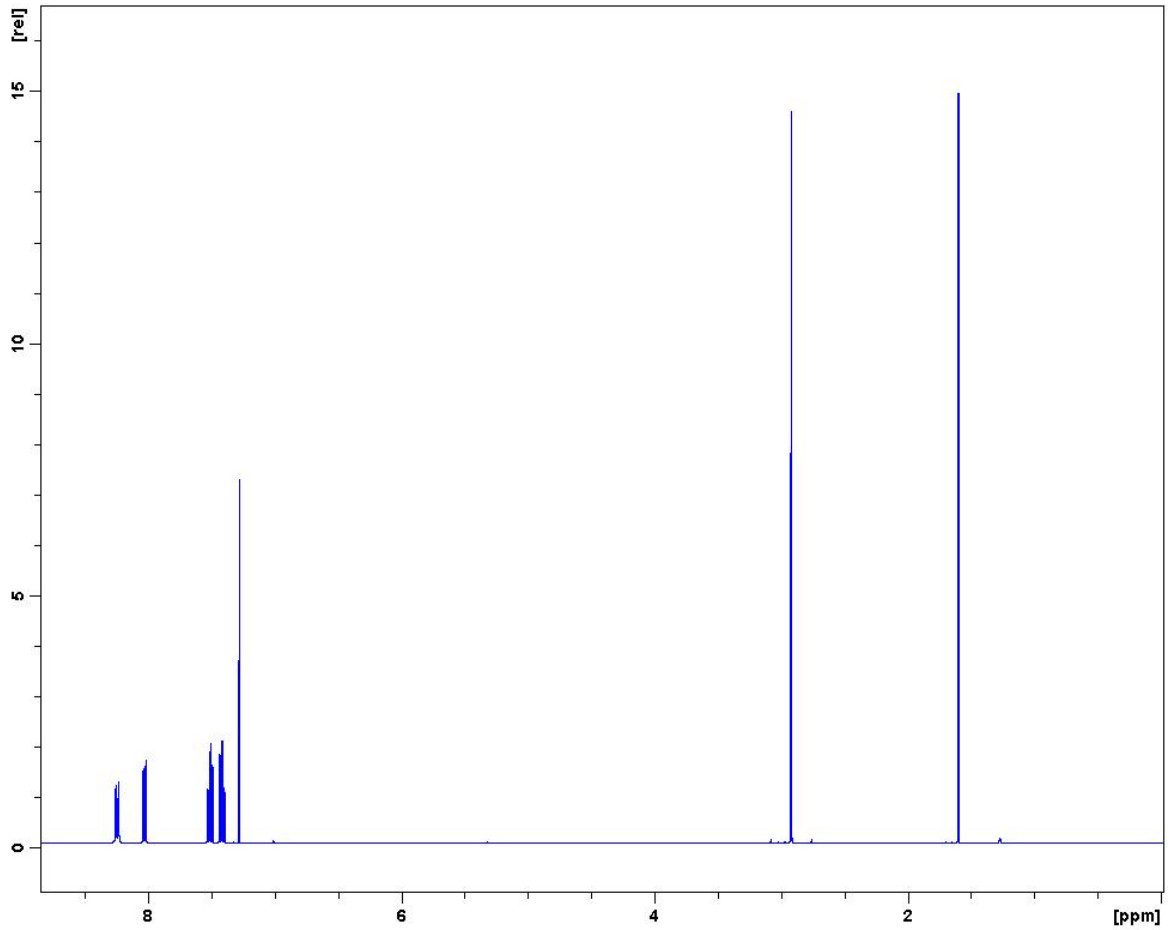
[a] Pd-based nanomaterials (0.00106 g of Pd) and molecular sieves (0.080 g) were heated in the solvent (1 mL) at 120°C under O_2 for 4 h. The mixture was filtered hot through two 0.45-μm Teflon syringe filters. ICP-MS analysis was performed on the filtrate to determine the amount of Pd that has leached into the solution. [b] Heated at 120°C under argon for 4 h.

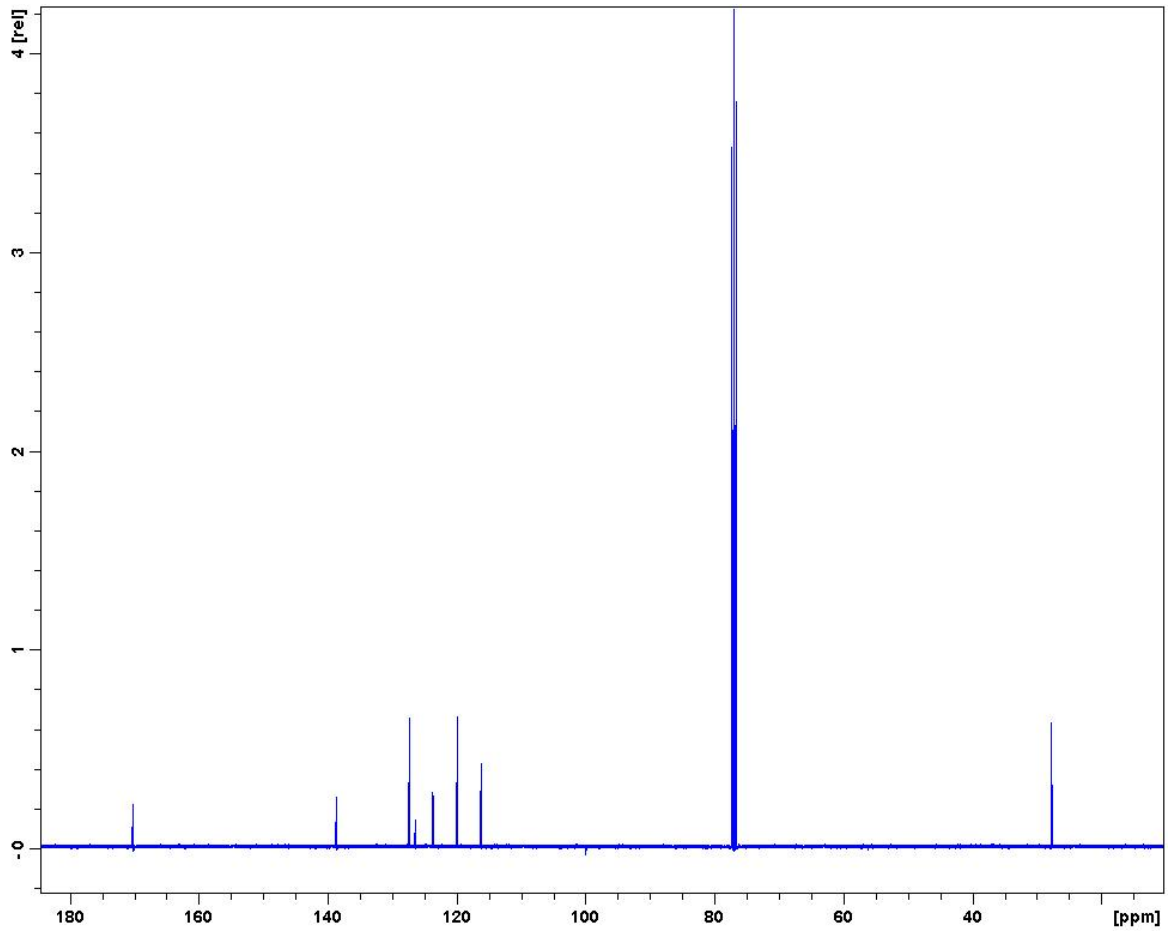
Scheme S1. Proposed mechanism for C-N bond formation *via* C-H functionalization catalyzed by supported Pd nanoparticles.



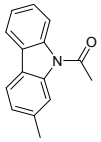
^{1}H and ^{13}C NMR spectra of 2a

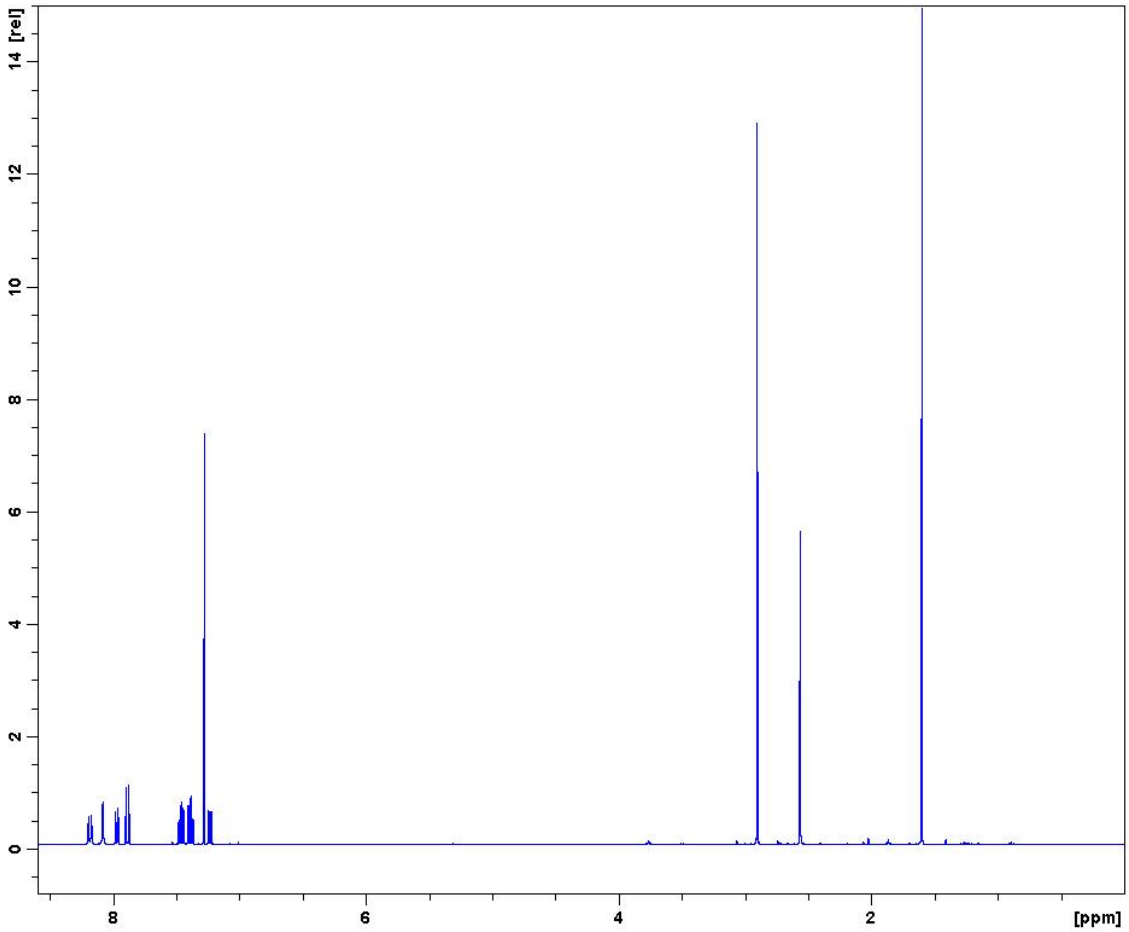


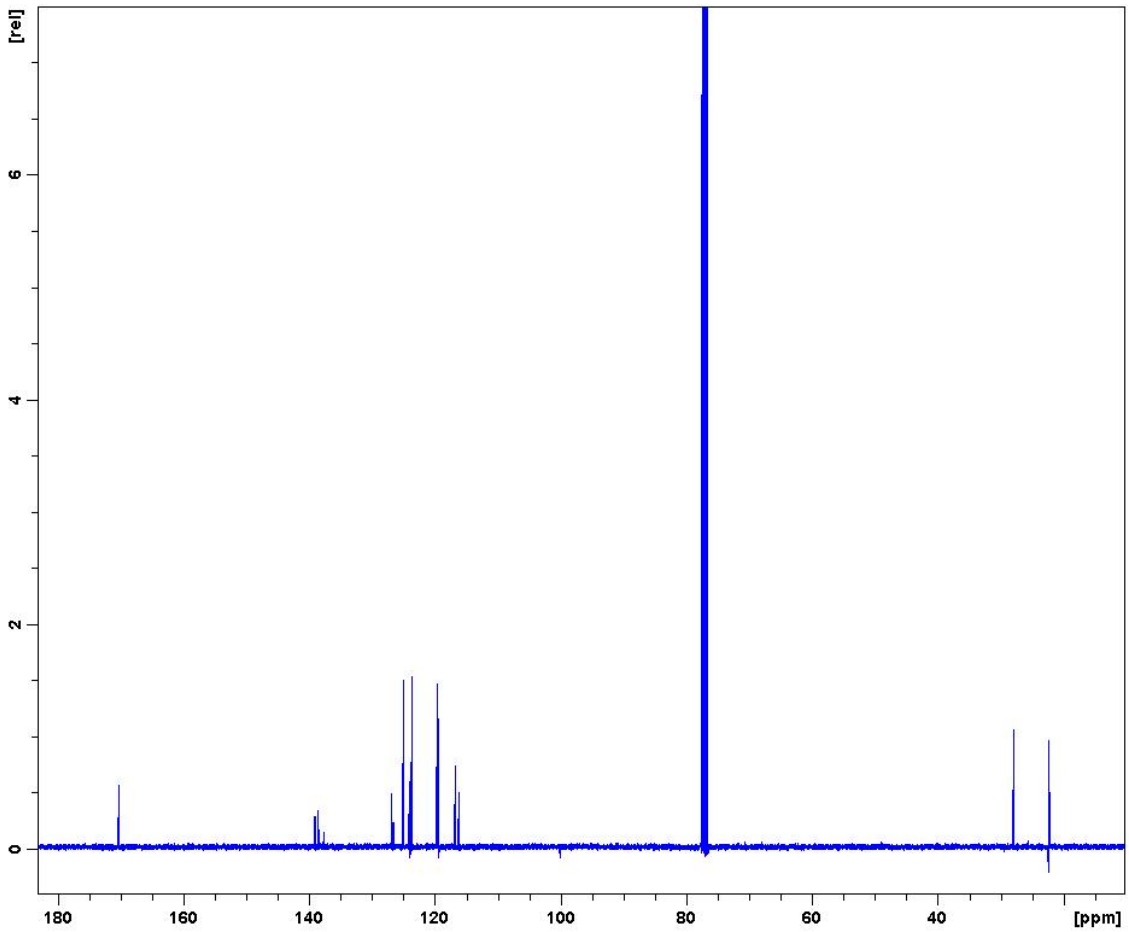




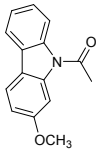
^{1}H and ^{13}C NMR spectra of 2b

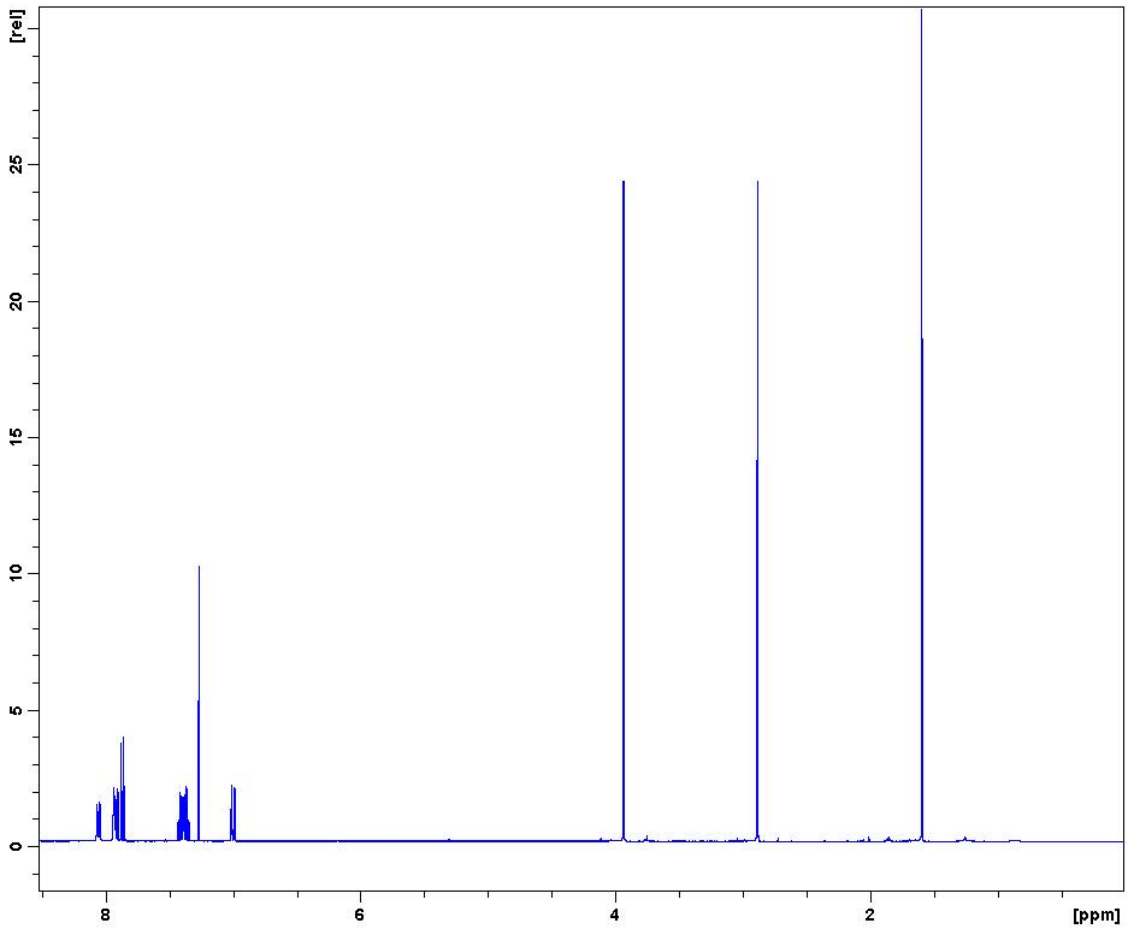


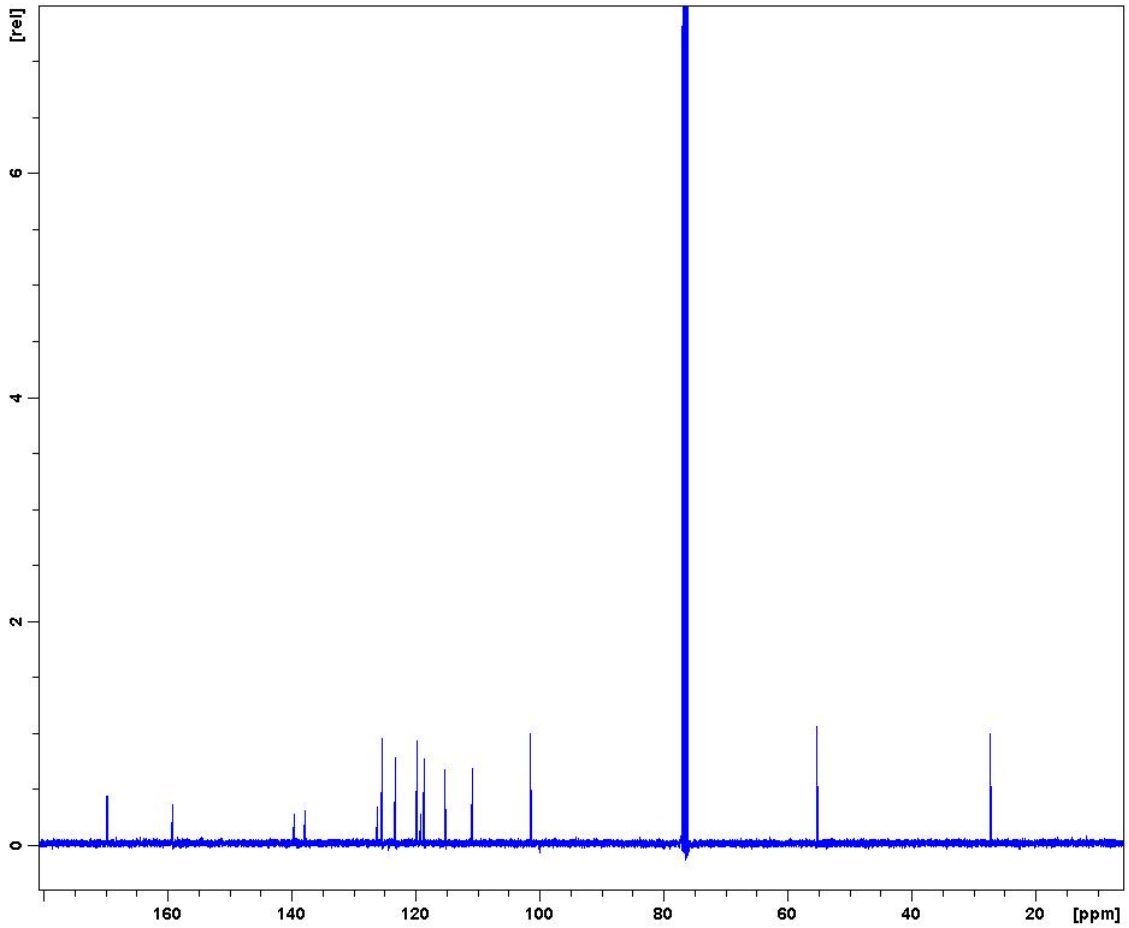




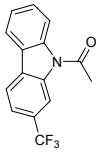
^{1}H and ^{13}C NMR spectra of 2c

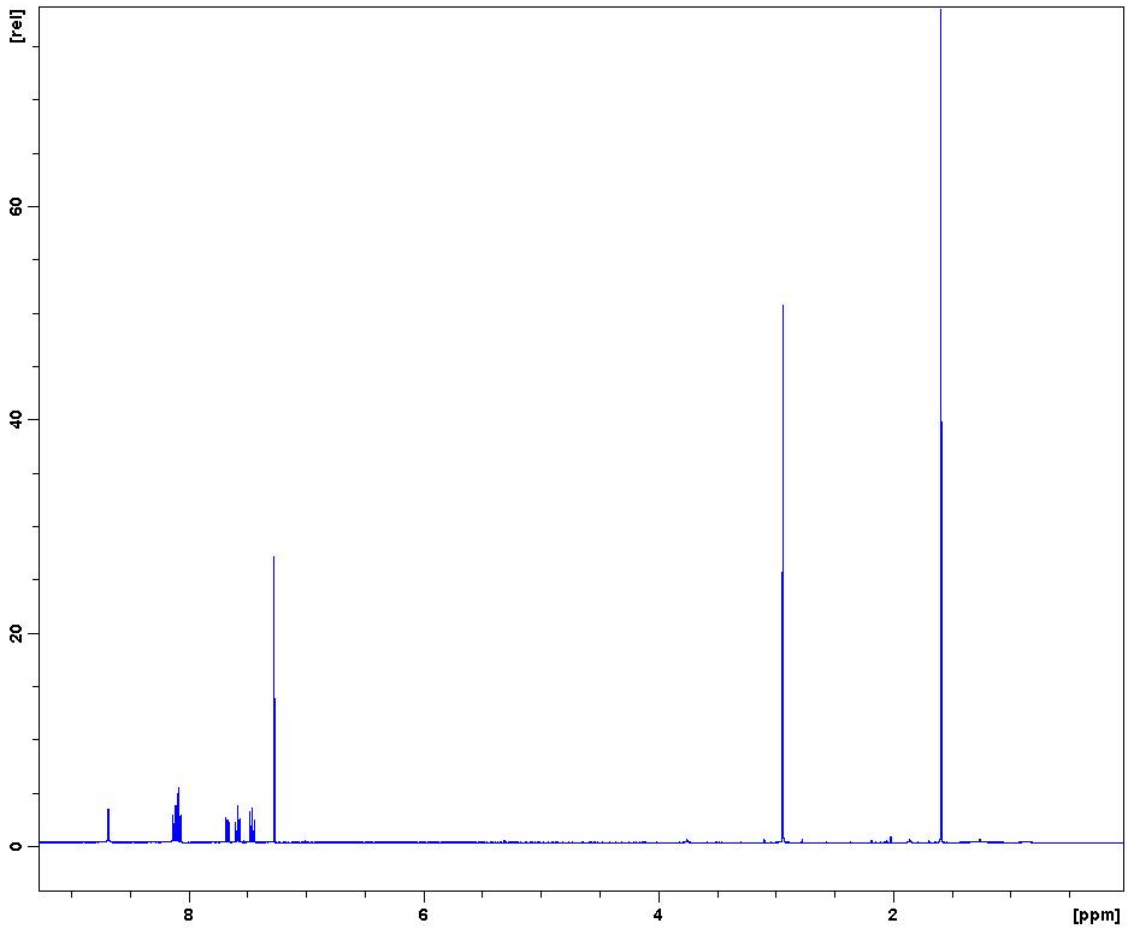


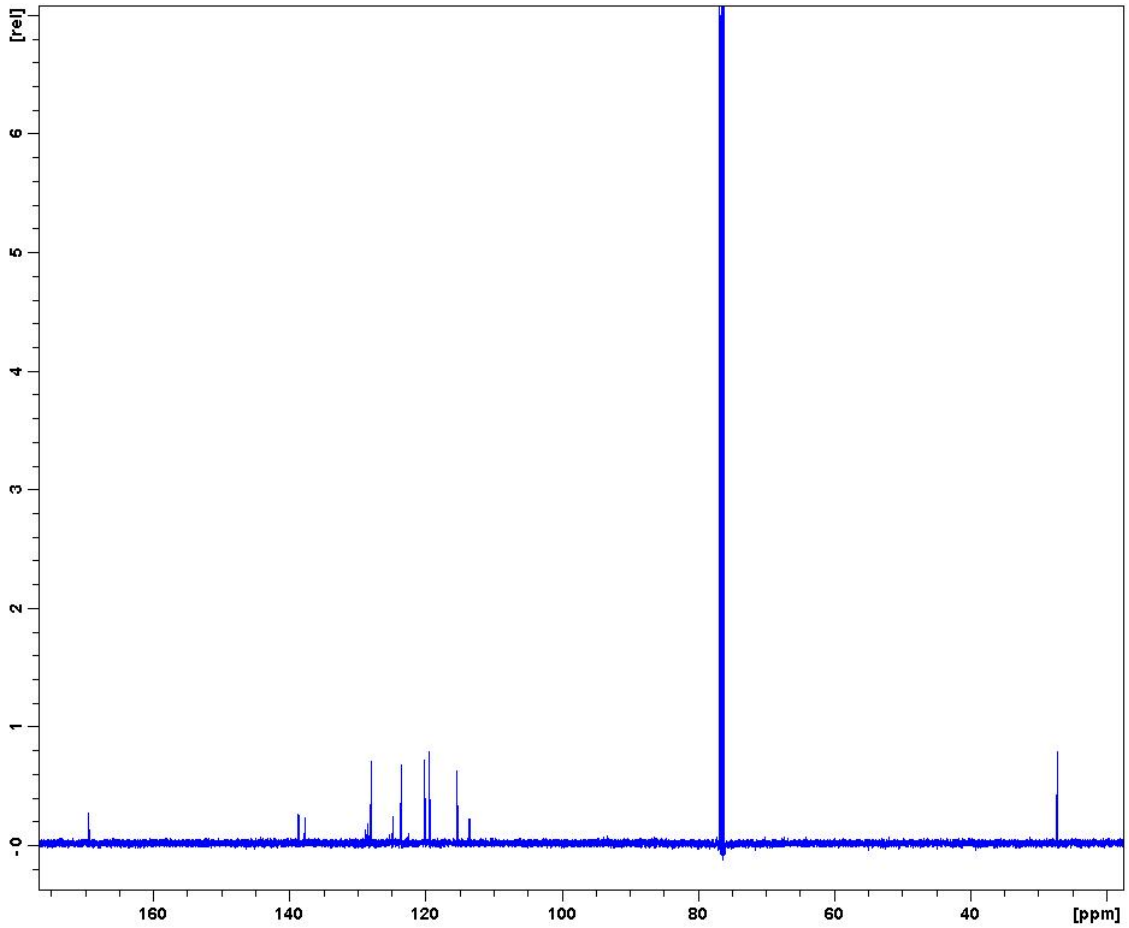




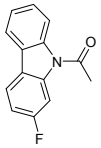
^{1}H and ^{13}C NMR spectra of 2d

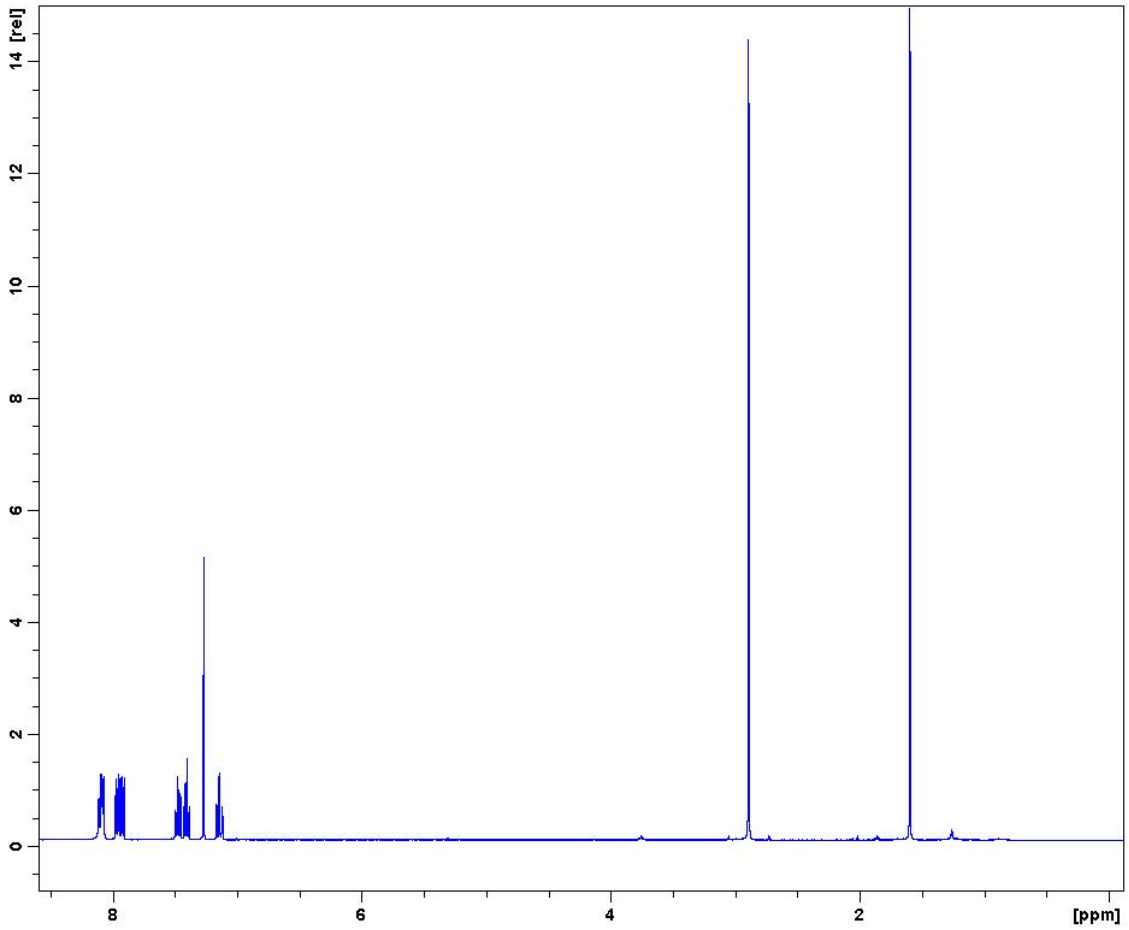


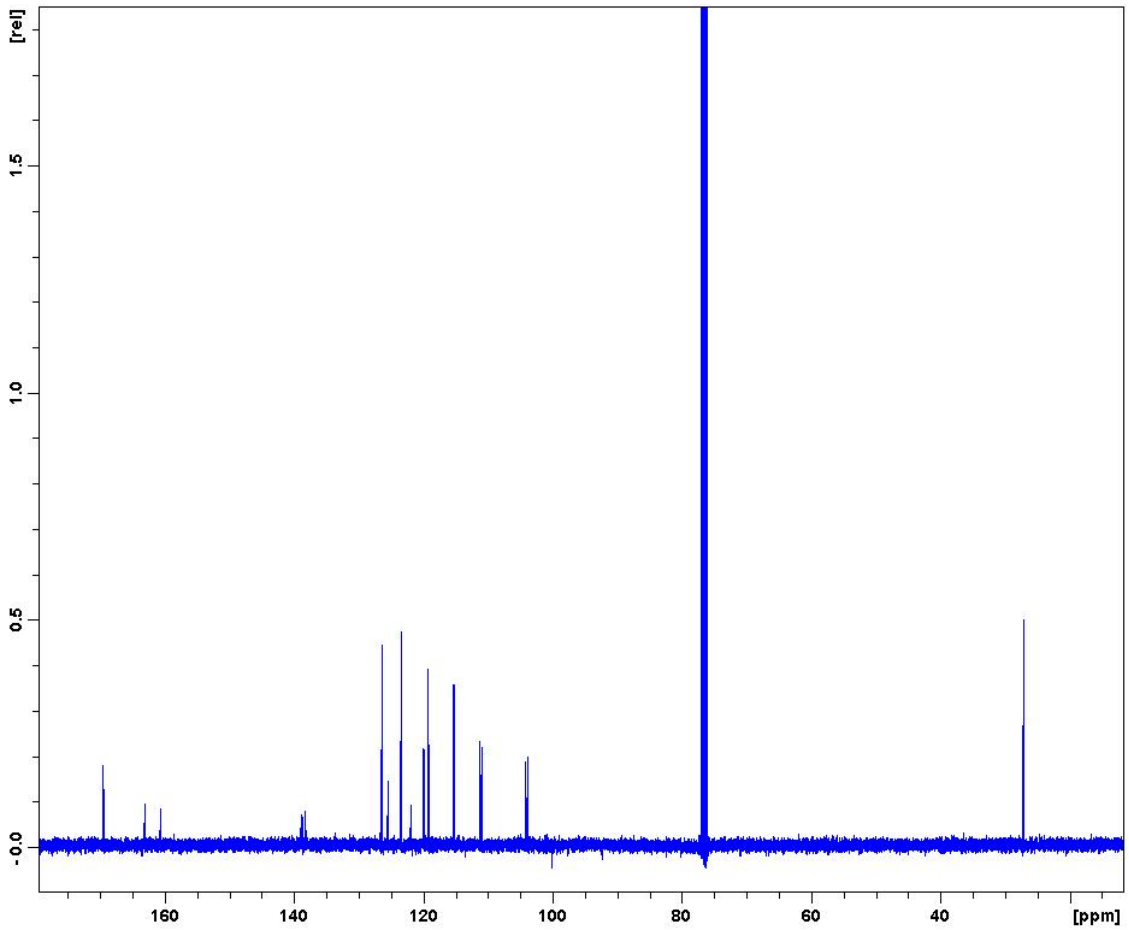




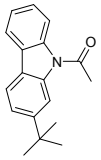
^{1}H and ^{13}C NMR spectra of 2e

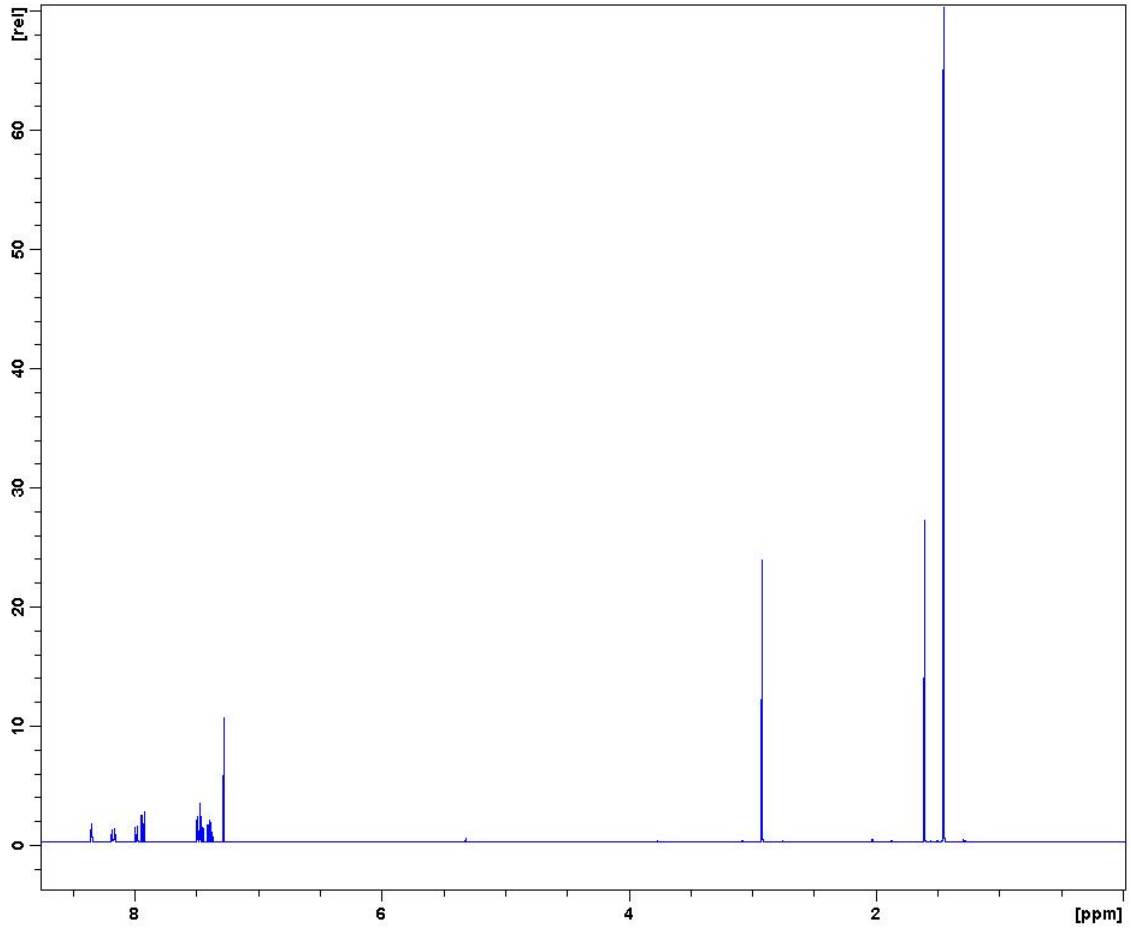


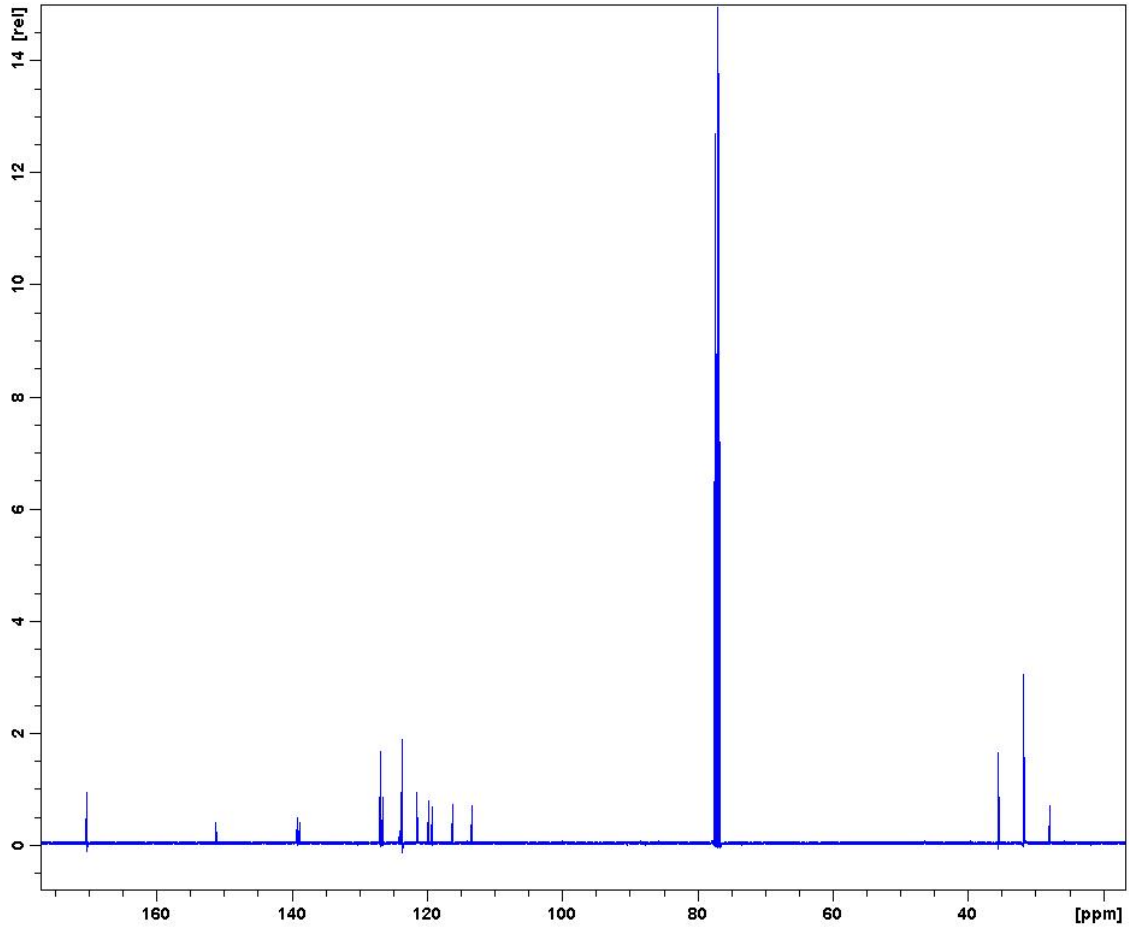




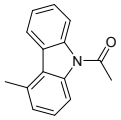
^{1}H and ^{13}C NMR spectra of 2f

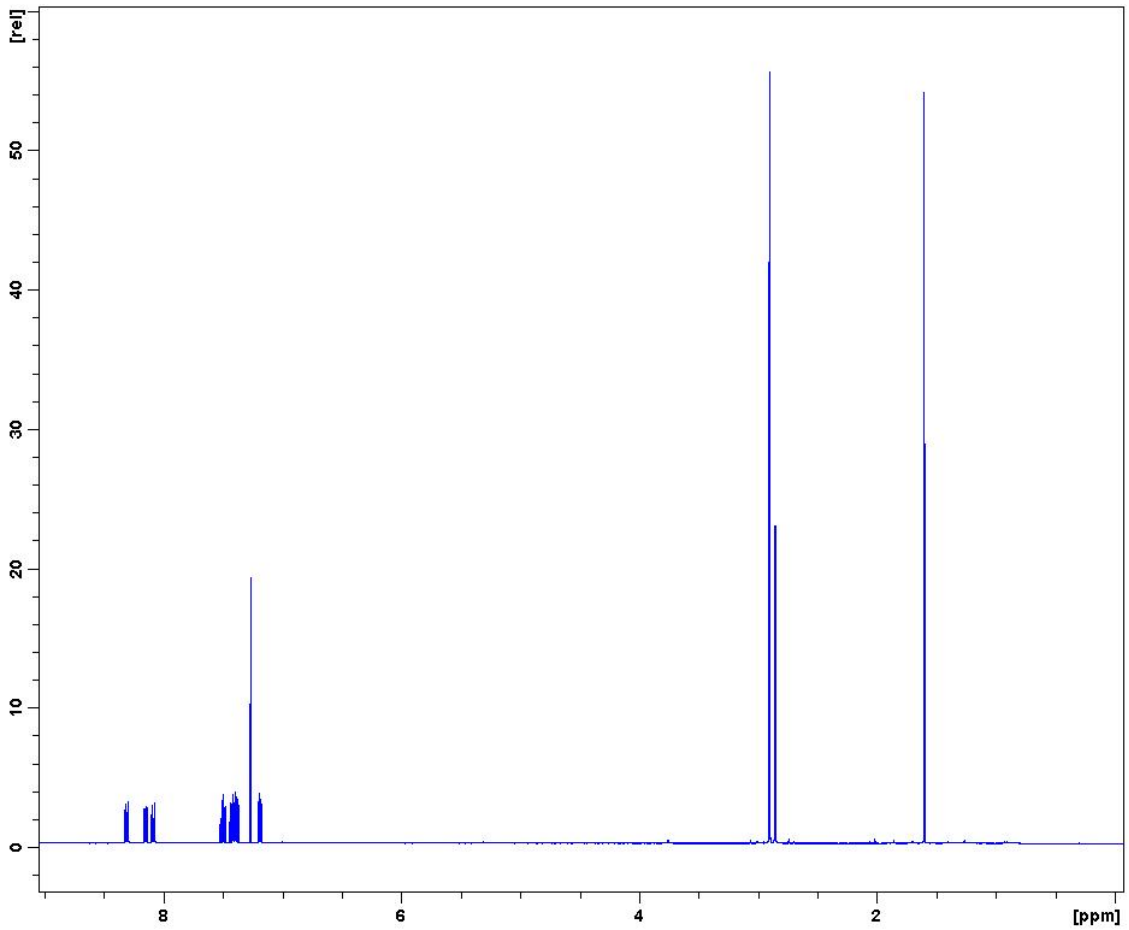


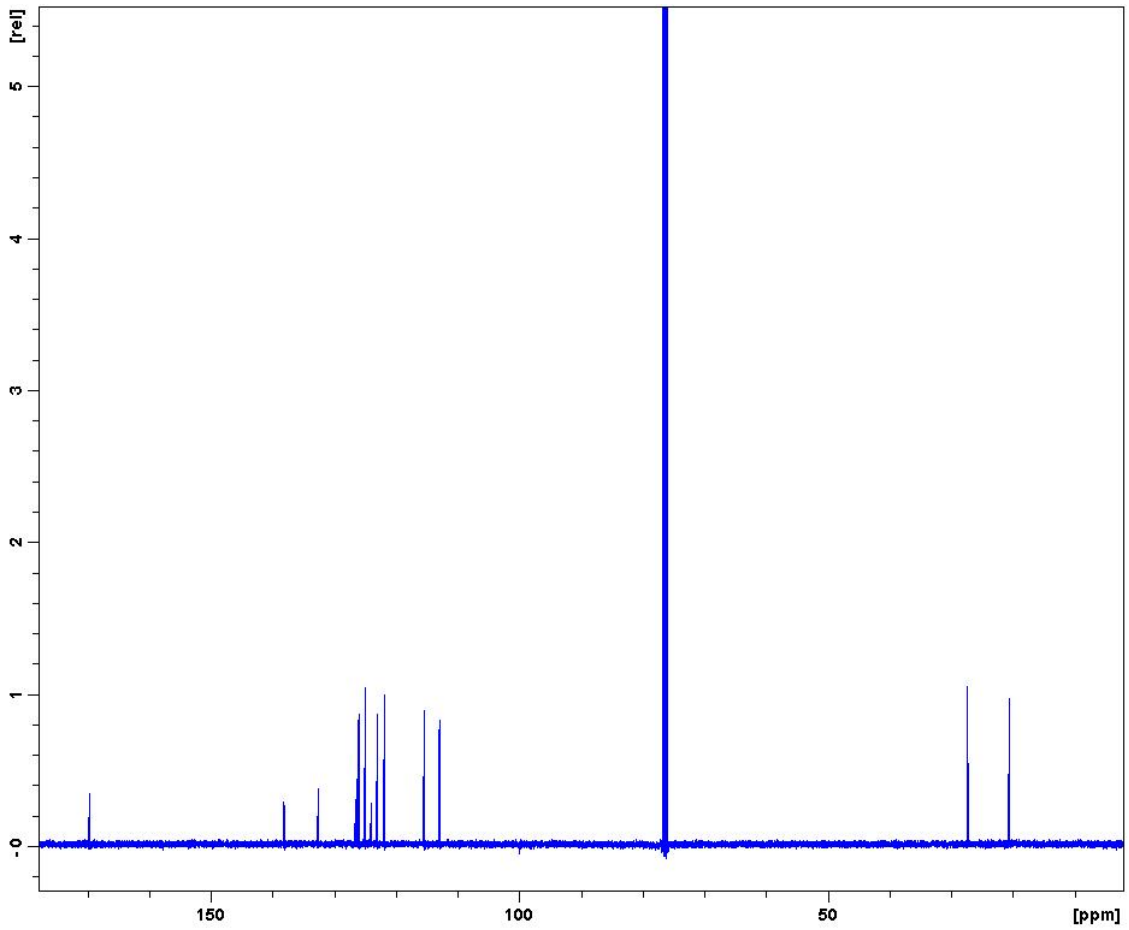




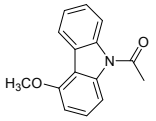
^{1}H and ^{13}C NMR spectra of 2g

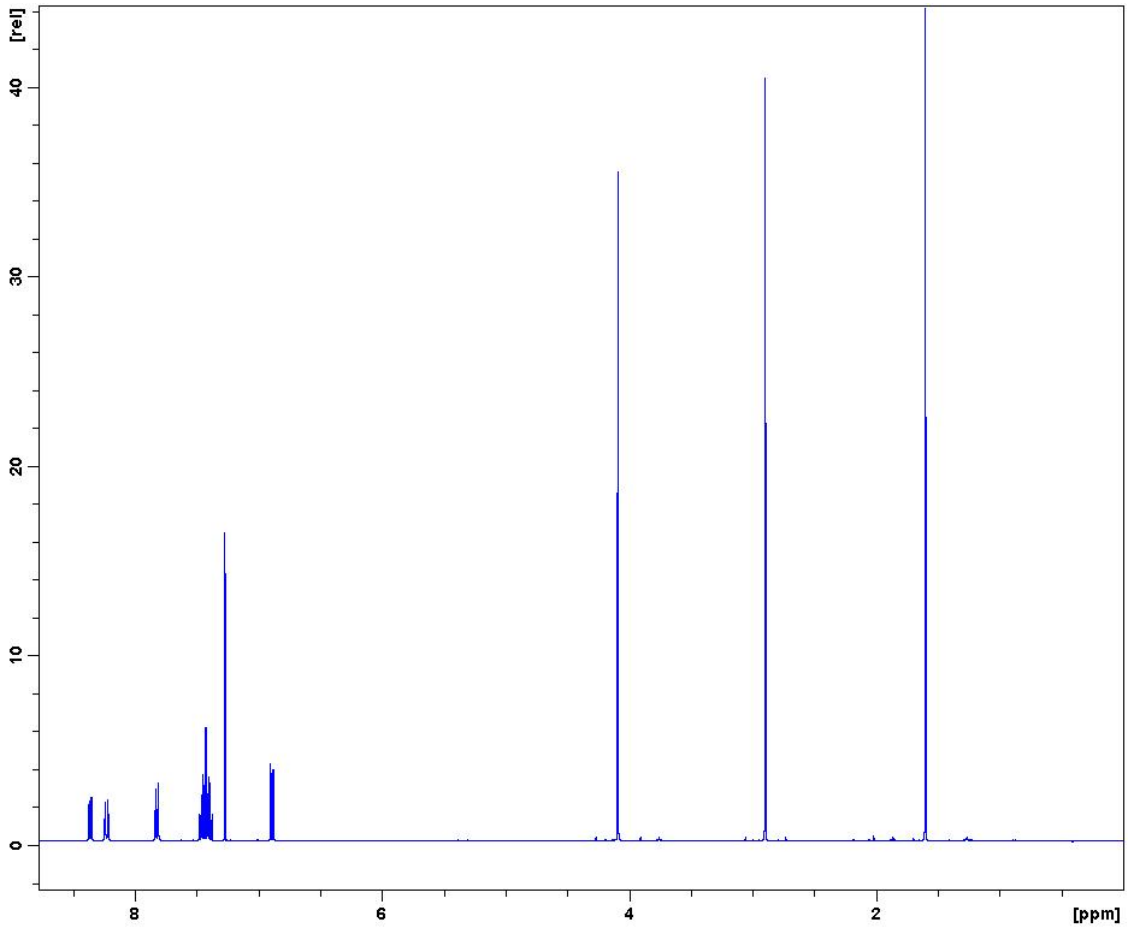


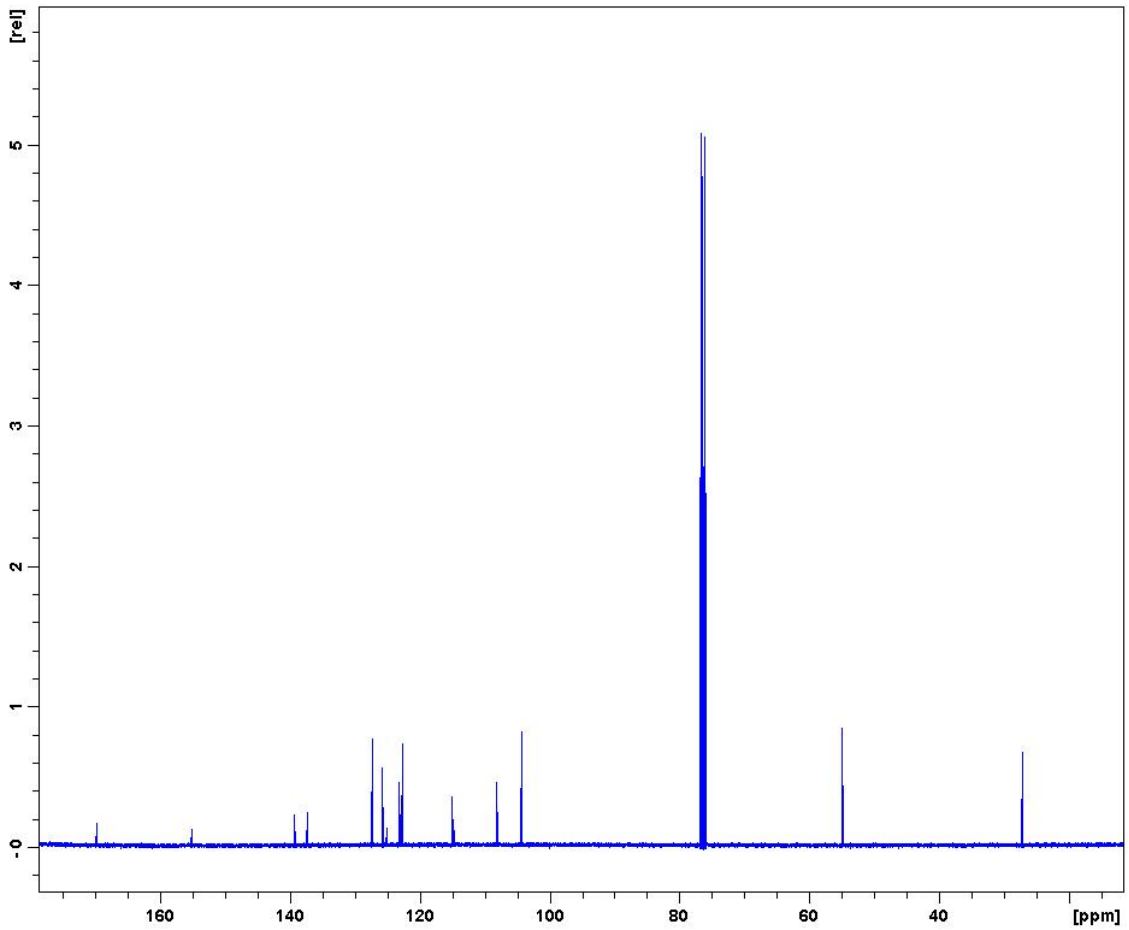




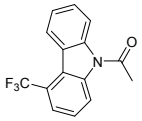
^{1}H and ^{13}C NMR spectra of 2h

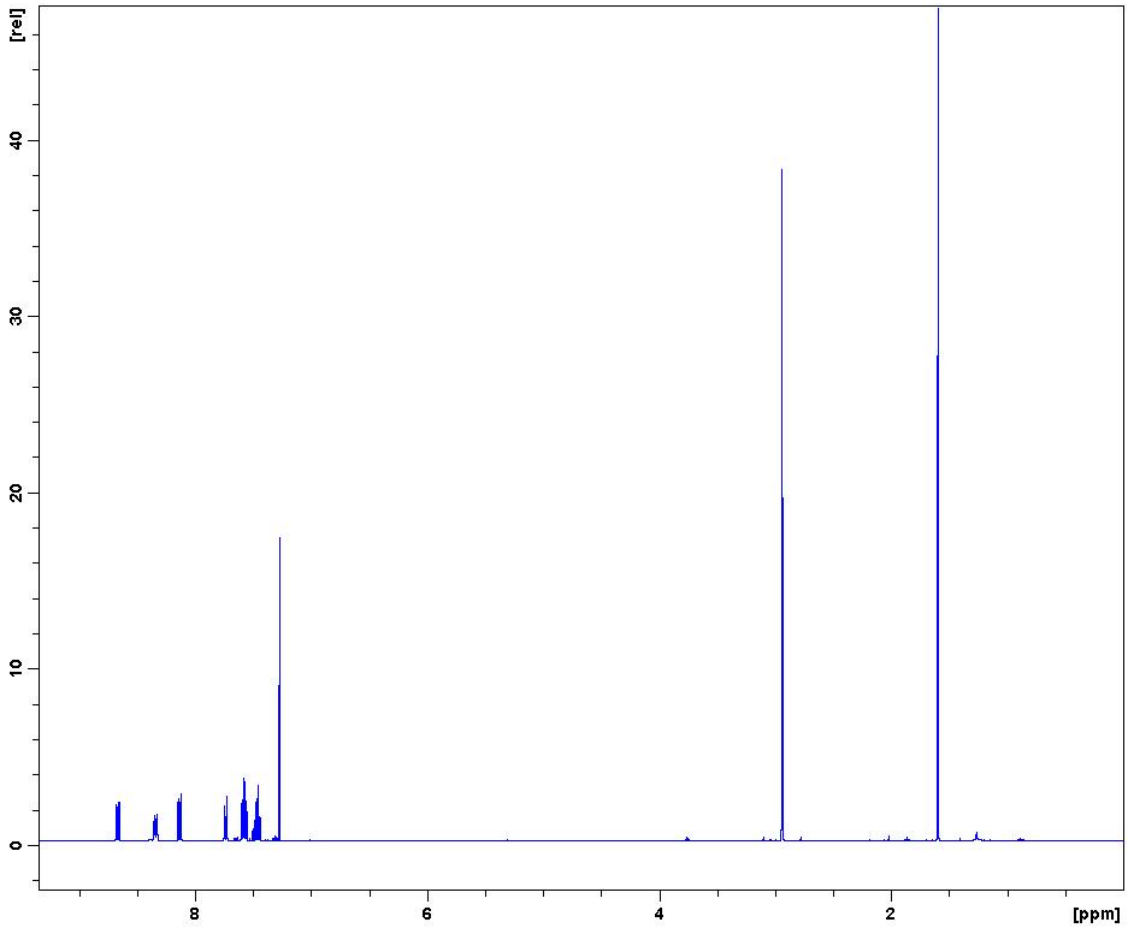


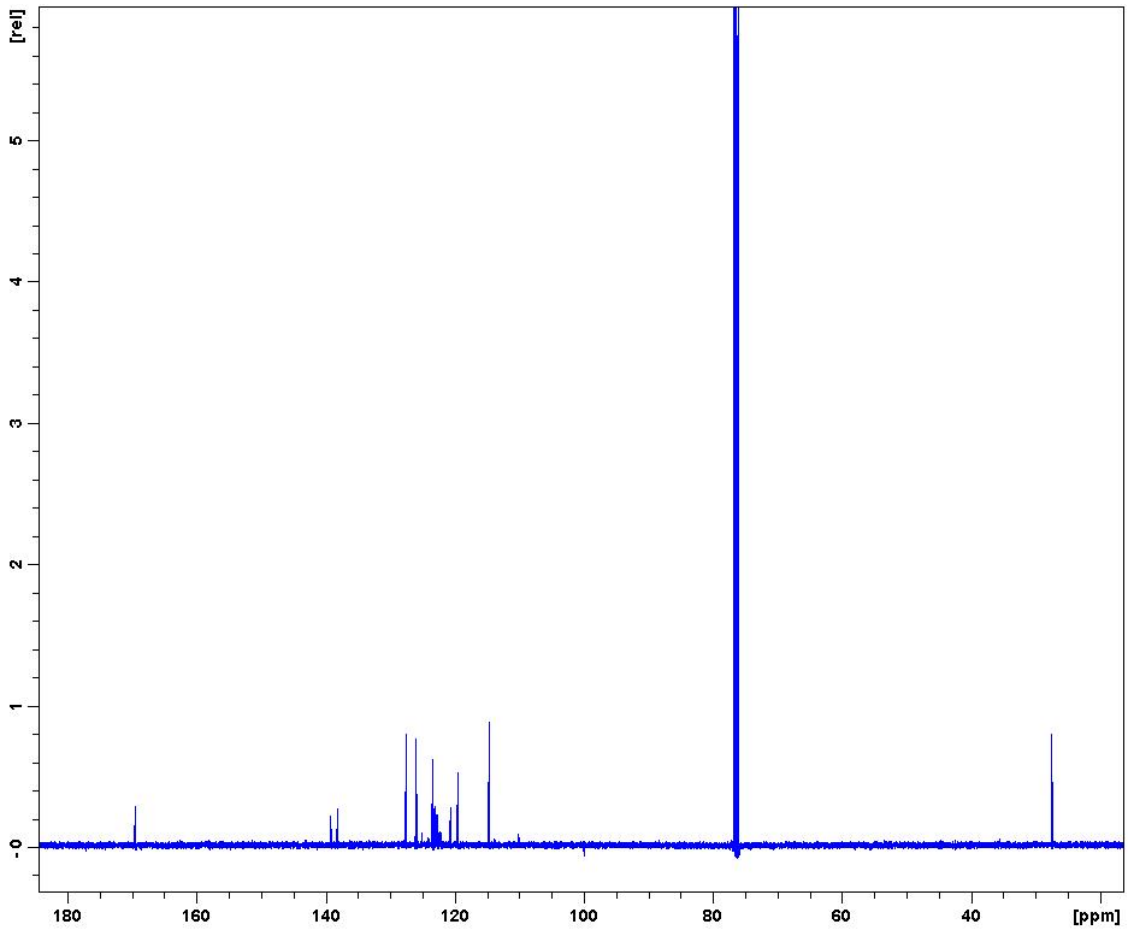




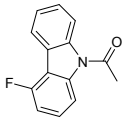
^{1}H and ^{13}C NMR spectra of 2i

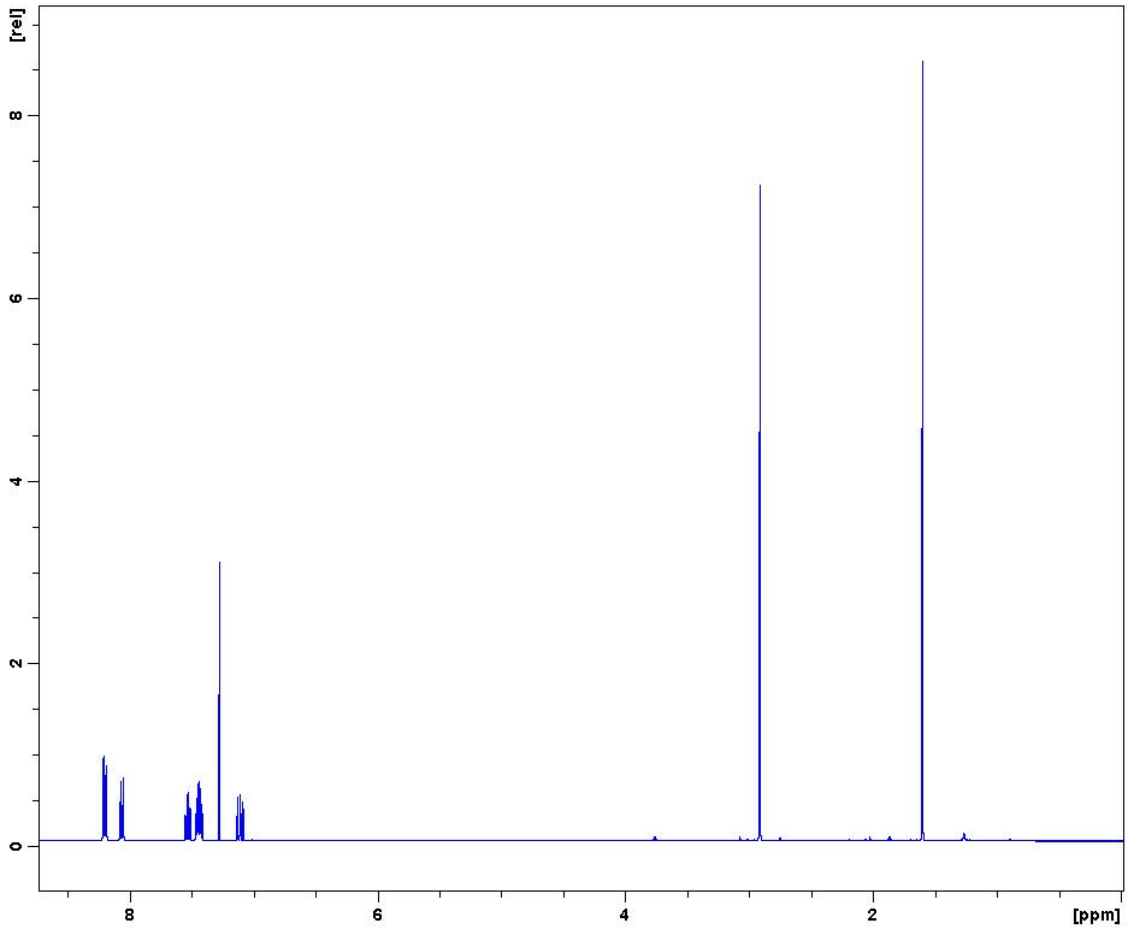


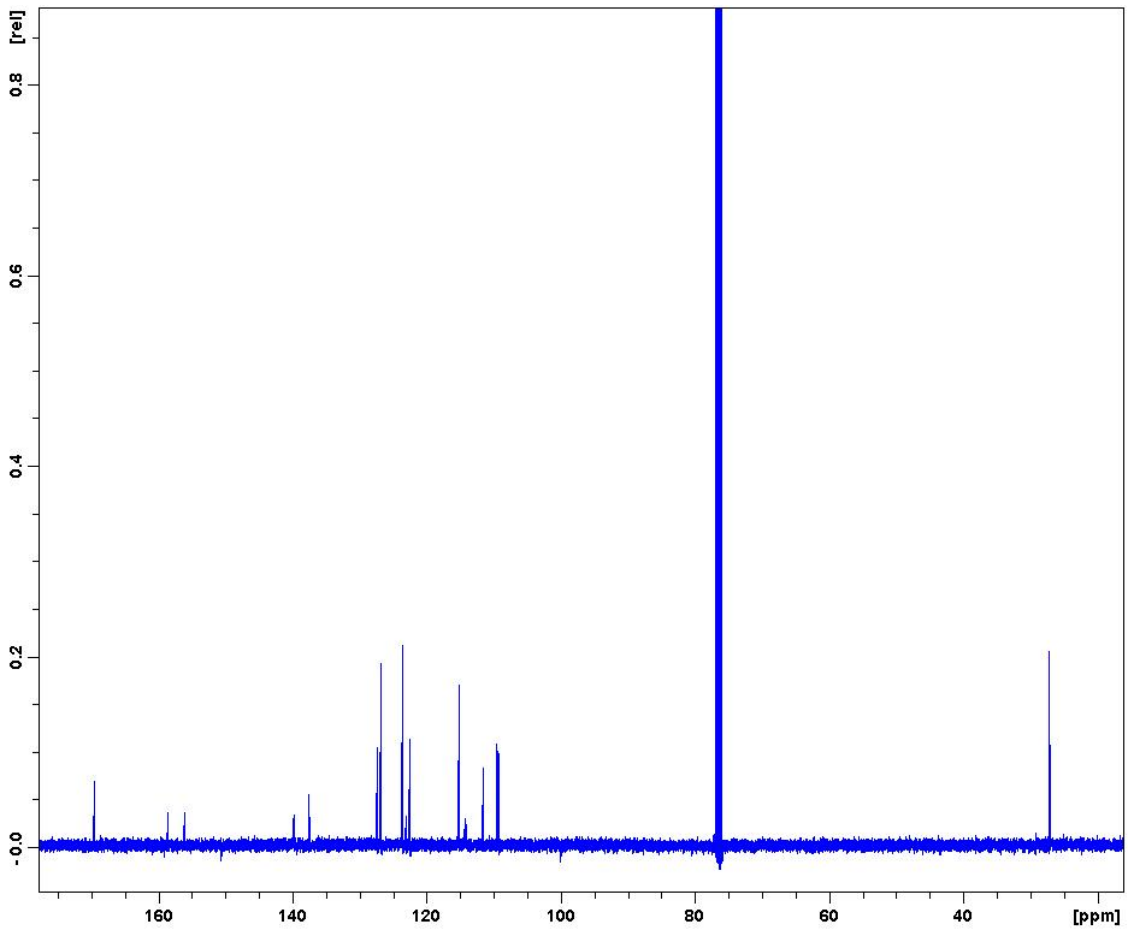




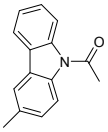
^{1}H and ^{13}C NMR spectra of 2j

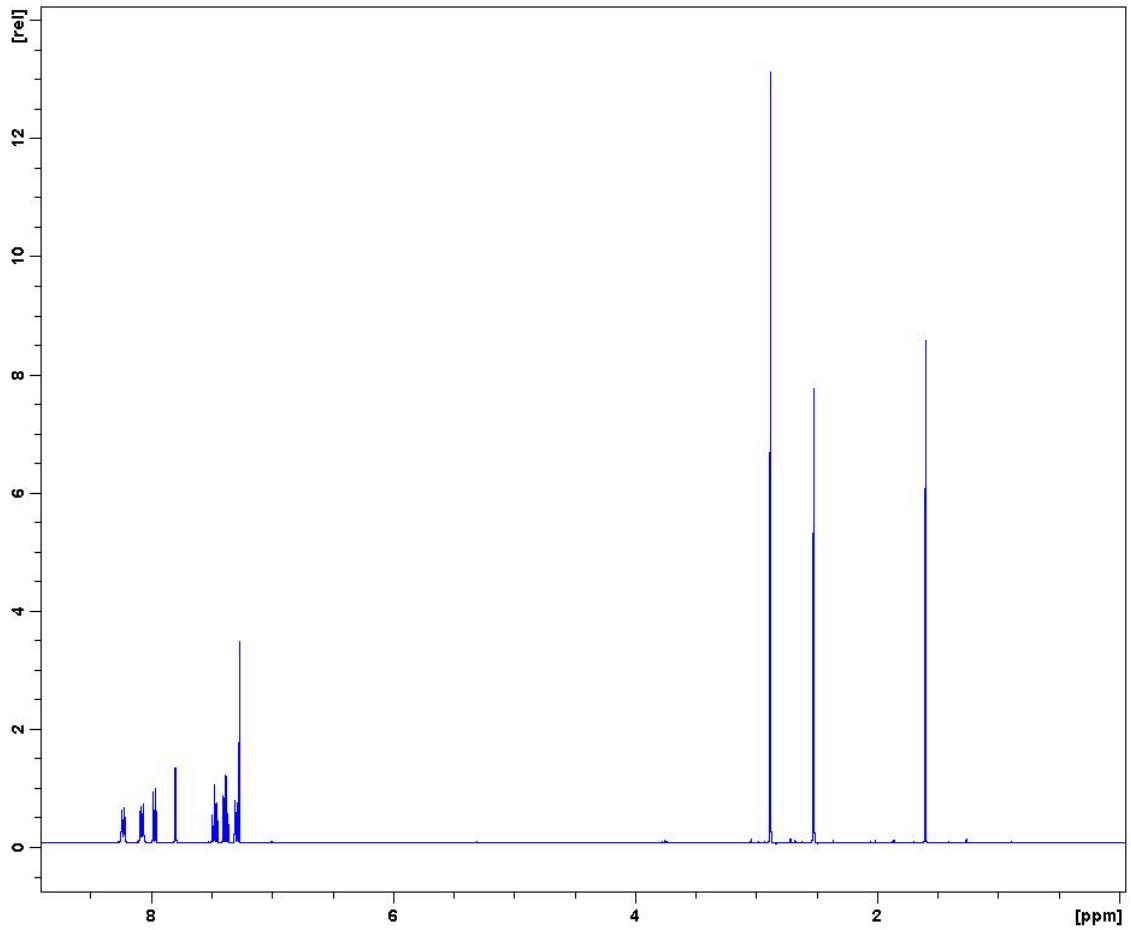


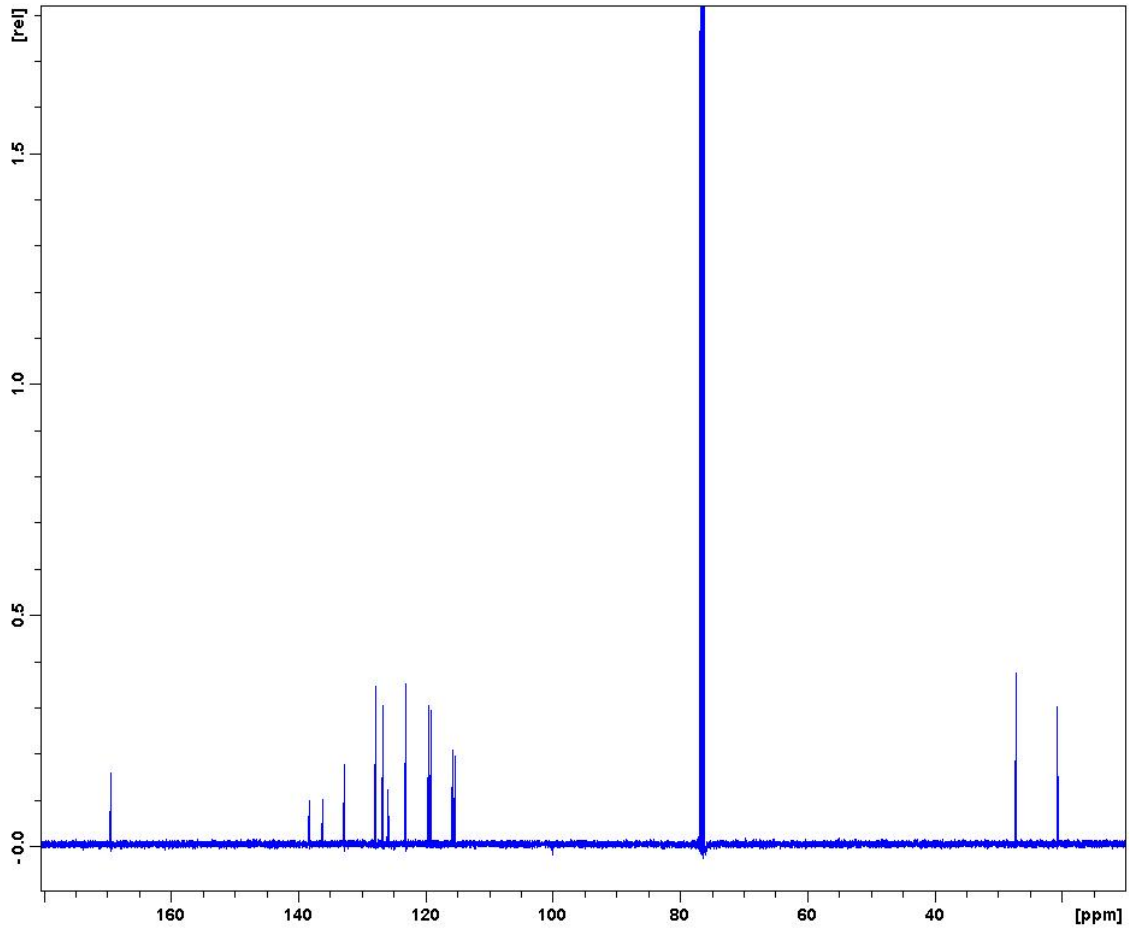




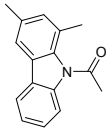
^{1}H and ^{13}C NMR spectra of 2k or 2n

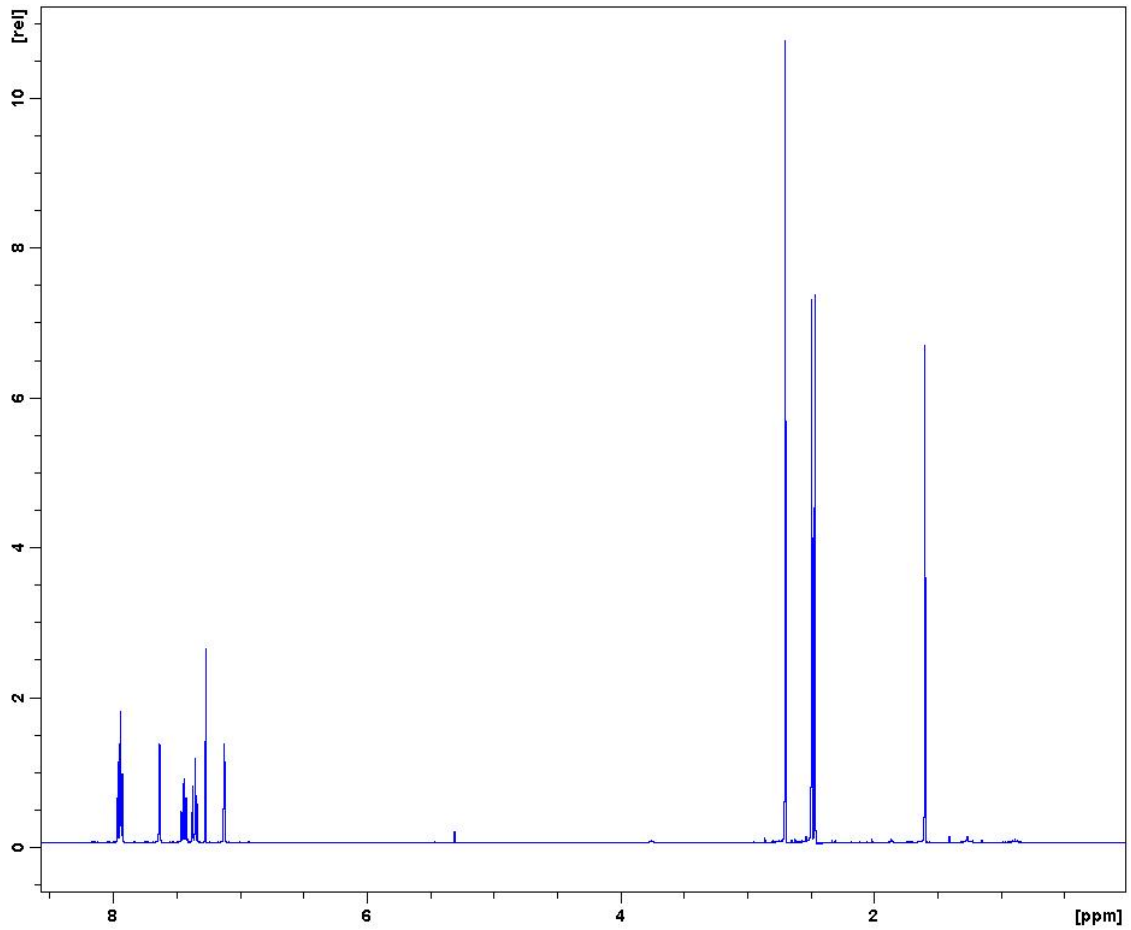


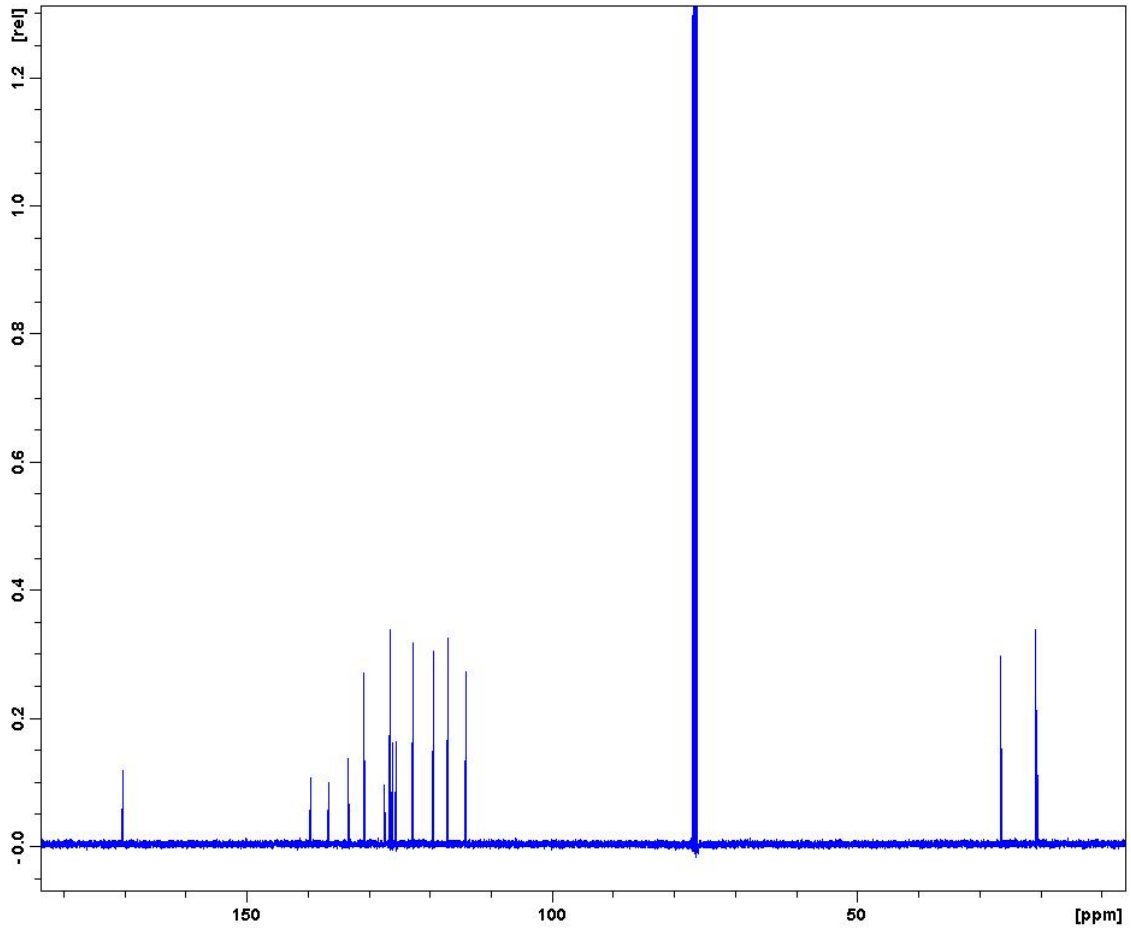




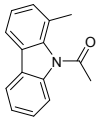
^{1}H and ^{13}C NMR spectra of 2l

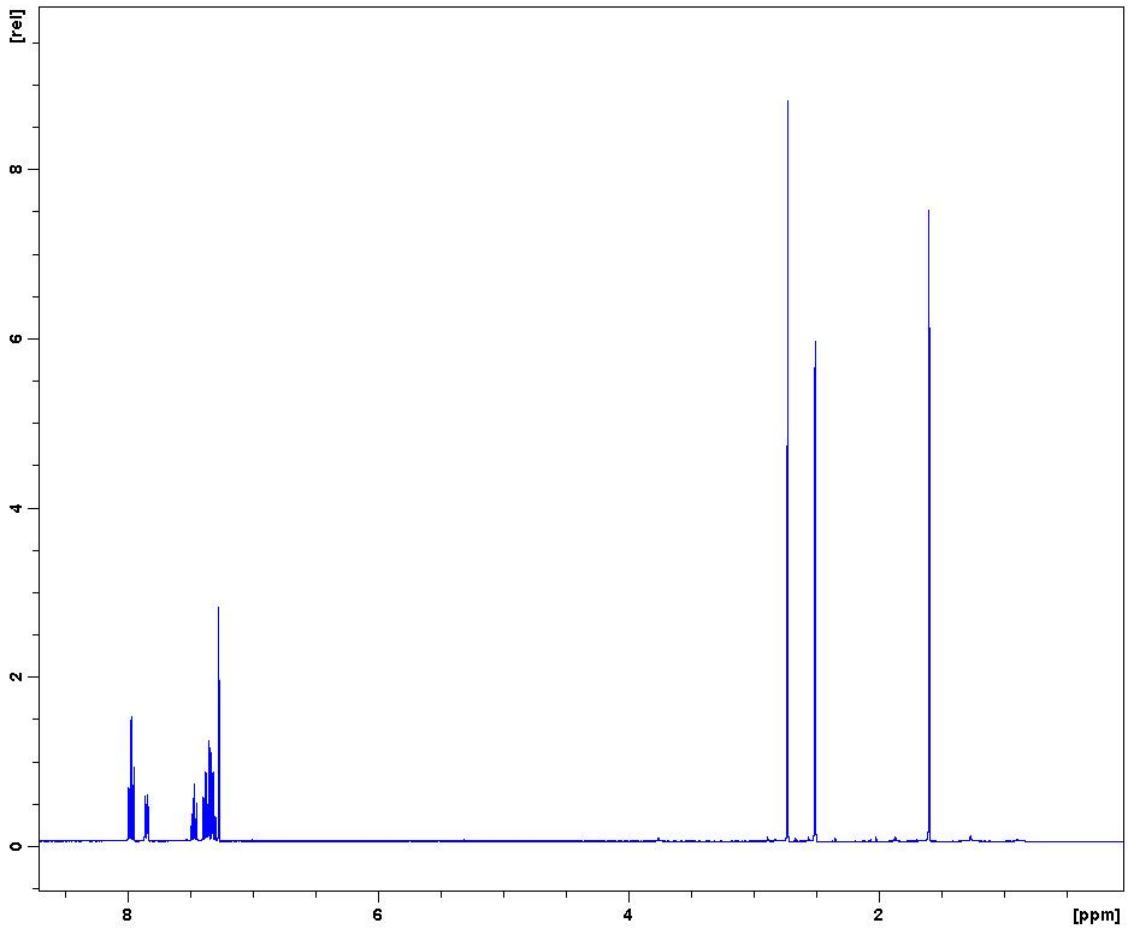


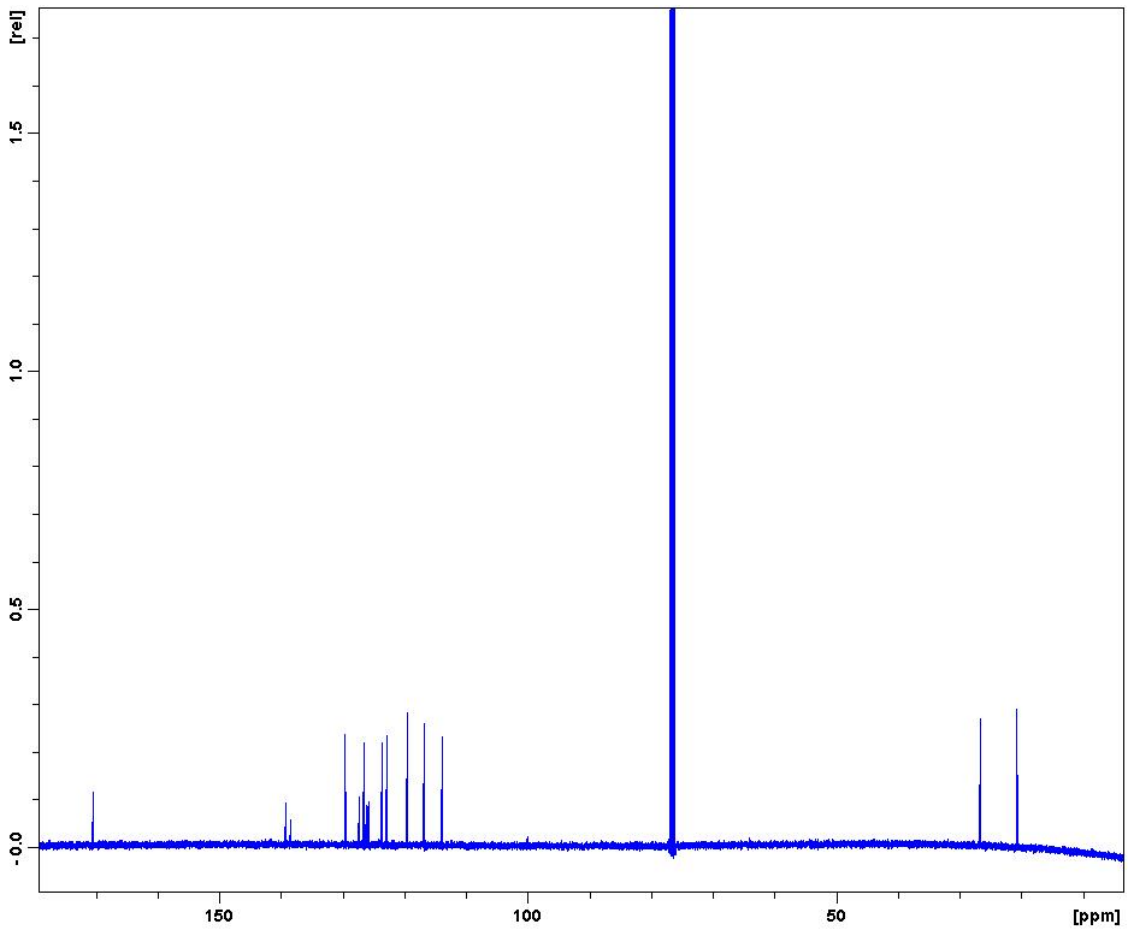




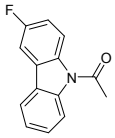
^{1}H and ^{13}C NMR spectra of 2m

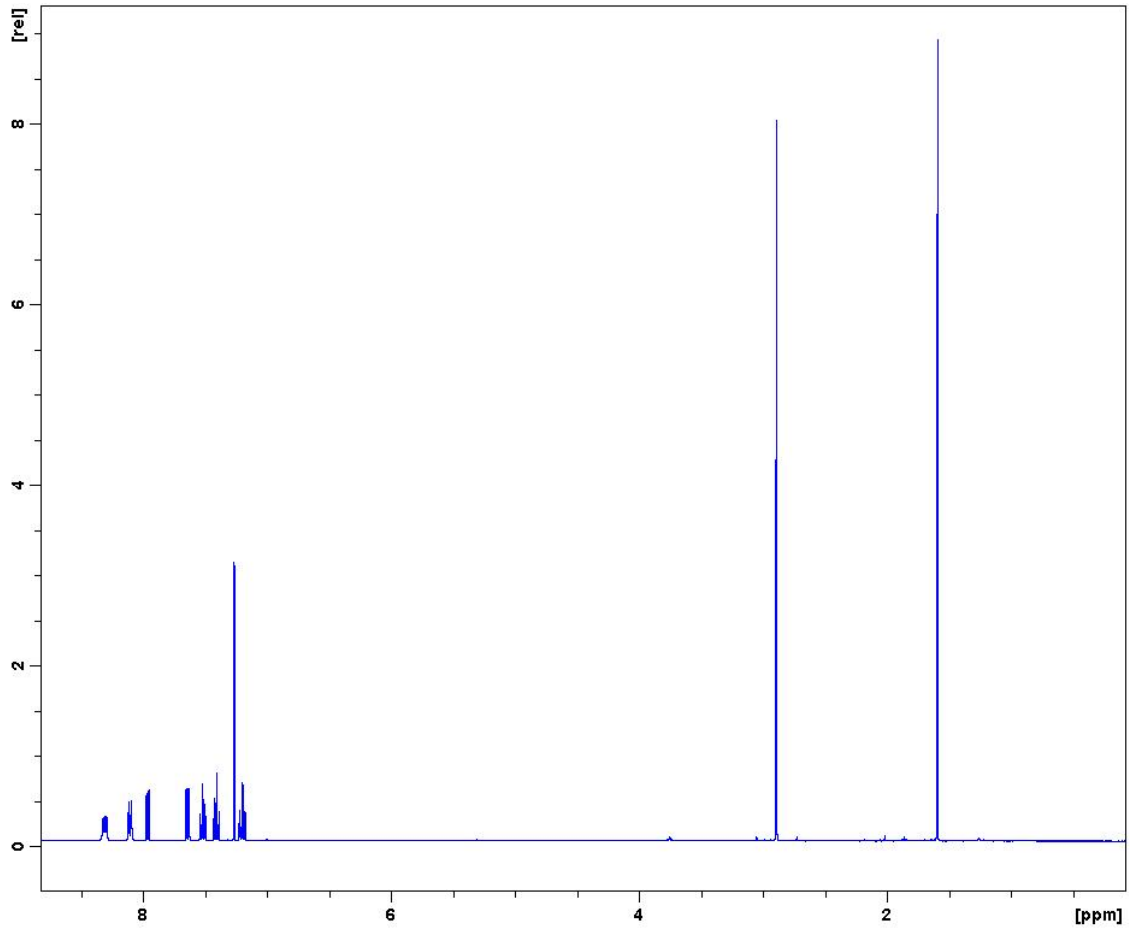


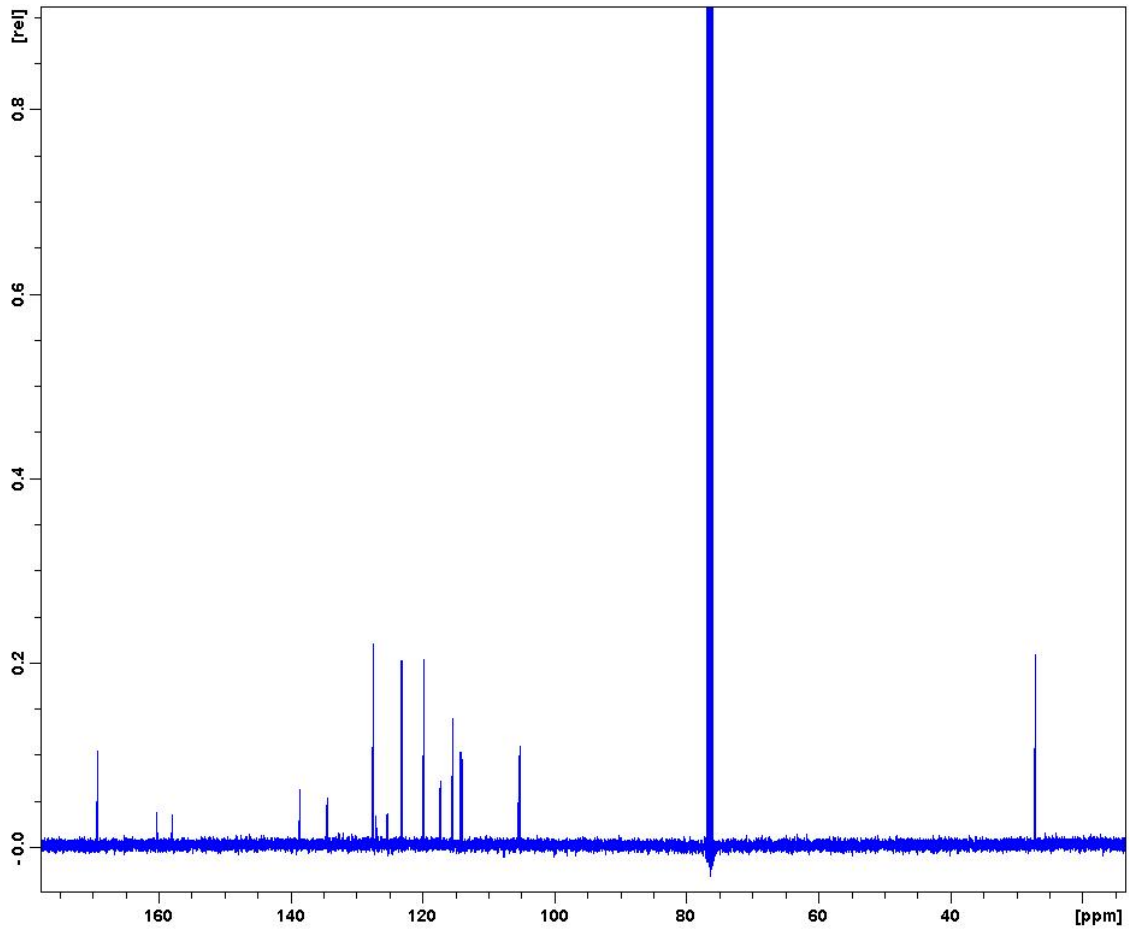




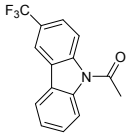
^{1}H and ^{13}C NMR spectra of 2o

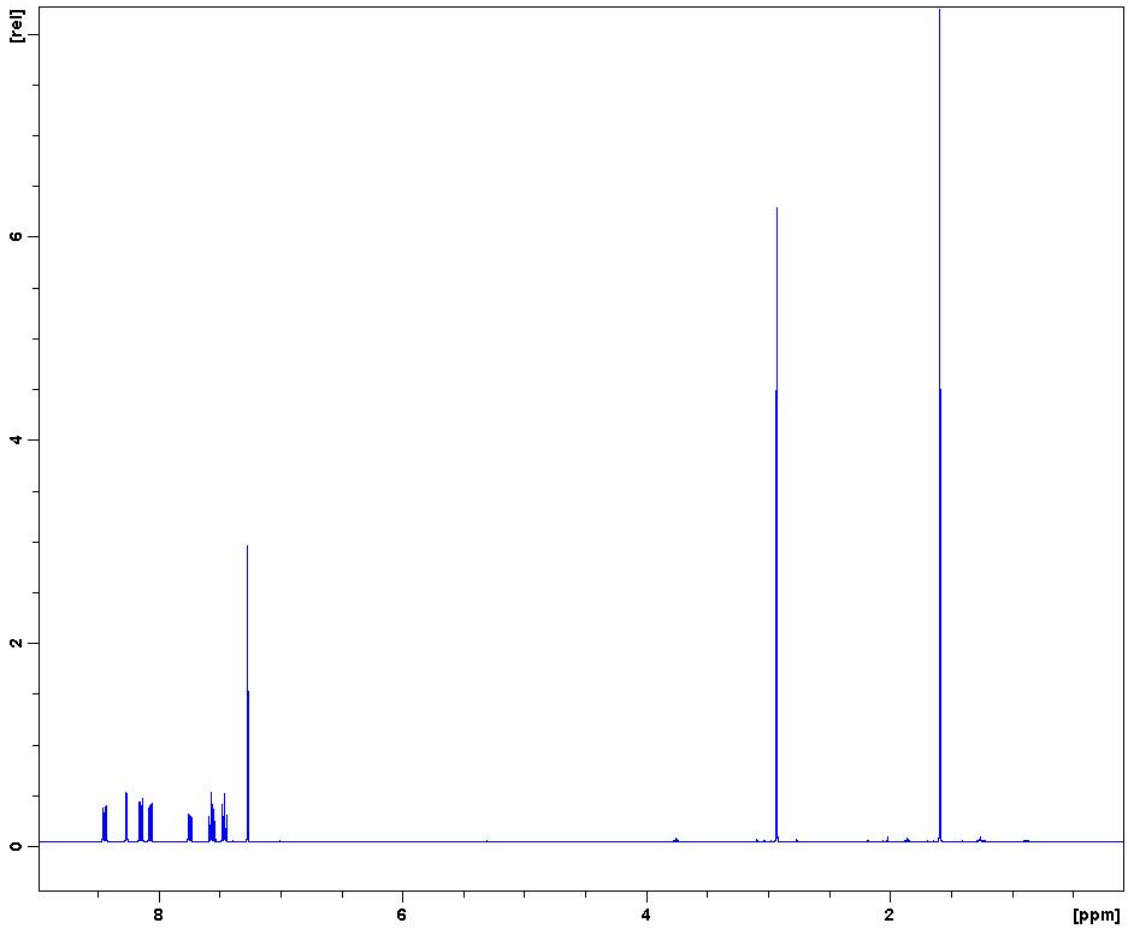


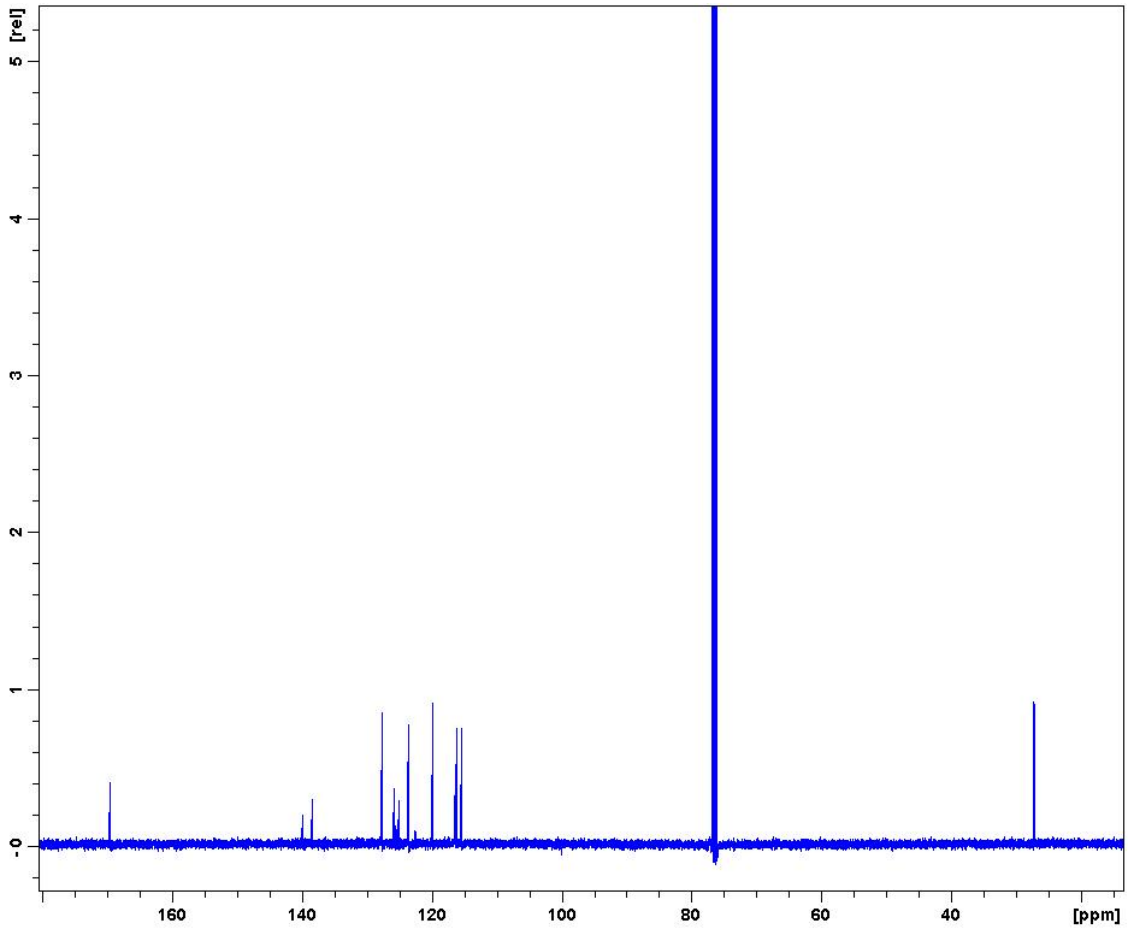




^{1}H and ^{13}C NMR spectra of 2p







^{1}H and ^{13}C NMR spectra of 2q