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Supporting Information

A mild CuBr-NMO oxidative system for the coupling of anilines leading to aromatic azo compounds

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1. General details

All glass apparatus were oven dried prior to use. Melting points were determined in open capillary tubes on an electrically heated block and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR RX1 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-300 and Bruker Ascend-400 using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Electrospray ionization mass spectrometry (ESI-MS) was obtained on Thermo LCQ Advantage Max Spectrometer and HRMS were recorded on Agilent 6520 Q-TOF. Column chromatography was performed over silica gel (60-120 Mesh) by using Smart flash EPCLC AI-700X YAMAZEN with minimal amount of solvent. All chemicals and reagents were obtained from Aldrich (USA), Alfa Aesar (England) and used without further purification. HPLC analysis was carried out using system consists of Shimazdu LC-10ATVp pumps and SIL-HTc auto sampler with temperature controller on a Supelco PKB C18 (4.6 X 150 mm, 5.0 μm). The system was run in gradient mode with mobile phase consisting of acetonitrile (A) and water (B) at flow rate of 1 mL/min for 25 minutes. Data acquisition was carried out on Class Vp software.

1. General Procedure and characterization data :

1.2 General procedure for preparation of symmetrical azobenzenes (2)

To a solution of Aniline **1a** (100mg, 0.81 mmol) in 2:1 CH_3CN/H_2O (6 mL), added CuBr (11.6mg, 0.081 mmol) and $NMO.H_2O$ (109.5 mg, 0.81 mmol) and stirred the reaction mixture at rt for 30 min. Progress of reaction was monitored by TLC. After completion of reaction, the mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give the crude product. Crude product was further purified by column chromatography over silica gel using 9:1 Hexane /Ethyl Acetate as an eluent to furnish azobenzene derivative (**2a**) 86mg (86%) as orange solid.

1.3 General procedure for preparation of unsymmetrical azobenzenes (3)

To a solution of aniline **1a** (100mg, 0.81) and **1g** (123mg, 0.97 mmol) in 2:1 CH_3CN/H_2O (6mL), added CuBr (11.6mg, 0.081 mmol) and $NMO.H_2O$ (110mg, 0.81 mmol) under air was stirred for 1.5 h, at room temperature. Progress of reaction was monitored by TLC. After completion of reaction, the mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give the crude product. Crude product was further purified by column chromatography over silica gel using 9:1 Hexane /ethyl acetate as an eluent. Quantitative yield of cross coupling products were carried out using system consists of Shimazdu LC-10ATVp pumps and SIL-HTc auto sampler with temperature controller to give 54% of **3b,** 19% of **2a** and 26% of **2g** by using Zorbax SB 100 C C18 column (4.6 X 150 μm) eluted with gradient of Water:Acetonitrile.

Compound Characterization data:

1,2-bis(4-methoxyphenyl)diazene (2a)[1]

Orange solid, yield 86%, mp 154.6−155.3 °C (lit.,[1] 155.4-158.7 °C) ; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3020, 1500, 1250, 1147, 1103, 1027, 841; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.88 (s, 6H), 6.99-7.02 (m, 4H), 7.86-7.89 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 55.6, 114.2, 124.4, 147.1, 161.6; **ESI-MS (m/z)**: 243 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1128; found: 243.1128.

1,2-diphenyldiazene (2b)[3]

Orange solid, Yield 78%, mp 67.2-68.1 °C (lit.,[3] 67.3-68.2 °C) ; **FT-IR** (KBr, ν_{max}/cm^{-1}) 1642, 1478, 1216, 1072, 760 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.46-7.55 (m, 6H), 7.92-7.94 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 122.9, 129.1, 131.0, 152.7; **ESI-MS (m/z)**: 183 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{12}H_{11}N_2$ $[M+H]^+$: 183.0917; found: 183.0922.

1,2-bis(3-methoxyphenyl)diazene(2c)[2]

Red solid, Yield 83%, mp 90.2- 91.6 °C (lit.,[9] 90-93 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 3140, 3020, 1599, 1402, 1216, 1038,763; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.90 (s, 6H), 7.03-7.06 (m, 2H), 7.41-7.46 (m, 4H), 7.55-7.57 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 55.5, 105.7, 117.1, 117.8, 129.7, 153.8, 160.4; **ESI-MS (m/z)**: 243 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1128; found: 243.1124.

1,2-bis(2-methoxyphenyl)diazene(2d)[2]

Red solid, Yield 84%, mp 149.7-150.2 °C (lit.,[10] 150-151 °C) ; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3396, 927, 1597, 1479, 1324, 1256, 1039, 785; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.02 (s, 6H), 6.98-7.02 (m, 2H), 7.06-7.07 (m, 2H), 7.39-7.44 (m, 2H), 7.61-7.64 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 56.3, 112.6, 117.6, 120.8, 132.2, 149.7, 156.8; **ESI-MS (m/z)**: 243 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$: 243.1128; found: 243.1129.

1,2-bis(4-methoxy-2-methylphenyl)diazene(2e)

Red solid, Yield 72%, mp 71.2-73.2 °C; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3146, 1636, 1402, 1216, 1034, 767; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 2.29 (s, 6H), 3.93 (s, 6H), 7.27 (d, J= 9.5 Hz, 2H), 7.40 (d, J= 1.6 Hz, 2H), 7.49 (dd, $J1$= 7.8 Hz, $J2$= 1.6 Hz, 2H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 16.5, 55.4, 101.8, 117.6, 130.3, 130.6, 152.2, 158.3; **ESI-MS (m/z)**: 271 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{16}H_{19}N_2O_2$ $[M+H]^+$: 271.1441; found: 271.1440.

1,2-bis(4-fluorophenyl)diazene(2f)[3]

Yellow solid, Yield 79%, mp 96.7-97.8 °C (lit.,[3] 97.1-99.8 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 2927, 1729, 1594, 1498, 1221, 1138, 846, 763; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.17-7.21 (m, 4H), 7.90-7.94 (m, 4H); **^{13}C NMR** (100 MHz, CD_3OH) δ_C 115.7 (d, *J*=4.5 Hz, 4XCH), 124.6 (d, *J*= 4.5 Hz, 4XCH), 149.0, 164.5 (d, *J*= 249.0 Hz, 2XC-F); **ESI-MS (m/z)**: 219 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{12}H_9F_2N_2$` $[M+H]^+$: 219.0728; found: 219.0728.

1,2-bis(4-chlorophenyl)diazene(2g)[3]

Yellow solid, Yield 83%, mp 181.8-183.7 °C (lit.,[3] 182.0-184.5 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 1479, 1402, 1215, 1084, 836, 758; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.47-7.51 (m, 4H), 7.84-7.88 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 124.2, 129.4, 137.2, 150.8; **ESI-MS (m/z)**: 251 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{12}H_9Cl_2N_2$ $[M+H]^+$: 251.0137; found: 251.0123.

1,2-bis(4-bromophenyl)diazene(2h)[3]

Yellow solid, Yield 73%, mp 200.3-201.6 °C (lit.,[3] 201.3-203.7 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 1522, 1472, 1215, 1067, 757; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.64-7.66 (m, 4H), 7.78-7.80 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 124.4, 125.8, 132.4, 151.2; **ESI-MS (m/z)**: 338 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{12}H_9Br_2N_2$ $[M+H]^+$: 338.9127; found: 338.9129.

1,2-bis(3,4-dimethylphenyl)diazene (2i)[3]

Red solid, Yield 74%, mp 154.8-156.7 °C (lit.,[3] 155.2-157.8 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 1602, 1403, 1215, 1069, 928, 757; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 2.33 (s, 6H), 2.35 (s, 6H), 7.26(d, *J*=7.8 Hz, 2H), 7.64-7.66 (m, 2H), 7.68 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 19.9, 120.7, 123.3, 130.2, 137.4, 139.8, 151.2; **ESI-MS (m/z)**: 239 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{16}H_{19}N_2$ $[M+H]^+$: 239.1543; found: 239.1543.

1,2-bis(4-ethylphenyl)diazene(2j)

Red solid, Yield 90%, mp 61.2-63.2 °C; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3402, 2966, 2401, 1720, 1602, 1410,1286, 1216, 1071, 845, 760; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 1.28 (t, *J*= 7.6 Hz, 2XCH_3), 2.73 (q, *J*= 7.6 Hz, 2XCH_2), 7.33 (d, *J*= 8.5 Hz, 4H), 7.81-7.84 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 15.4, 28.8, 122.8, 128.5, 147.5, 151.0; **ESI-MS (m/z)**: 239 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{16}H_{19}N_2$ $[M+H]^+$: 239.1543; found: 239.1548.

1,2-di([1,1'-biphenyl]-2-yl)diazene (2k)[3]

Yellow solid, Yield 69%, mp 132.4-133.5 °C (lit.,[3] 133.5 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 3018, 2399, 1638, 1384, 1215, 1083, 928, 758; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.36-7.58 (m, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 116.4, 127.3, 127.7, 128.0, 130.9, 138.9, 141.5, 149.8; **ESI-MS (m/z)**: 335 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{24}H_{19}N_2$ $[M+H]^+$: 335.1543; found: 335.1540.

1,2-di(pyridin-3-yl)diazene (2l)

yellow solid, Yield 70%, 98.6-99.1 °C; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3685, 3019, 2400, 1634, 1525, 928, 757, 669, 626; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.46-7.48 (m, 2H), 8.16-8.18 (m, 2H), 8.72-8.74 (m ,2H), 9.22 (d, *J*= 1.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 124.1, 127.0, 147.6, 147.7, 152.3; **ESI-MS (m/z)**: 185 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{10}H_9N_4$ $[M+H]^+$: 185.0822; found: 185.0821.

1,2-di(quinolin-3-yl)diazene (2m)

Orange solid, Yield 62%, 204-206 °C; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3399, 1644, 1582, 1403, 1216, 1070, 761, 669; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.66 (t, *J*=7.24 Hz, 2H), 7.83 (t, *J*=7.12 Hz, 2H), 8.04 (d, *J*=8.12 Hz, 2H), 8.21 (d, *J*=8.36 Hz, 2H), 8.73 (s, 2H), 9.58 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 128.0, 129.9, 130.9, 131.5, 145.2, 145.7, 149.7; **ESI-MS (m/z)**: 185 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{18}H_{13}N_4$ $[M+H]^+$: 285.1135; found: 285.1132

1-(4-methoxyphenyl)-2-phenyldiazene (3a)[4]

Red solid, Yield 45%, mp 52.0-53.4 °C (lit.,[11] 52.0-54.0 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 3153, 3019, 2399, 1650, 1215, 1034, 929, 759; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.89 (s,3H), 7.00-7.04 (m, 2H), 7.41-7.46 (m, 1H), 7.47-7.52 (m, 2H), 7.86-7.89 (m, 2H), 7.91-7.94 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 55.6, 114.2, 122.6, 124.7, 129.0, 130.3, 147.0, 152.8, 162.0; **ESI-MS (m/z)**: 213 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{13}H_{13}N_2O$ $[M+H]^+$: 213.1022; found: 213.1024.

1-(4-chlorophenyl)-2-(4-methoxyphenyldiazene (3b)[5]

Red solid, HPLC Yield 54%, mp 121-123 °C (lit.,[8] 121 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 3137, 1602, 1402, 1217, 1030, 842, 768; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.89 (s, 3H), 6.99-7.03 (m, 2H), 7.45-7.47 (m, 2H), 7.81-7.84 (m, 2H), 7.89-7.93 (m, 2H); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ_C 55.6, 114.3, 123.8, 124.8, 129.2, 136.1, 146.8, 151.1, 162.3; **ESI-MS (m/z)**: 247 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{13}H_{12}ClN_2O$ $[M+H]^+$: 247.0633; found: 247.0638.

1-(4-fluorophenyl)-2-(4-methoxyphenyldiazene (3c)[4]

Yellow solid, Yield 50%, mp 72.2-73.6 °C; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3019, 1403, 1215, 1032, 756; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.89 (s, 3H), 6.99-7.03 (m, 2H), 7.15-7.19 (m, 2H), 7.87-7.91 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 55.6, 114.2, 115.8, (d, *J*= 22 Hz, 2XCH), 124.5 (d, *J*= 9.0 Hz, 2X CH), 124.7, 146.8, 149.3(d, *J*= 2.0 Hz, C), 162.7, 164.0 (d, *J*=249 Hz, C-F); **ESI-MS (m/z)**: 231 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{13}H_{12}FN_2O$ $[M+H]^+$: 231.0928; found: 231.0929.

1-(3,4-dimethylphenyl)-2-(4-methoxyphenyl)diazene (3d)

Yellow solid, HPLC Yield 52%, mp 74-75.5 °C; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3400, 1601, 1502, 1403, 1254, 1215, 839, 759, 669 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 2.33 (s, 3H), 2.35 (s, 3H), 3.89 (s, 3H), 6.99-7.01 (m, 2H), 7.64-7.67 (m, 3H), 7.88-7.90 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 19.8, 55.5, 114.2, 120.6, 123.2, 124.5, 130.2, 137.3, 139.5, 147.2, 151.2, 161.8; **ESI-MS (m/z)**: 241 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$: 241.1335; found: 241.1322.

1-(3-methoxyphenyl)-2-phenyldiazene (3e)[6]

Red solid, Yield 48%, mp 40.0-41.0 °C (lit.,[6] 38-42 °C); **FT-IR** (KBr, ν_{max}/cm^{-1}) 3139, 2924, 1637, 1402, 1035, 769; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.90 (s, 3H), 7.05 (dd, *J*1= 8.0 Hz, *J*2= 2.2 Hz, 1H), 7.41-7.58 (m, 6H), 7.92 (d, *J*= 6.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 55.5, 105.8, 117.1, 117.8, 122.9, 129.1, 129.8, 131.0, 152.6, 153.9, 160.4; **ESI-MS (m/z)**: 213 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{13}H_{13}N_2O$ $[M+H]^+$: 213.1022; found: 213.1024.

1-(4-chlorophenyl)-2-(3-methoxyphenyldiazene (3f)[7]

Red solid, HPLC Yield 53%, mp 70.6-71.7 °C; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3139, 2924, 1637, 1402, 1035, 769; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 3.90(s, 3H), 7.05 (d, *J*= 6.4 Hz 1H), 7.41-7.56 (m, 5H), 7.87 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 55.5, 105.8, 117.3, 118.1, 124.2, 129.4, 129.8, 136.9, 150.9, 153.7, 160.4; **ESI-MS (m/z)**: 247 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{13}H_{12}ClN_2O$ $[M+H]^+$: 247.0633; found: 247.0633.

1-(4-ethylphenyl)-2-(3-methoxyphenyl)diazene (3g)

Red liquid, HPLC Yield 50%, **FT-IR** (KBr, ν_{max}/cm^{-1}) 3400, 3019, 1403, 1216, 1037, 770; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 1.29 (t, *J*= 7.6 Hz, 3H), 2.73 (q, *J*= 7.6 Hz, 2H), 3.90 (s, 3H), 7.03 (dd, *J*1= 8.1 Hz, *J*2=2.6 Hz, 2H), 7.33-7.42 (m, 3H), 7.44-7.45 (m, 1H), 7.53-7.56 (m, 1H), 7.85 (d, *J*=8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 15.4, 28.8, 55.4, 105.7, 116.9, 117.5, 122.9, 128.5, 129.7, 147.8, 150.9, 154.0, 160.3; **ESI-MS (m/z)**: 241 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$: 241.1335; found: 241.1332.

1-(2-methoxyphenyl)-2-phenyldiazene (3h)[6]

Red liquid, HPLC Yield 45%, **FT-IR** (KBr, ν_{max}/cm^{-1}) 3400, 1593, 1486, 1280, 1243, 1159, 1026, 768 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.03 (s, 3H), 7.02 (t, *J*= 8.04 Hz, 1H), 7.10 (d, *J*= 7.8 Hz, 1H), 7.42-7.52 (m, 4H), 7.66 (d, *J*= 7.9 Hz, 1H), 7.91-7.92 (m, 2H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 56.4, 112.8, 117.0, 120.8, 123.0, 129.0, 130.8, 132.5, 142.4, 153.2, 157.0; **ESI-MS (m/z)**: 213 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{13}H_{13}N_2O$ $[M+H]^+$: 213.1022; found: 213.1025.

1-(4-chlorophenyl)-2-(2-methoxyphenyldiazene (3i)

Red liquid, HPLC Yield 51%, **FT-IR** (KBr, ν_{max}/cm^{-1}) 3150, 3018, 1629, 1053, 1010, 819, 757; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 4.03 (s, 3H), 6.99-7.04 (m, 1H), 7.09-7.11 (m, 1H), 7.17-7.21 (m, 1H), 7.45-7.48 (m, 2H), 7.66 (dd, *J*1= 8 Hz, *J*2= 1.7 Hz, 1H), 7.84-7.87(m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 56.4, 112.8, 116.9, 120.8, 124.2, 129.3, 132.8,136.7, 142.1, 151.5, 157.2; **ESI-MS (m/z)**: 247 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{13}H_{12}ClN_2O$ $[M+H]^+$: 247.0633; found: 247.0637.

1-(4-ethylphenyl)-2-(2-methoxyphenyldiazene (3j)

Red liquid, HPLC Yield 49%, **FT-IR** (KBr, ν_{max}/cm^{-1}) 3131, 2400, 1640, 1215, 1083, 929; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 1.29 (t, *J*= 7.6 Hz, 3H), 2.7 (q, *J*=7.6 Hz, 2H), 4.02 (s, 3H), 7.00-7.05 (m, 1H), 7.08-7.10 (m, 1H), 7.32 (d, *J*= 8.6 Hz, 2H), 7.40-7.45 (m, 1H), 7.64 (dd, *J*1= 8.0 Hz, *J*2 =1.7 Hz, 1H), 7.83- 7.86 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 15.4, 28.8, 56.4, 117.0, 120.8, 123.0, 128.1, 128.5, 132.0, 142.5, 147.6, 151.5, 156.8; **ESI-MS (m/z)**: 241 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$: 241.1335; found: 241.1334.

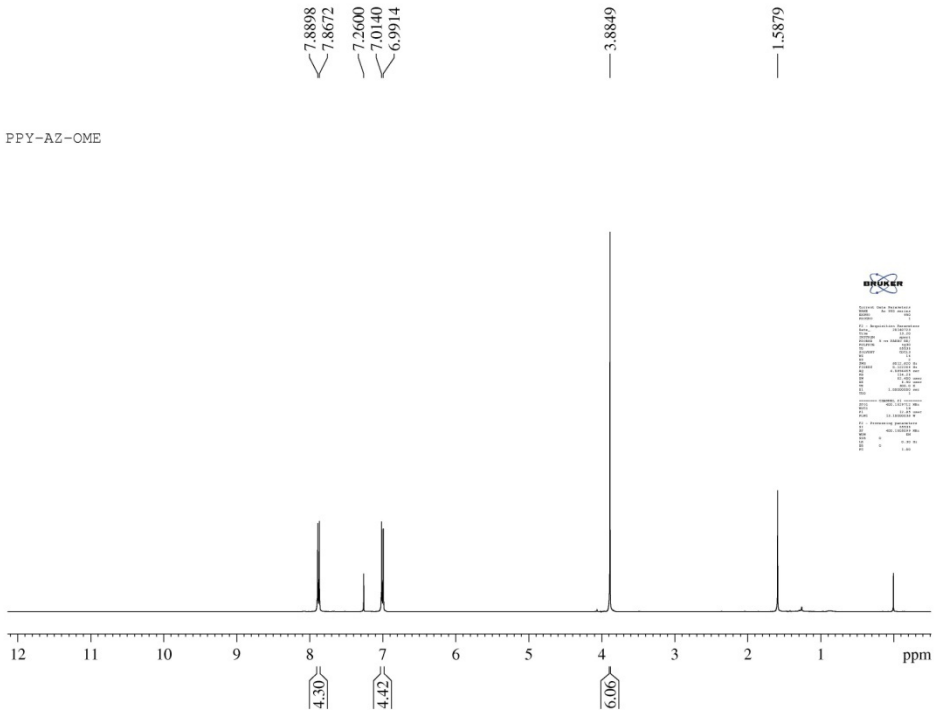
1-(4-chlorophenyl)-2-phenyldiazene (3k) [8]

Red solid, HPLC Yield 50%, mp 90.6-91.1 °C (lit.,[8] 91 °C) ; **FT-IR** (KBr, ν_{max}/cm^{-1}) 3136, 1635, 1402, 1216, 1085, 762; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.21-7.28 (m, 1H), 7.47-7.53 (m , 4H), 7.85-7.92 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 122.9, 124.1, 129.1, 129.4,

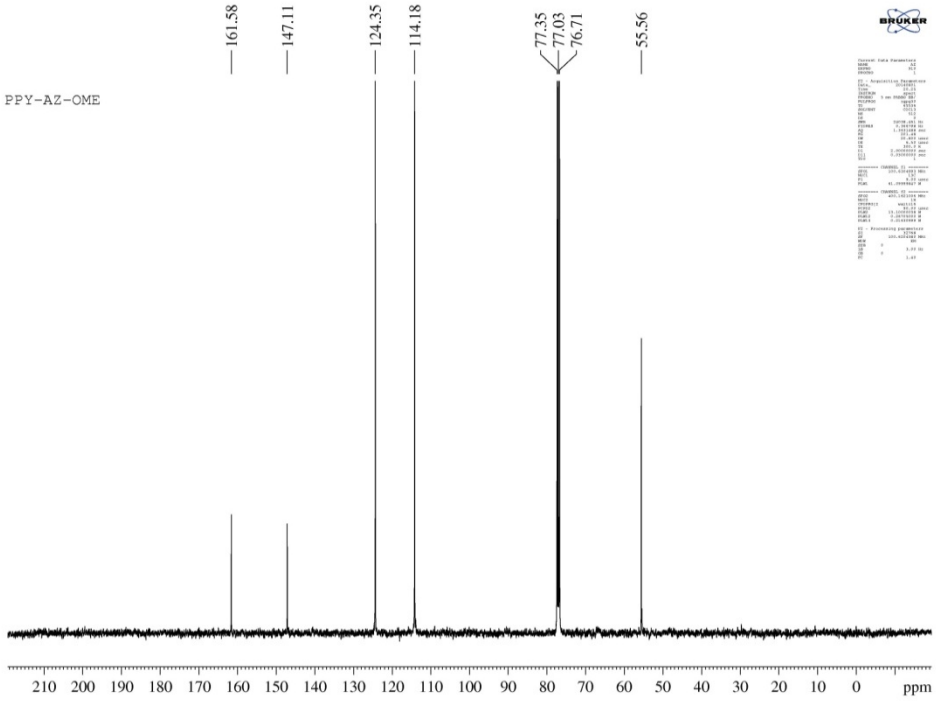
131.3, 136.9, 151.0, 152.5; **ESI-MS (m/z)**: 217 $[M+H]^+$; **HR-MS (ESI)** calcd for $C_{12}H_{10}ClN_2$ $[M+H]^+$: 217.0527; found: 217.0533.

References:

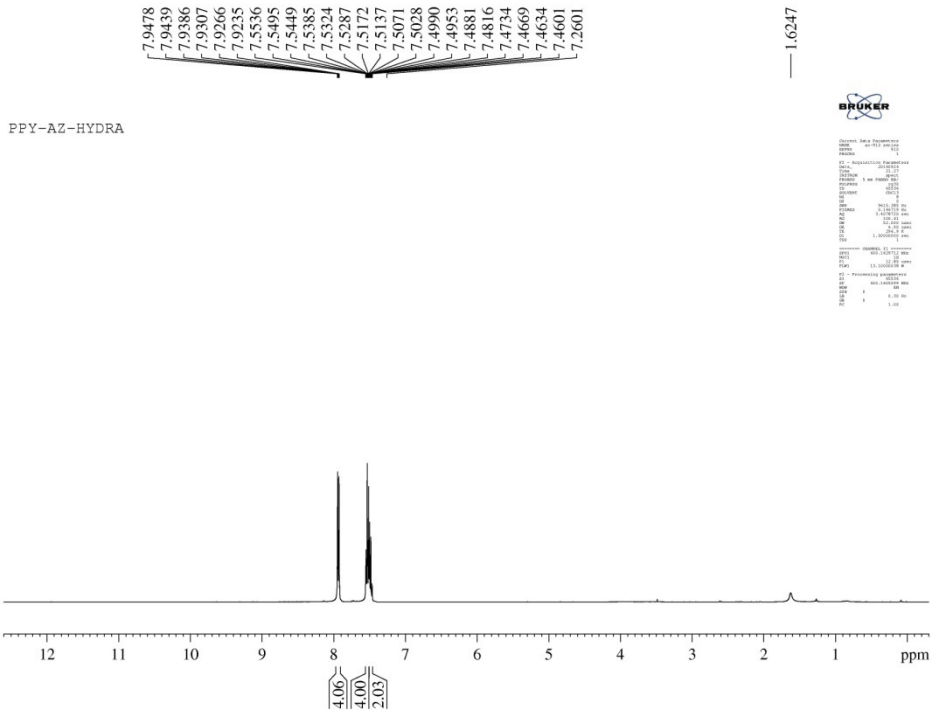
1. I. Cepanec, M. Litvić, J. Udiković, I. Pogorelić and M. Lovric, *Tetrahedron*., 2007, **63**, 5614.
2. W. Lu and C. Xi *Tetrahedron Lett*., 2008, **49**, 4011.
3. S. Okumura, C.-H Lin, Y. Takeda and S. Minakata *J. Org. Chem*., 2013, **78**, 12090.
4. C. Zhang and N. Jiao, *Angew. Chem., Int. Ed.,* 2010, **49**, 6174.
5. K. Monir, M. Ghosh, S. Mishra, A. Majee and A. Hajara, *Eur. J. Org. Chem.,* 2014, 1096.
6. R. Zhao, C. Tan, Y. Xie, C. Gao, H. Liu and Y. Jiang, *Tetrahedron Lett*., 2011, **52**, 3805.
7. M. Barbero, I. Degani, S. Dughera, R. Fochi and P. Perracino, *Synthesis,* 1998, **9**, 1235.
8. N. R. Ayyanger, *Tetrahedron Lett.,* 1989, **30**, 7253.
9. G. R., Srinivasa, K. Abiraj and D. C. Gowda, Tetrahedron Lett., 2003, **44**, 5835.
10. M. Zhang, R. Zhang, A.-Q. Zhang, X. Li and H. Liang, *Synth. Commun*., 2009, **39**, 3428.
11. R. Zhao, C. Tan, Y. Xie, C. Gao, H. Liu and Y. Jiang, *Tetrahedron Lett*., 2011, **52**, 3805.



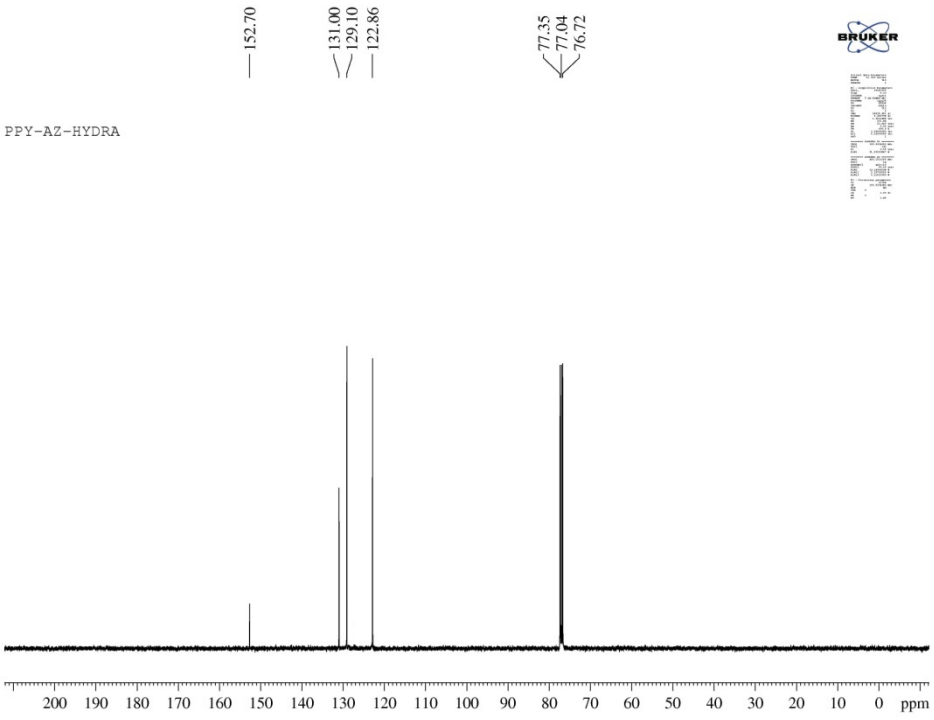
^{1}H NMR Spectra of (**2a)** (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of (**2a)** (100 MHz, $CDCl_3$)



^{1}H NMR Spectra of (**2b)** (400 MHz, $CDCl_3$)



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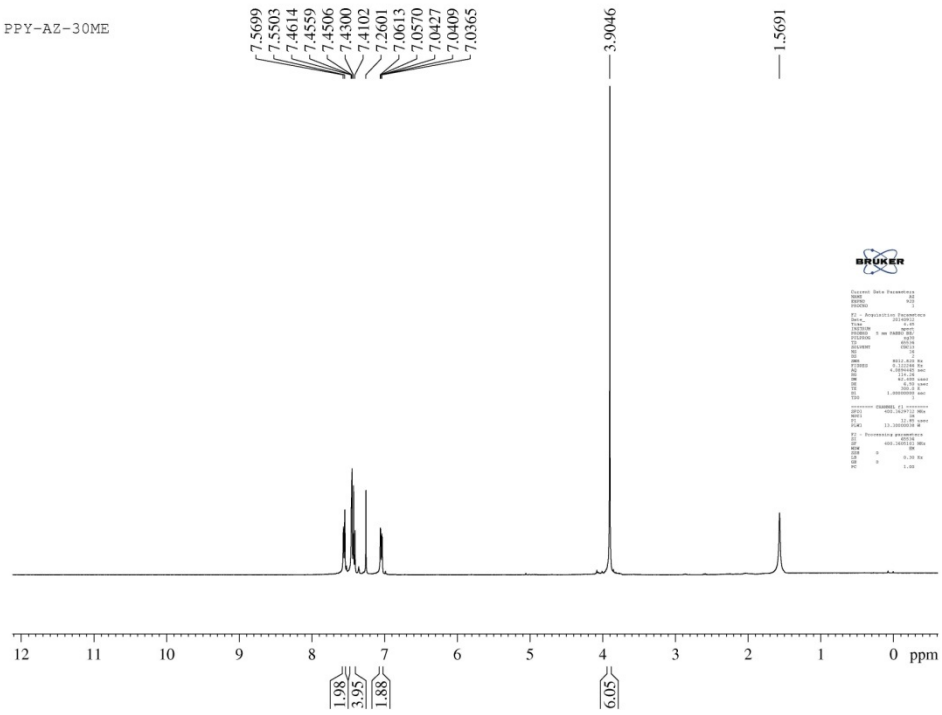
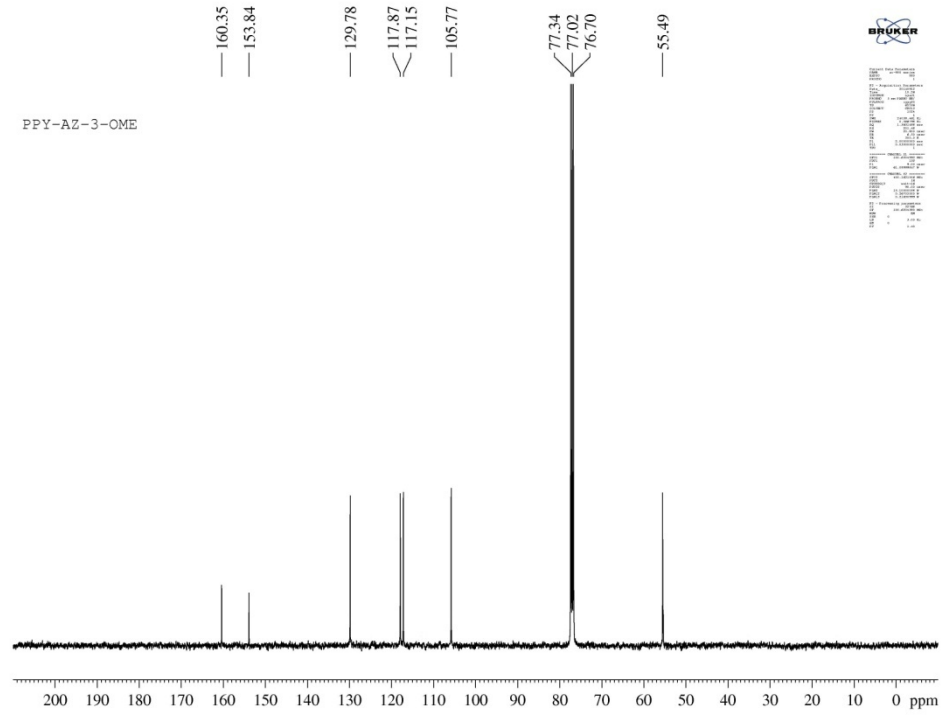
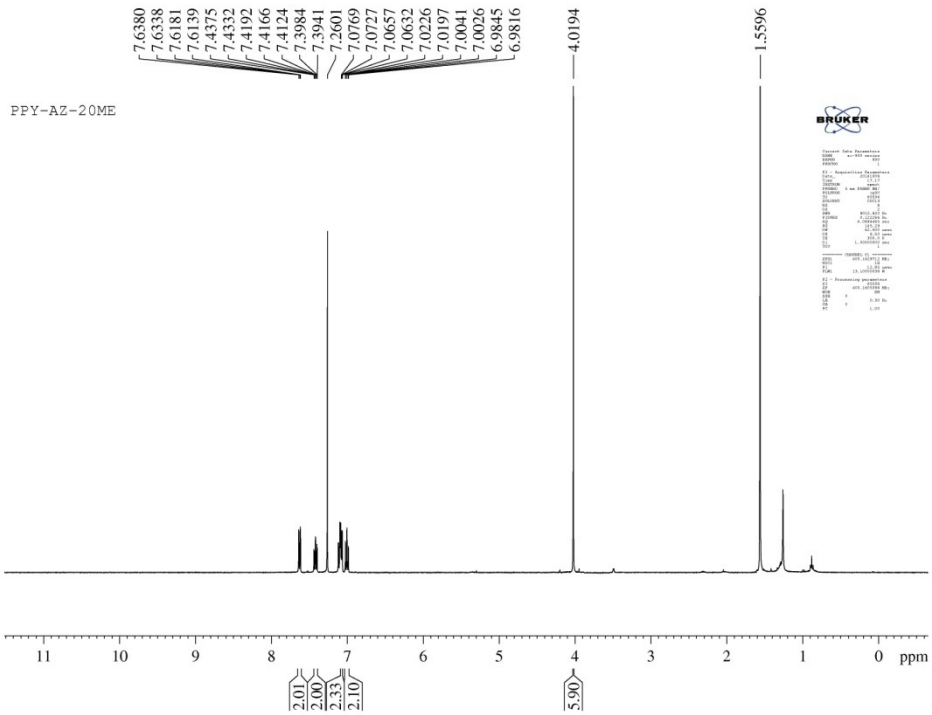


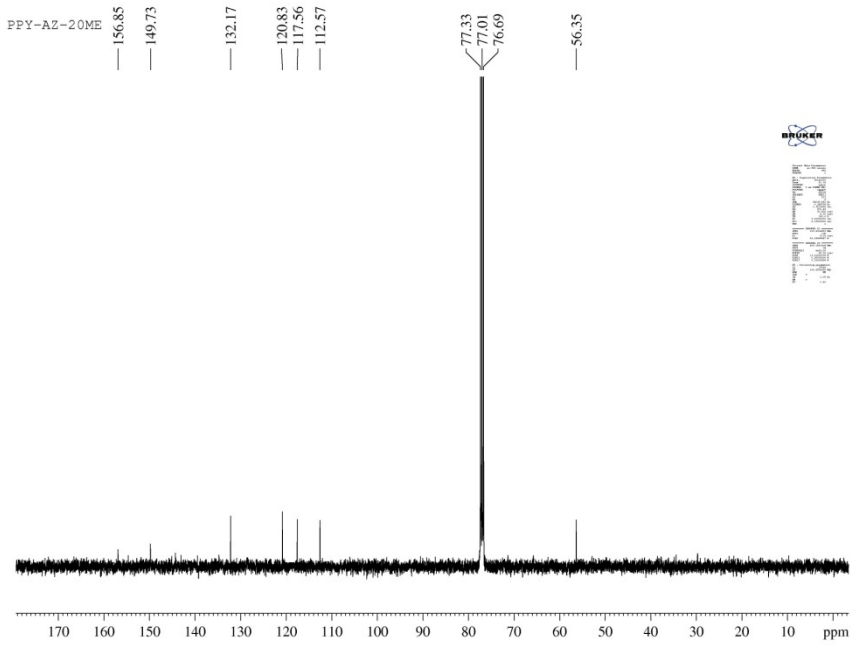
^{1}H NMR Spectra of (**2c)** (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of (**2c)** (100 MHz, $CDCl_3$)



^{1}H NMR Spectra of (**2d)** (400 MHz, $CDCl_3$)



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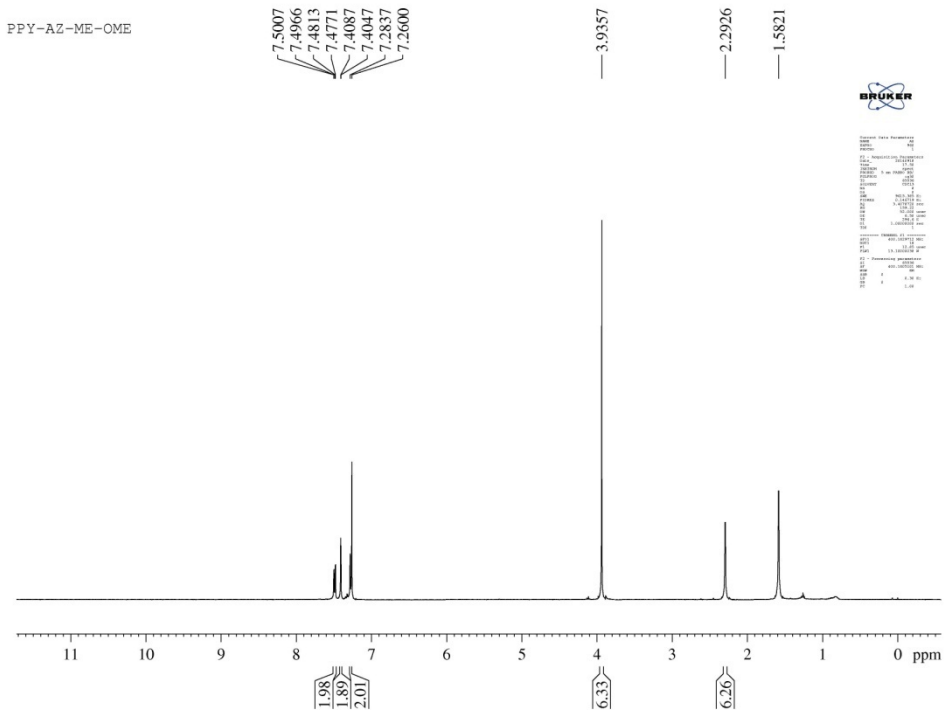

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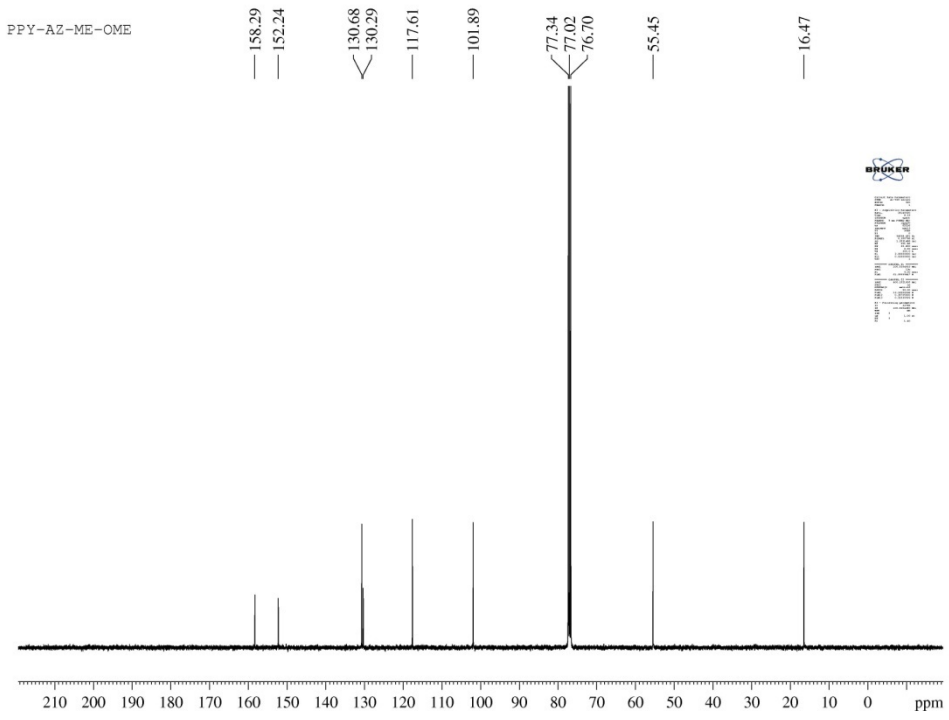

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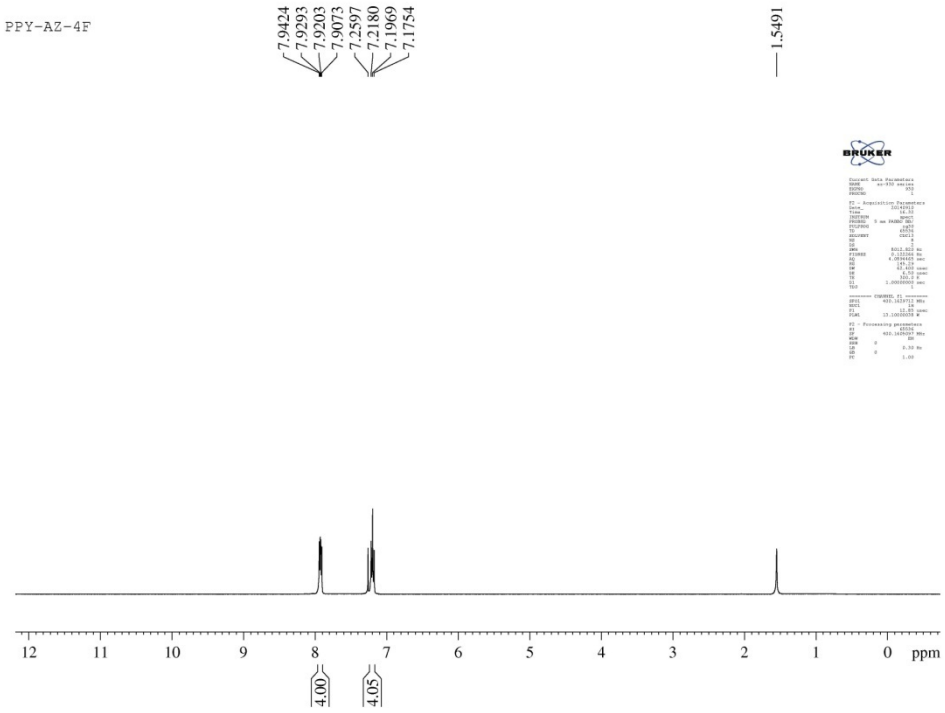
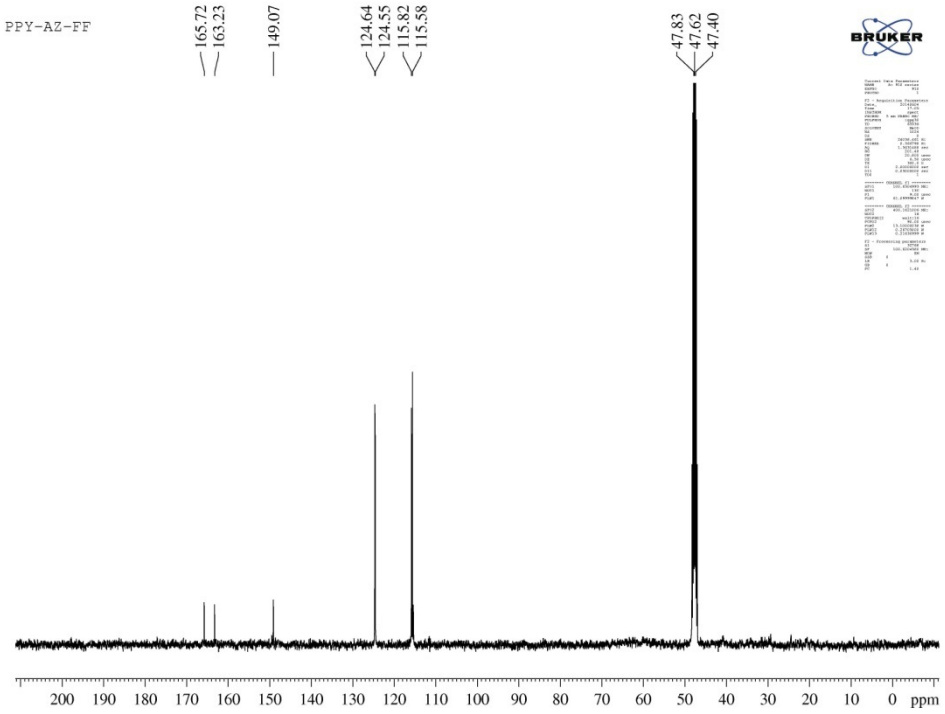


^{1}H NMR Spectra of (**2f**) (400 MHz, $CDCl_3$)



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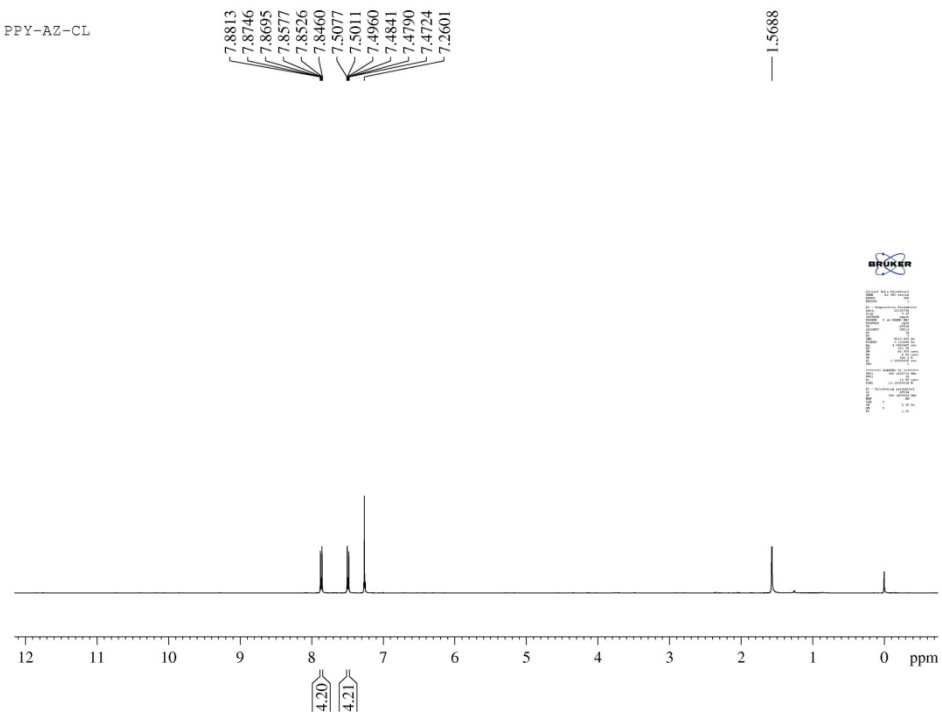

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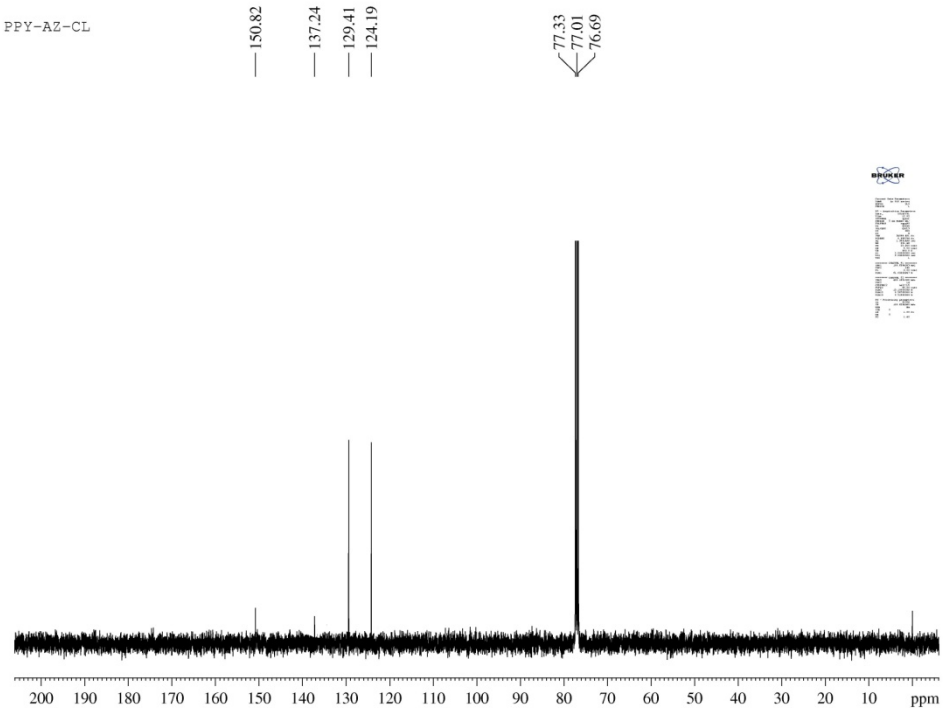

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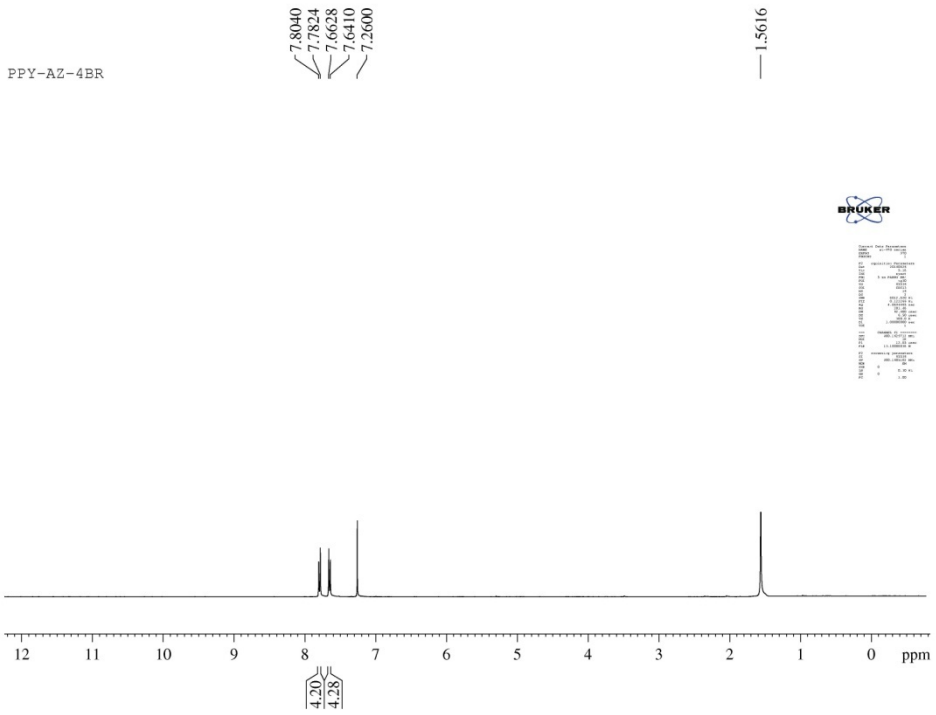

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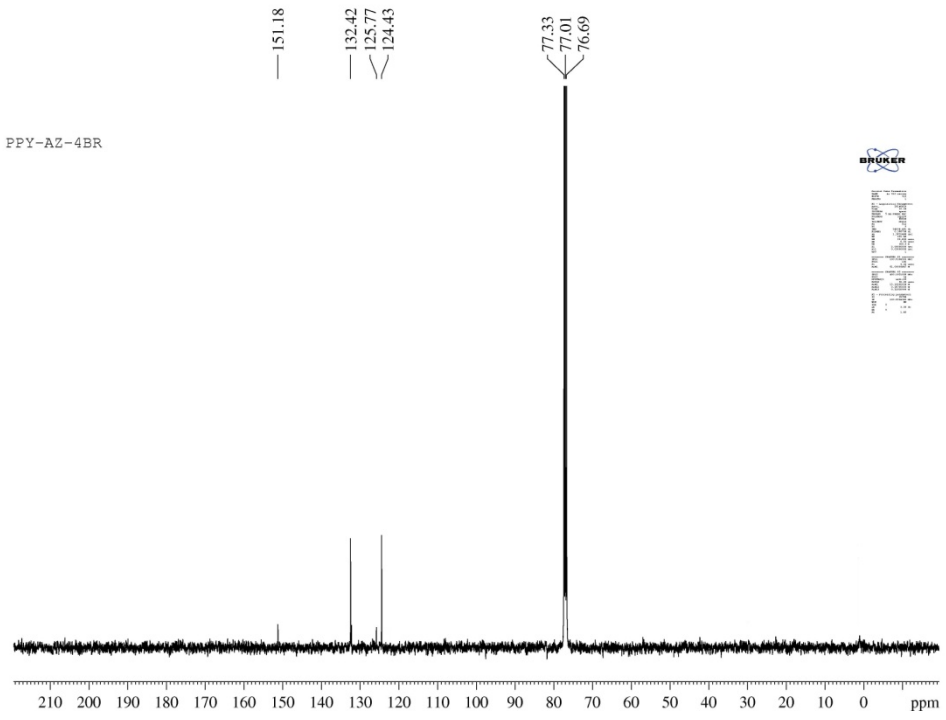

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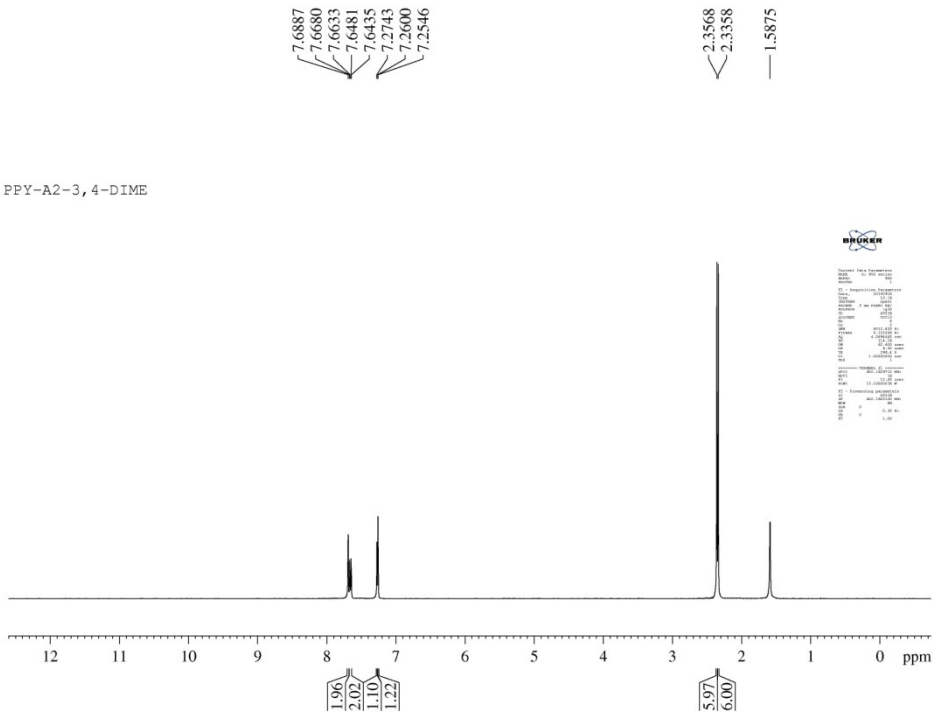

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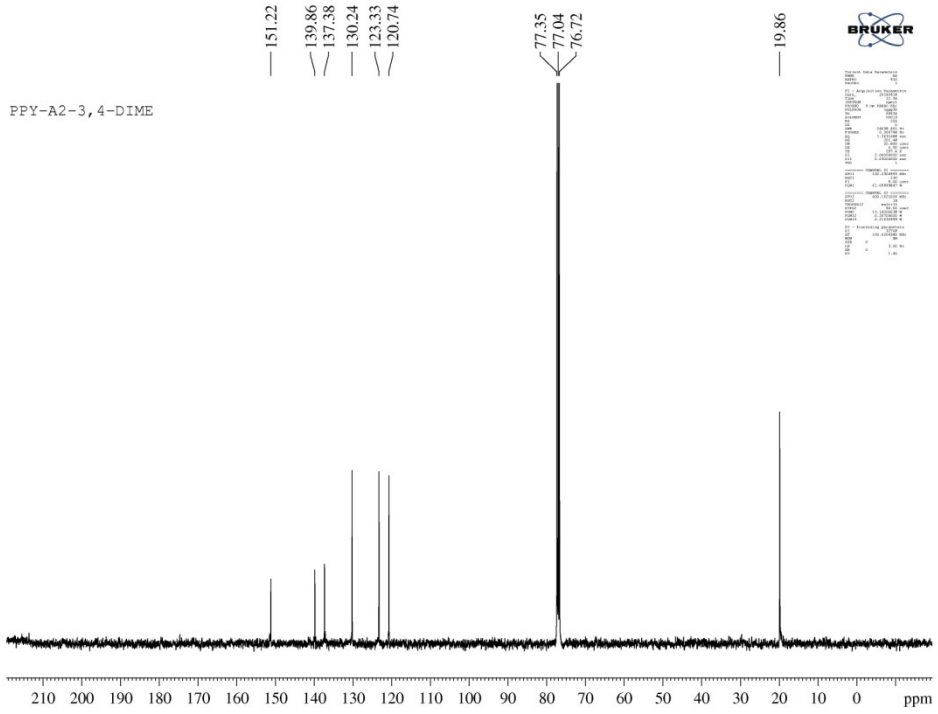

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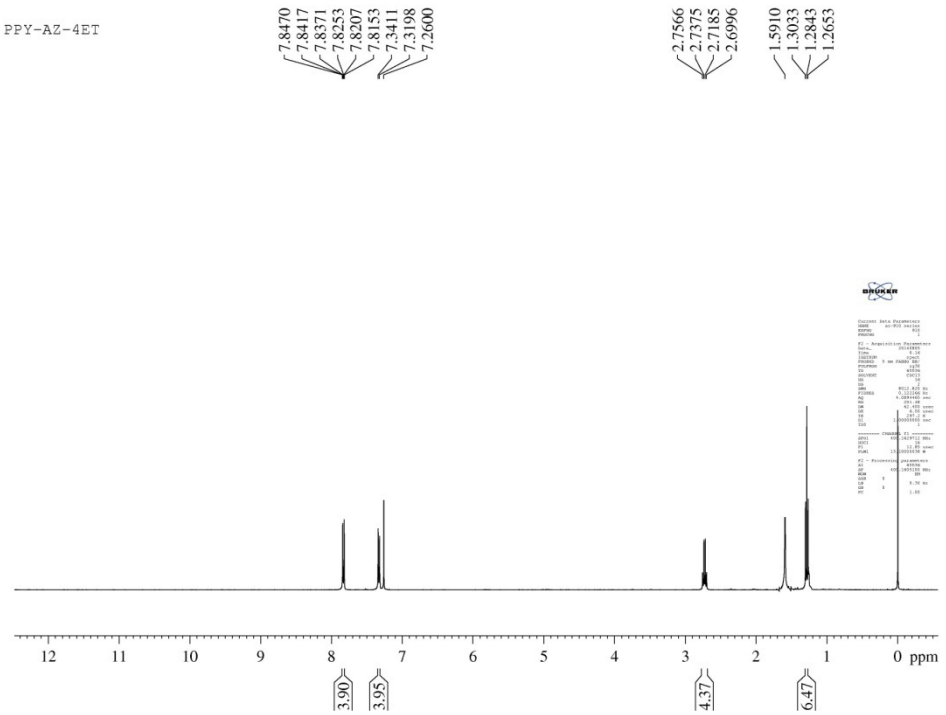

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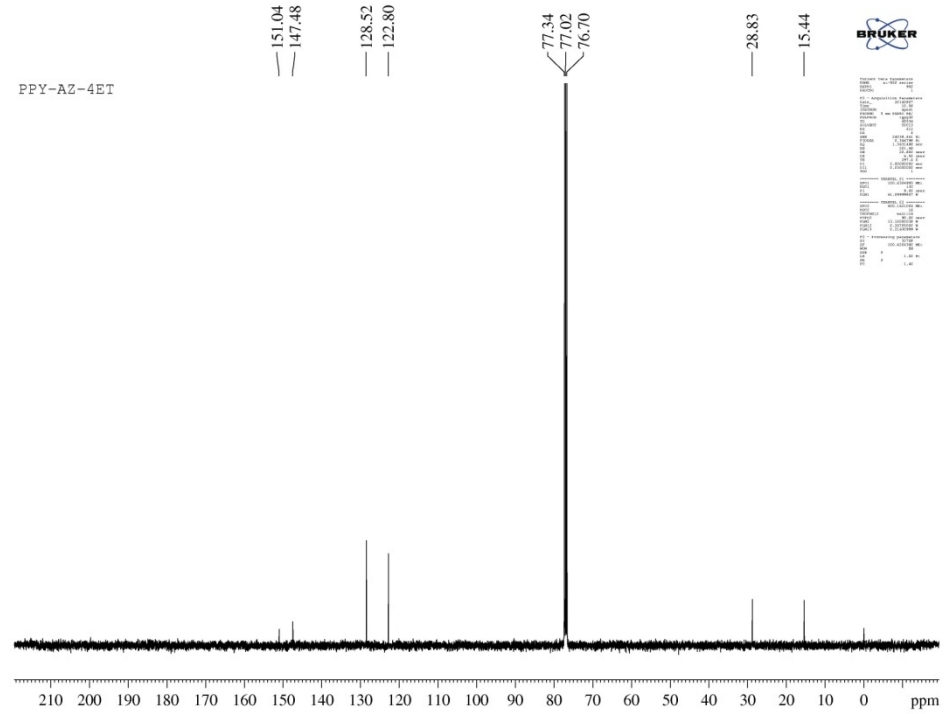

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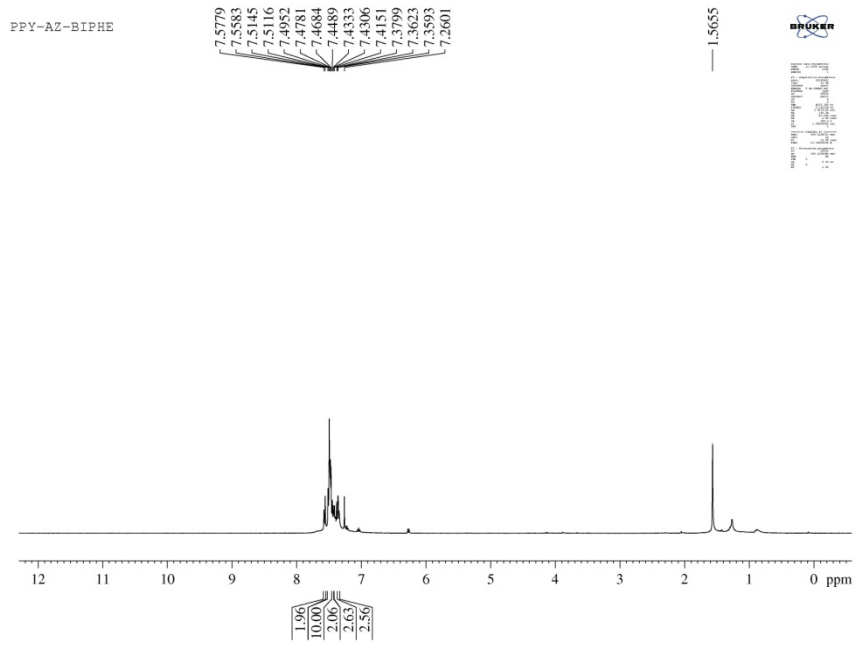

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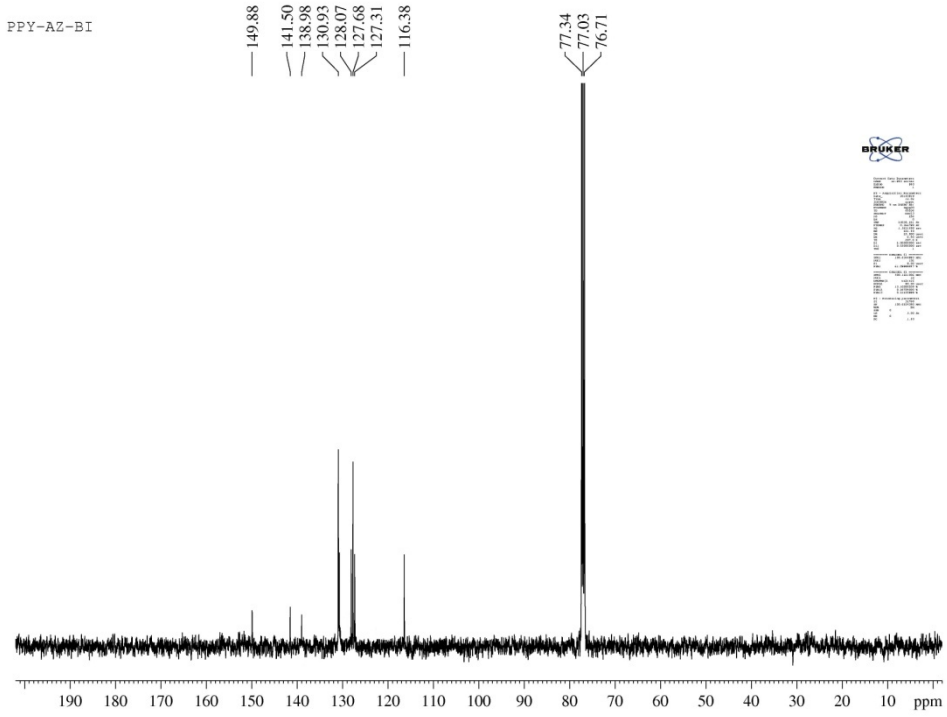

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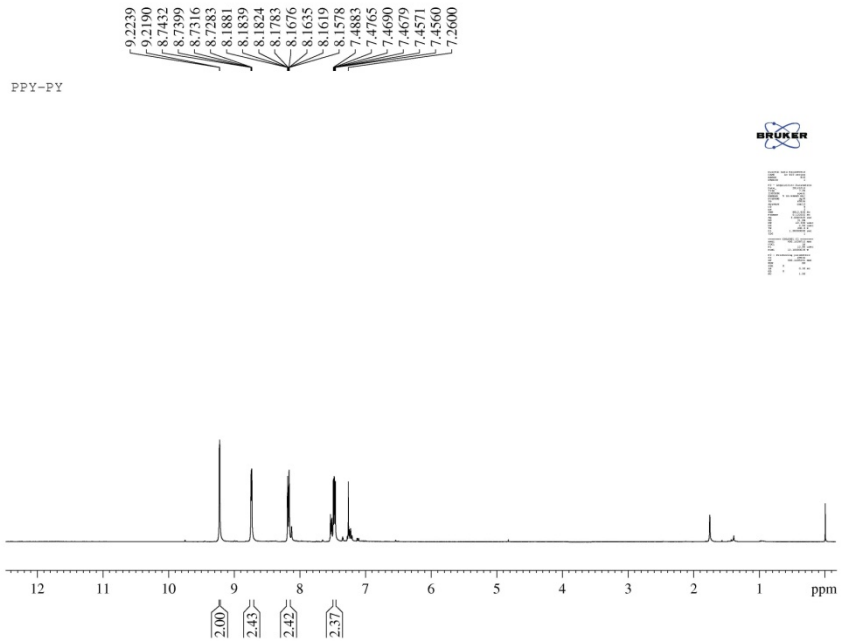

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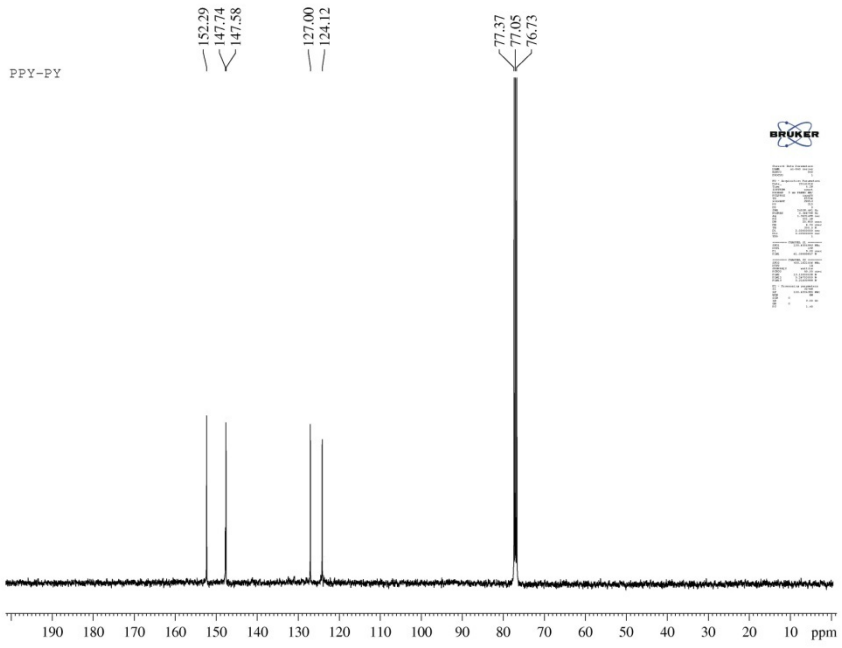

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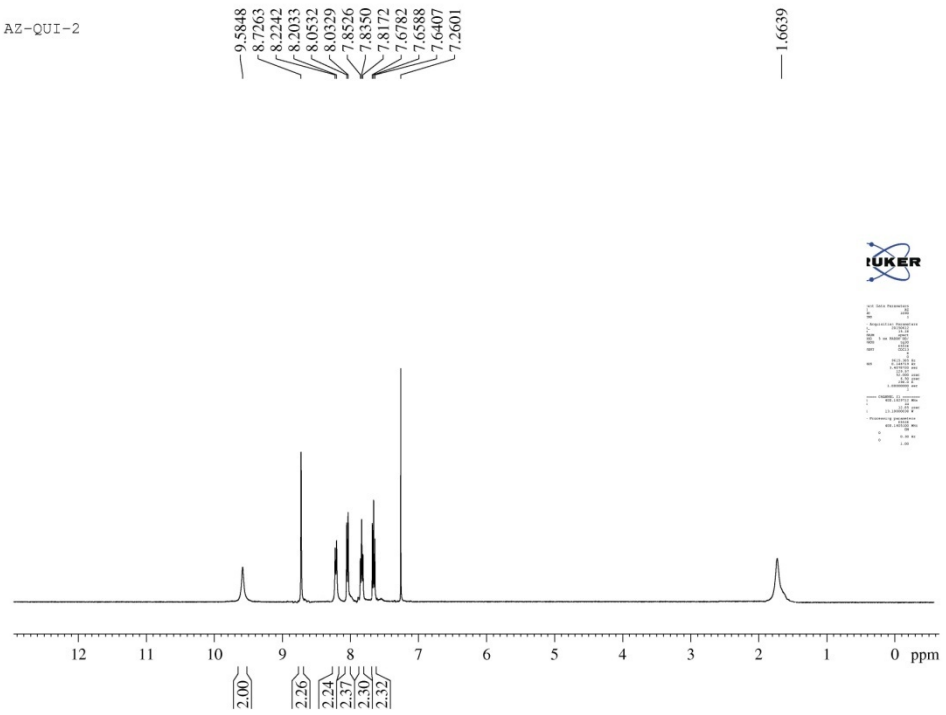

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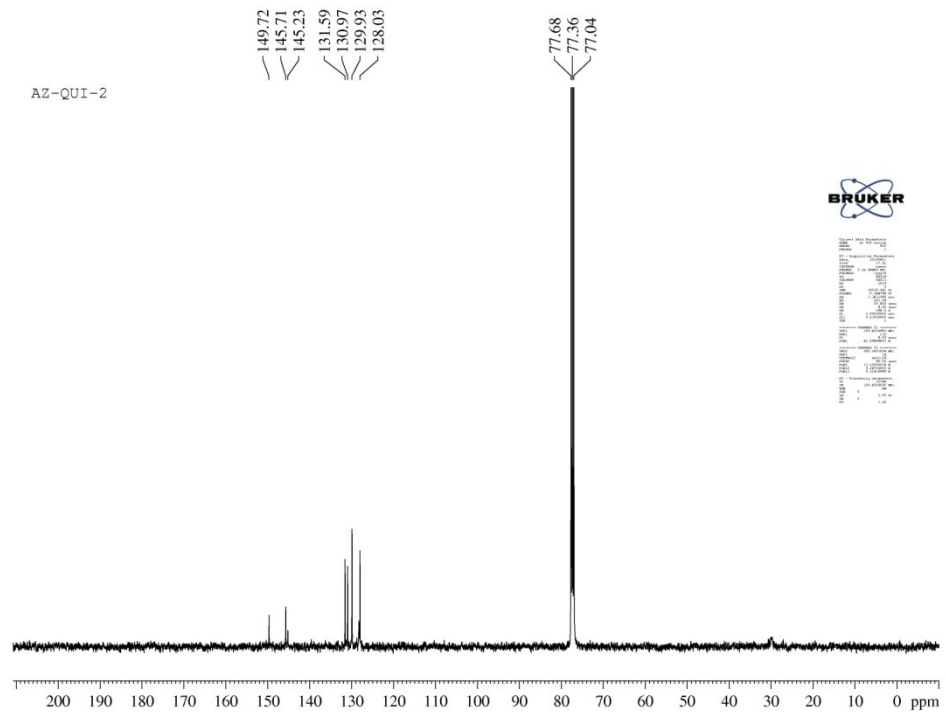

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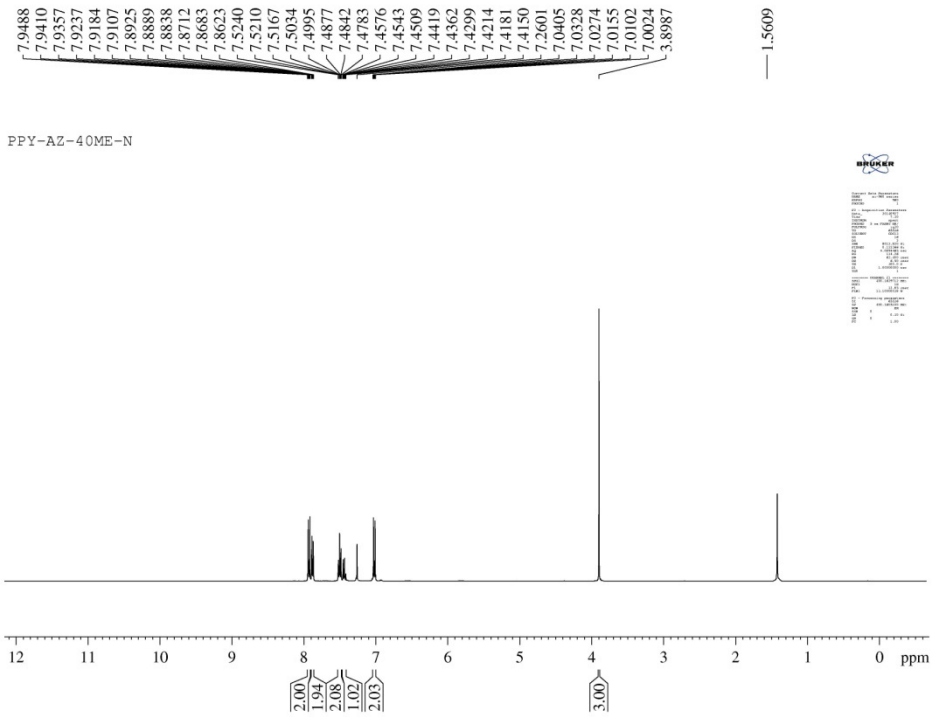
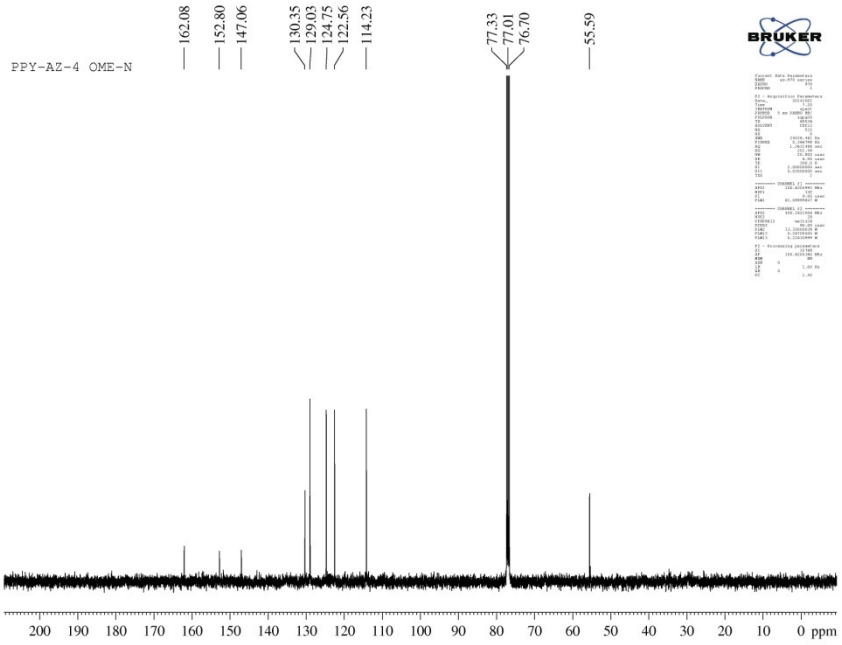


^{1}H NMR Spectra of (**3a)** (400 MHz, $CDCl_3$)



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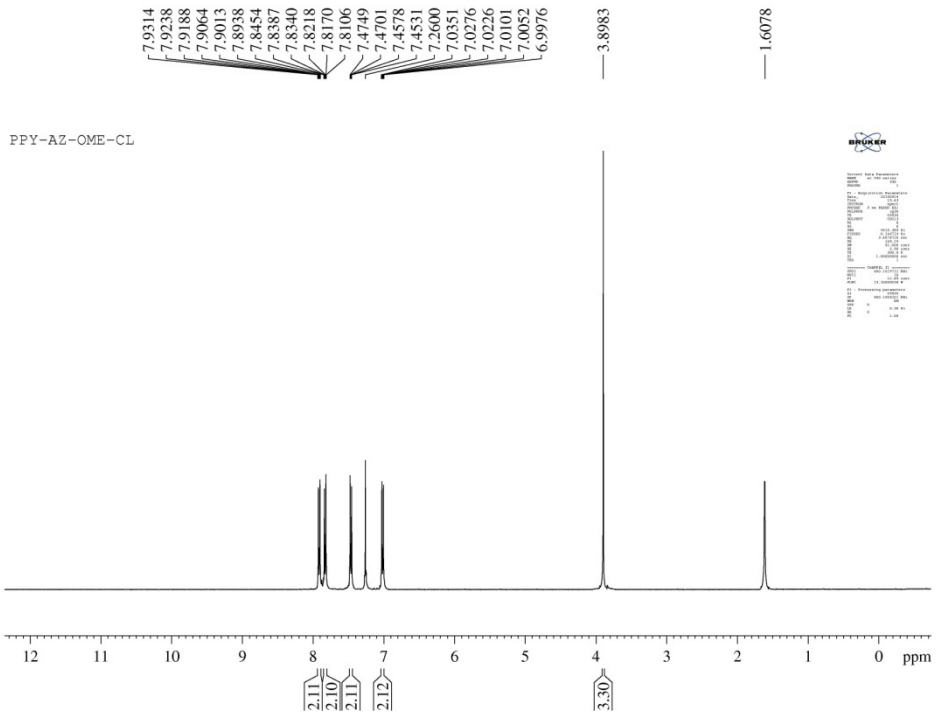
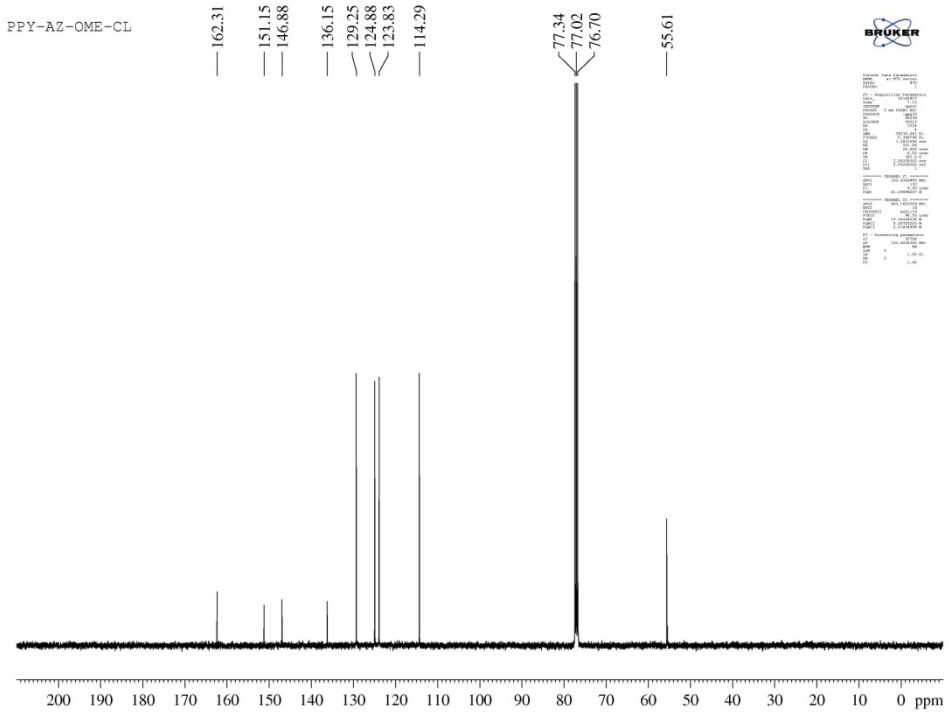
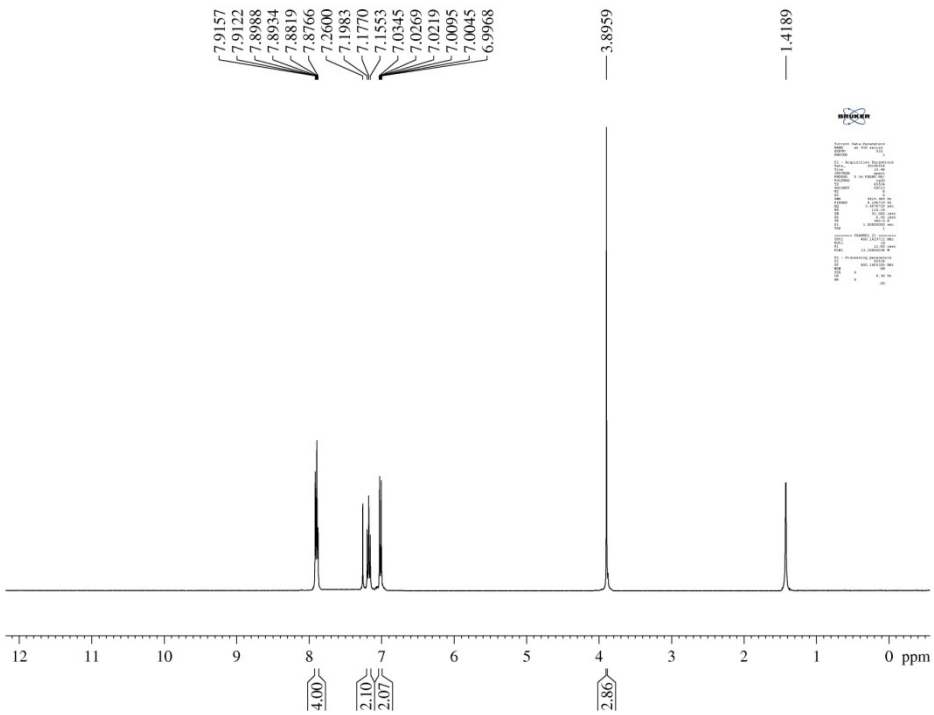


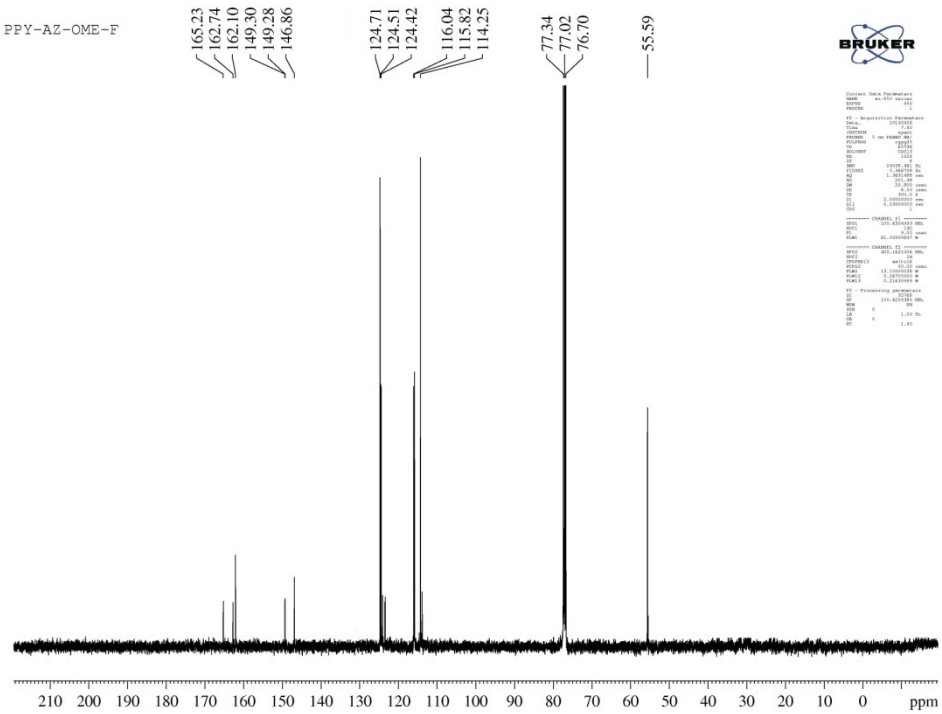
^{1}H NMR Spectra of (**3b)** (400 MHz, $CDCl_3$)



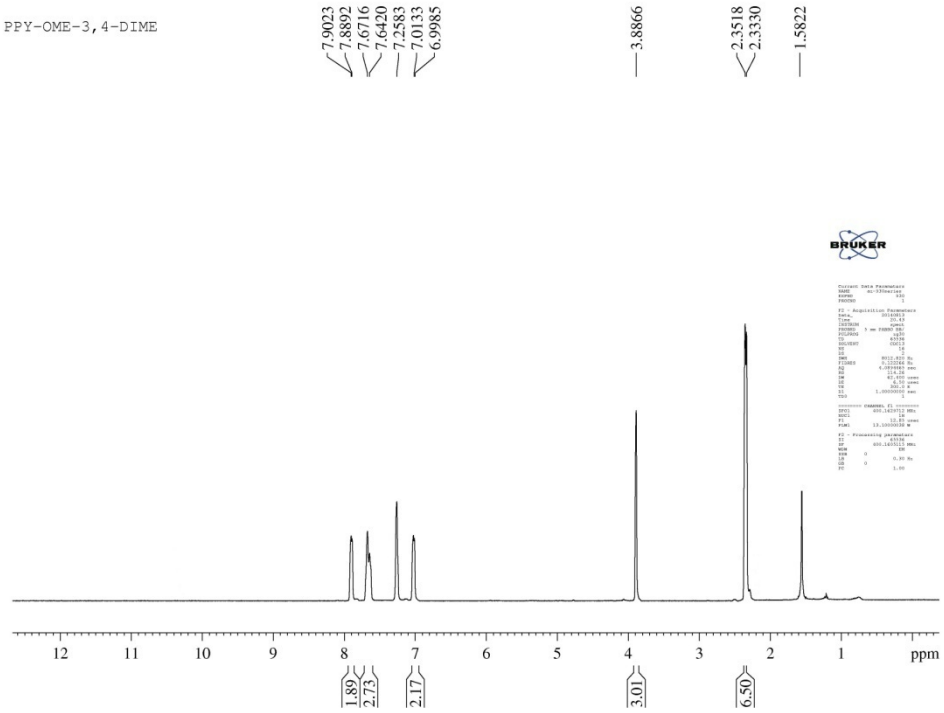
^{13}C NMR Spectra of (**3b)** (100 MHz, $CDCl_3$)



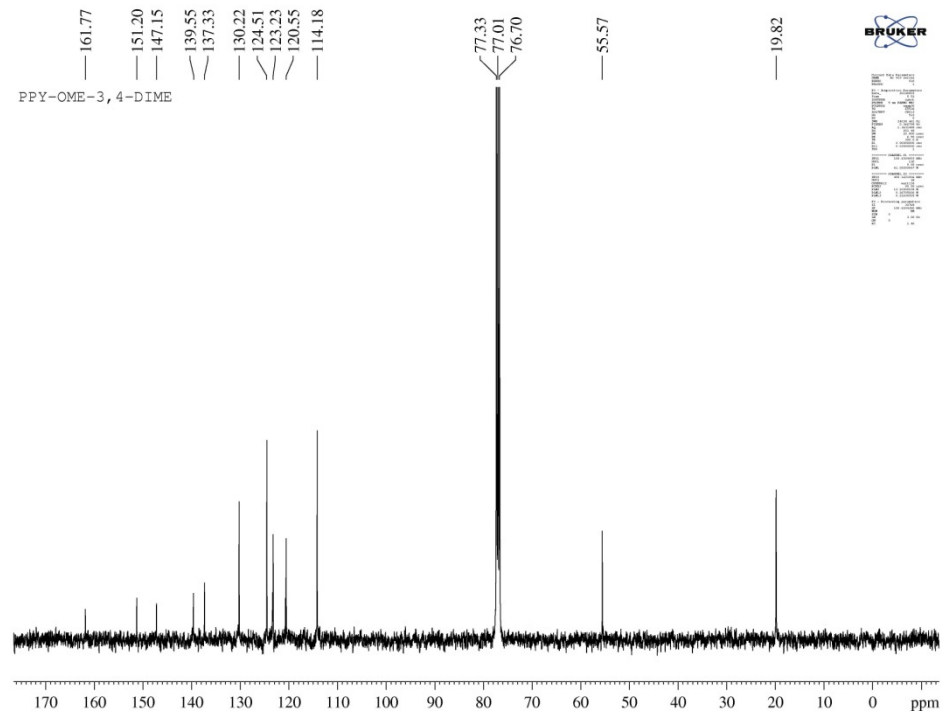
^{1}H NMR Spectra of (**3c)** (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of (**3c)** (100 MHz, $CDCl_3$)



^{1}H NMR Spectra of (**3d)** (400 MHz, $CDCl_3$)



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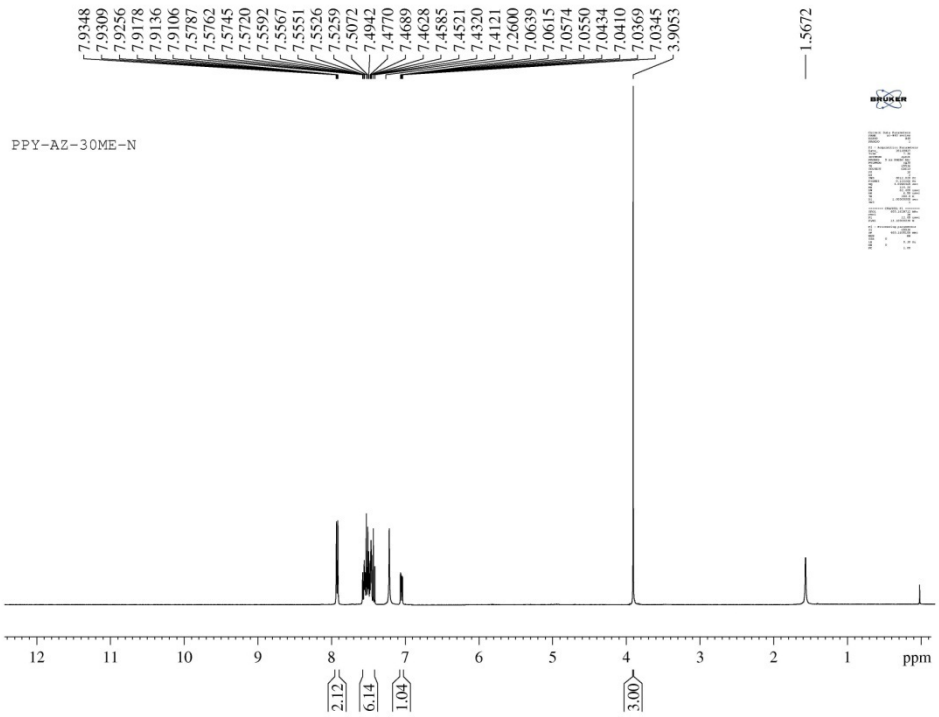

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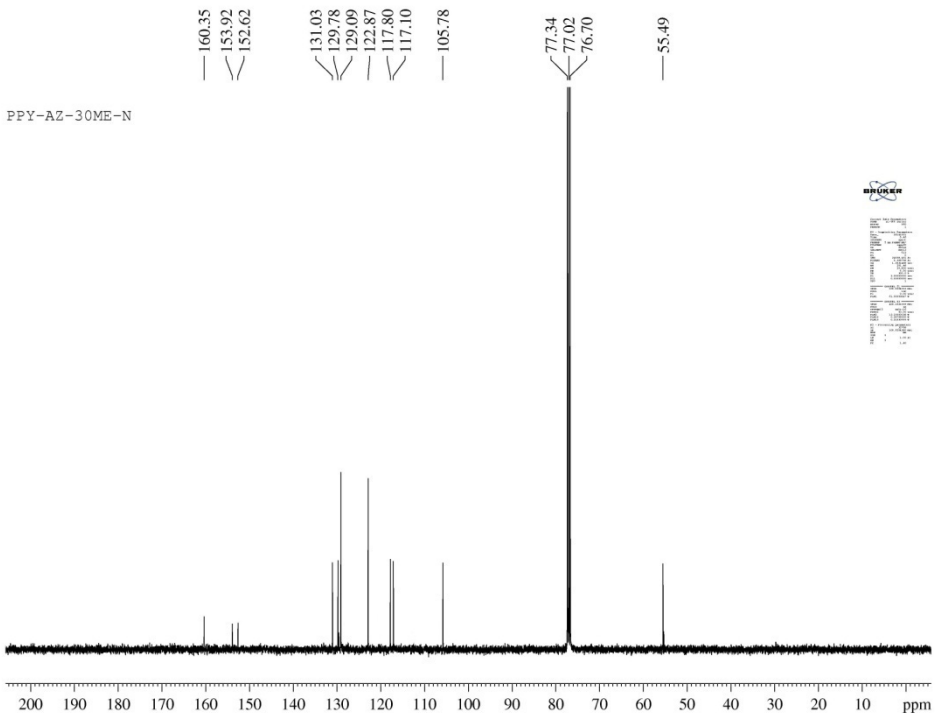

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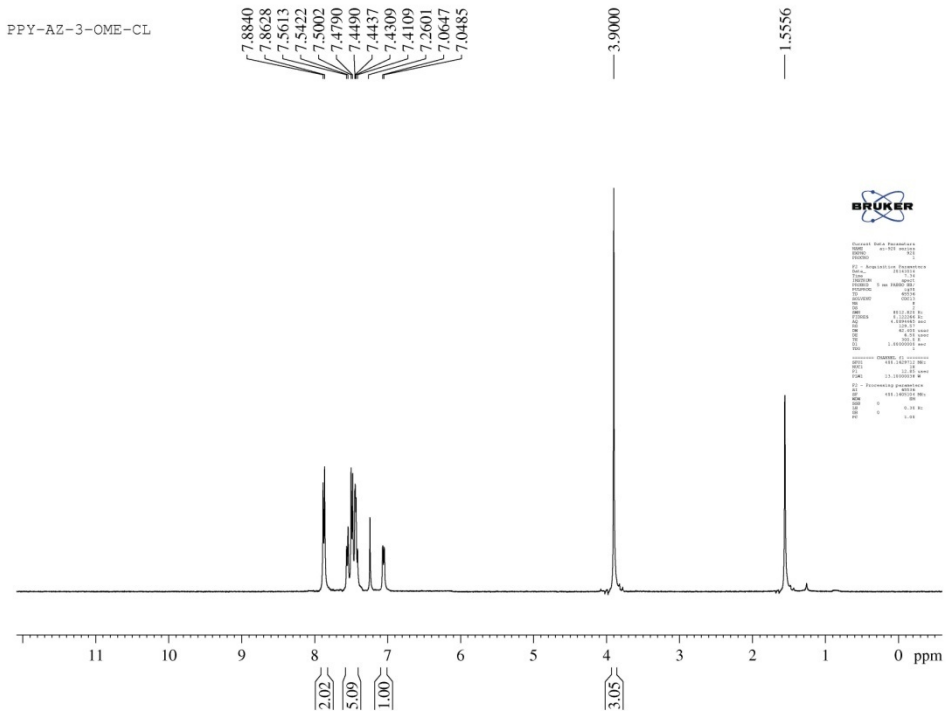
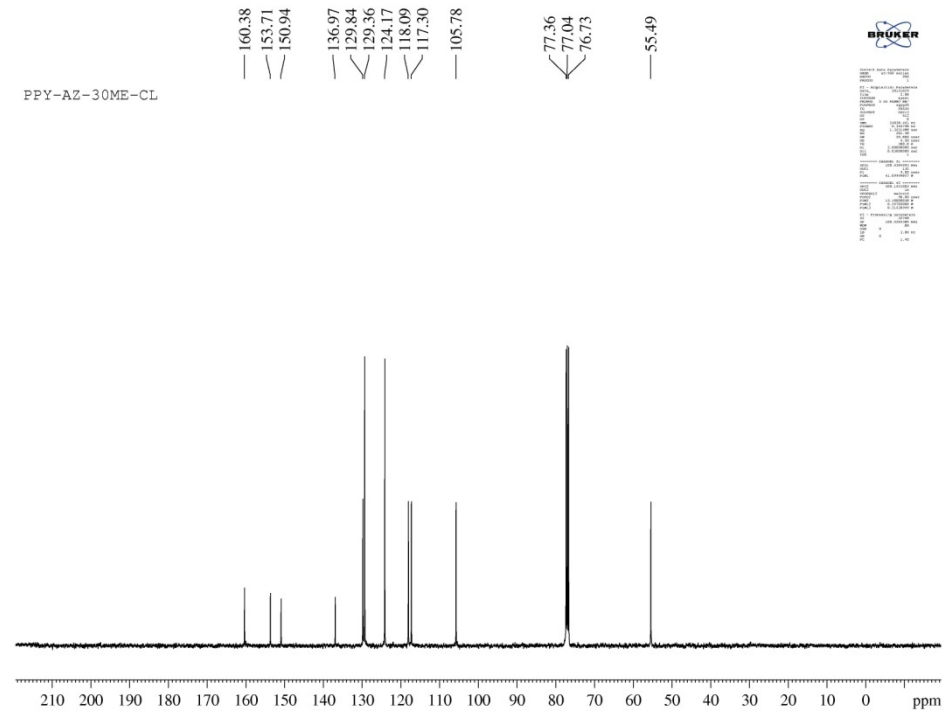


^{1}H NMR Spectra of (**3f)** (400 MHz, $CDCl_3$)



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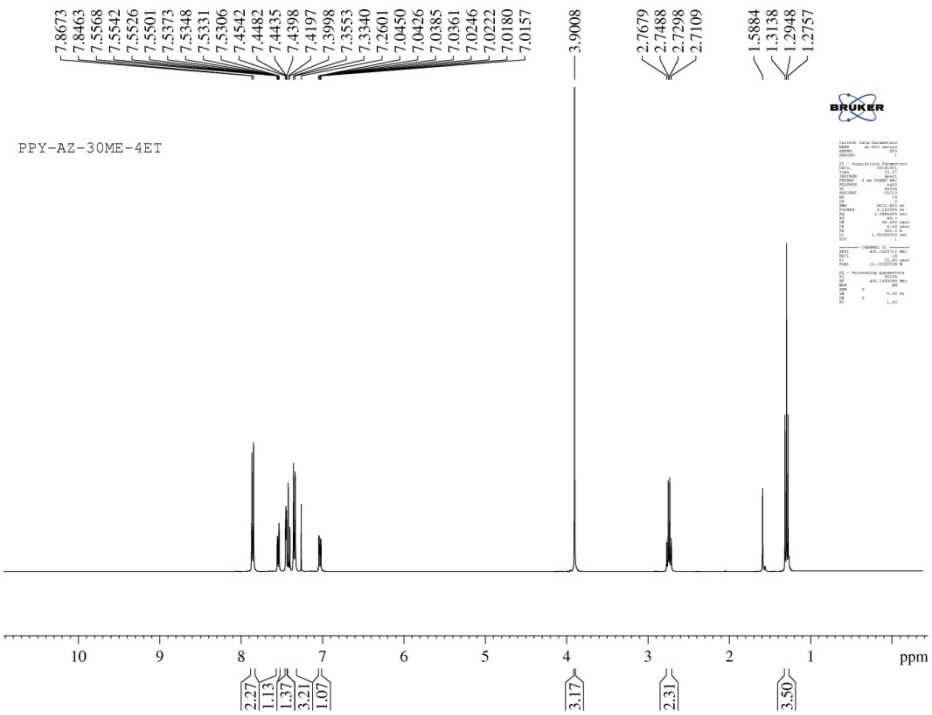
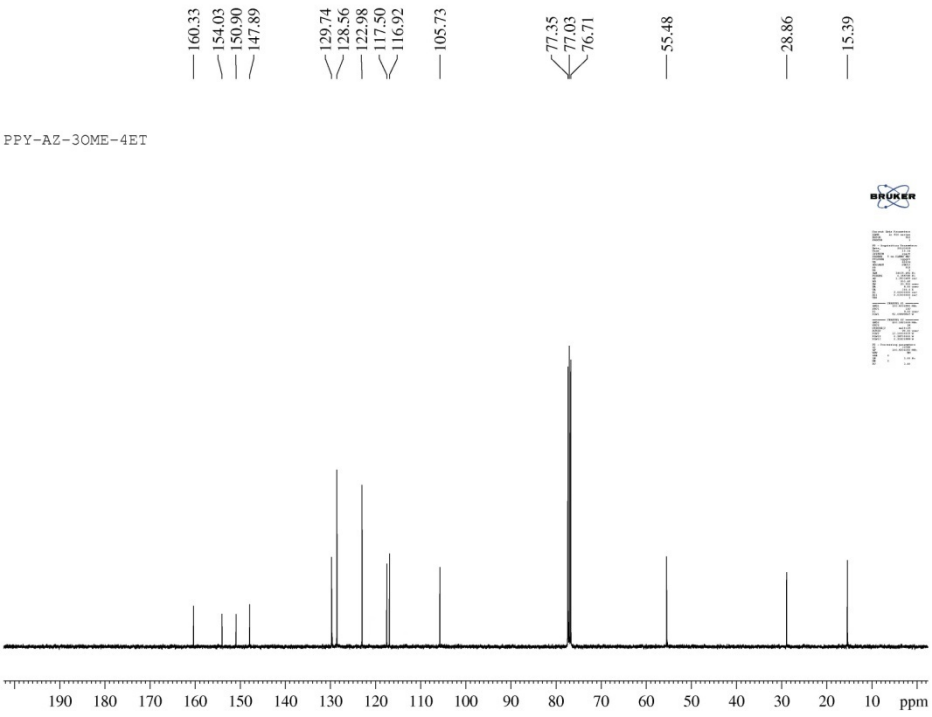


^{1}H NMR Spectra of (**3g)** (400 MHz, $CDCl_3$)



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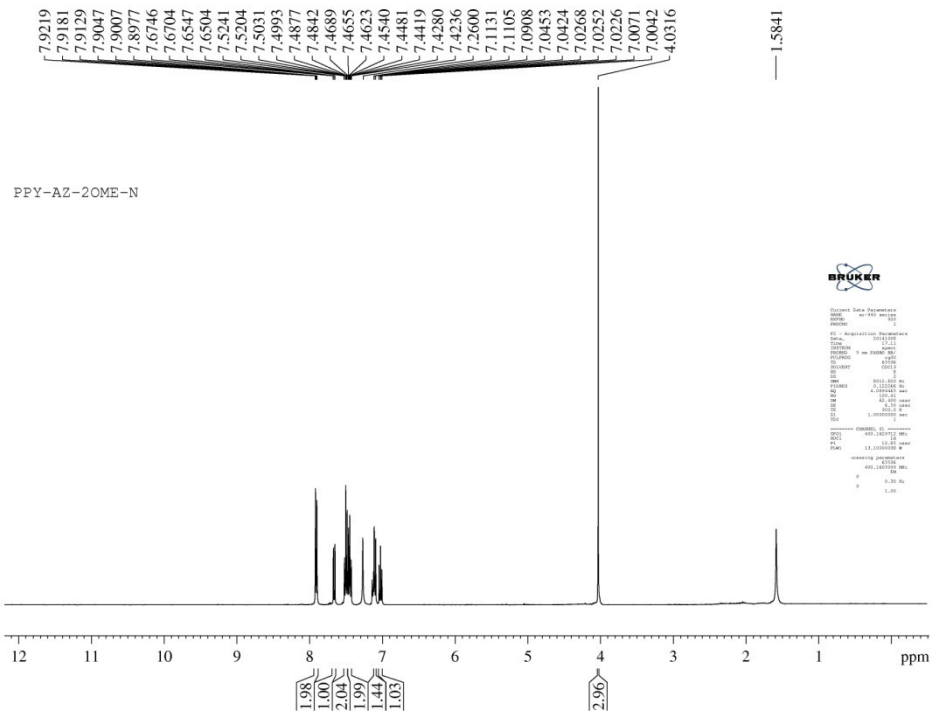
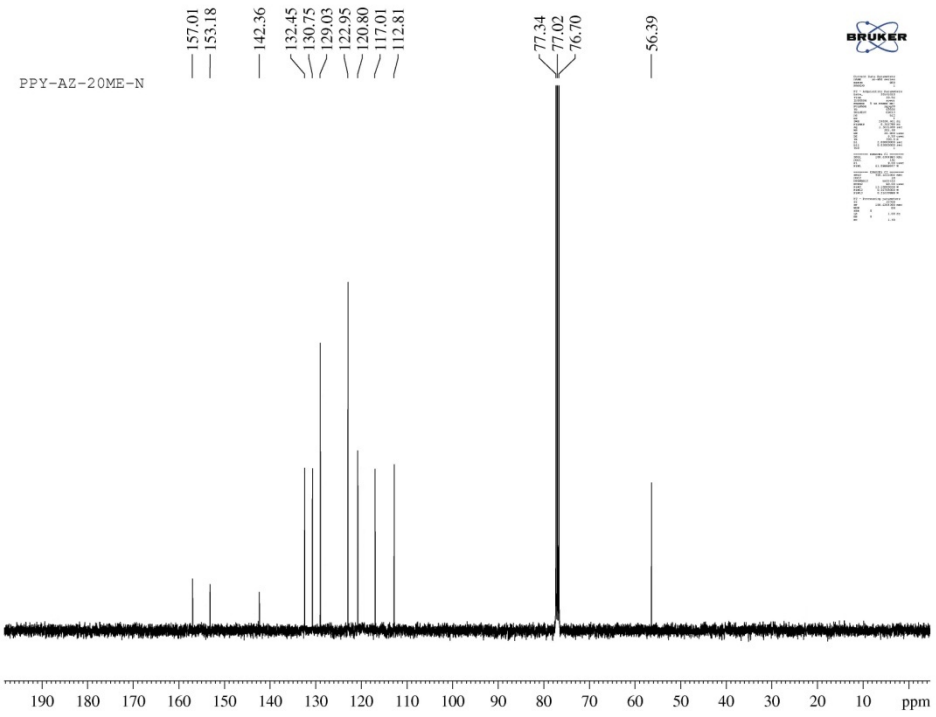


^{1}H NMR Spectra of (**3h)** (400 MHz, $CDCl_3$)



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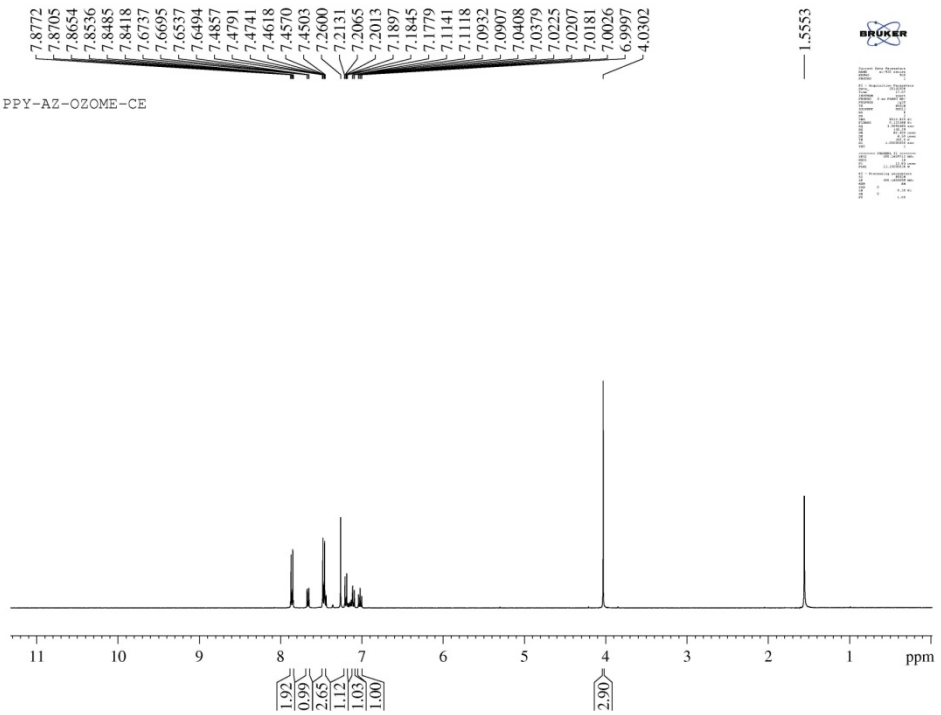
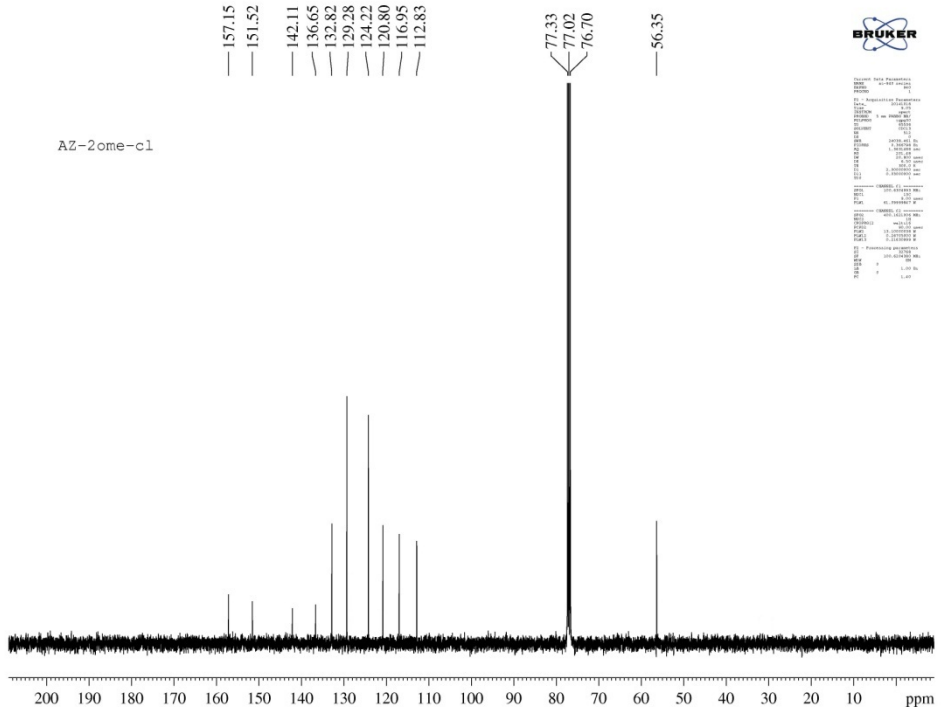


^{1}H NMR Spectra of (**3i)** (400 MHz, $CDCl_3$)



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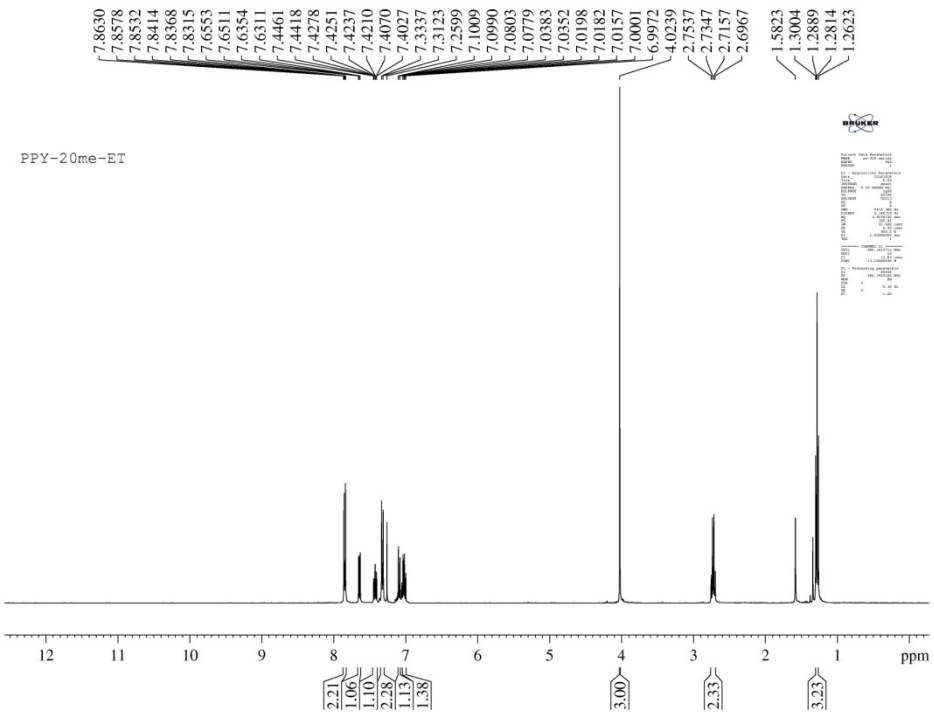

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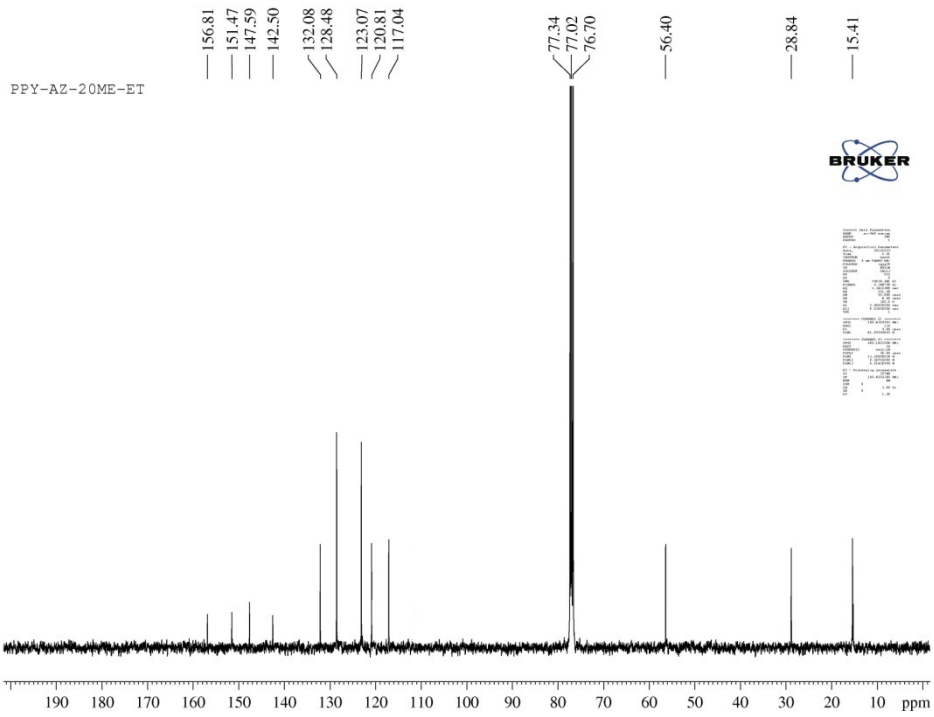

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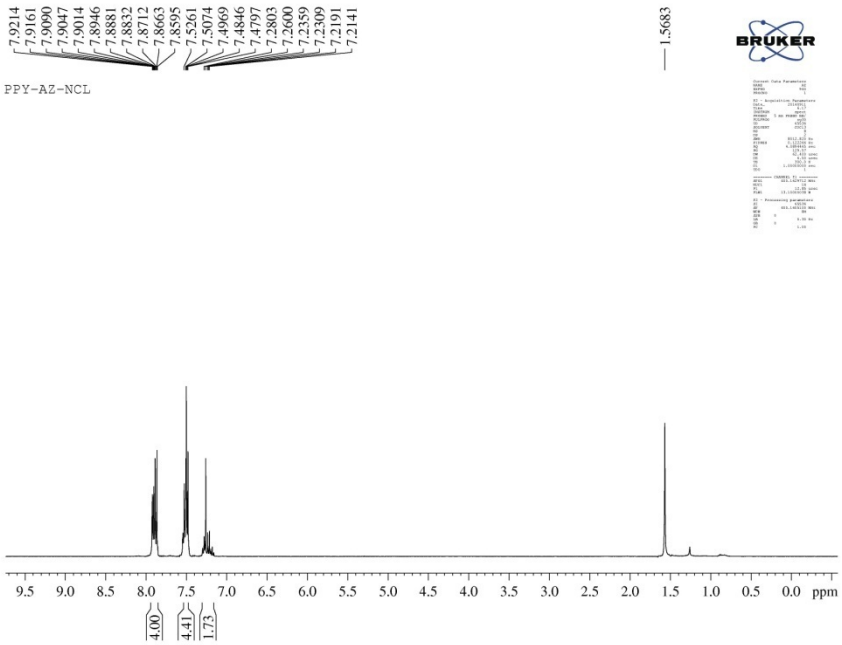

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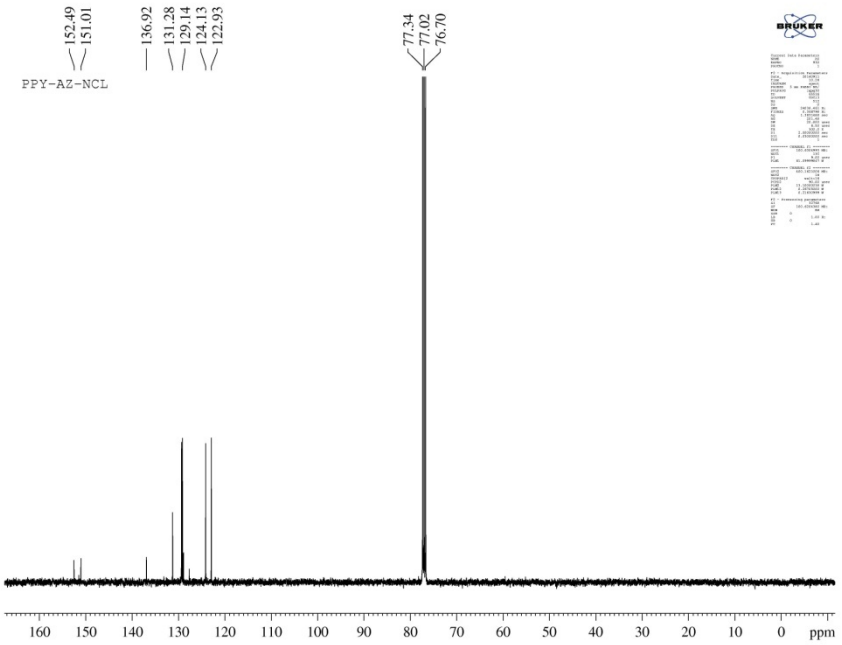

^{13}C NMR Spectra of (**3k)** (100 MHz, $CDCl_3$)