Supporting information

Gold and Palladium Supported on Ionic Liquid Modified Fe-based Metal–Organic Framework (MOF) as Highly Efficient Catalysts for Reduction of Reduction of Nitrophenols, Dyes and Sonogashira-Hagihara Reactions

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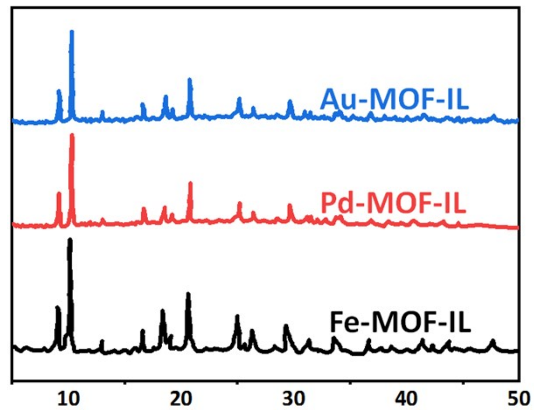


Figure S 1. XRD pattern dates of Fe-MOF-IL, Au@Fe-MOF-IL and Pd@Fe-MOF-IL.

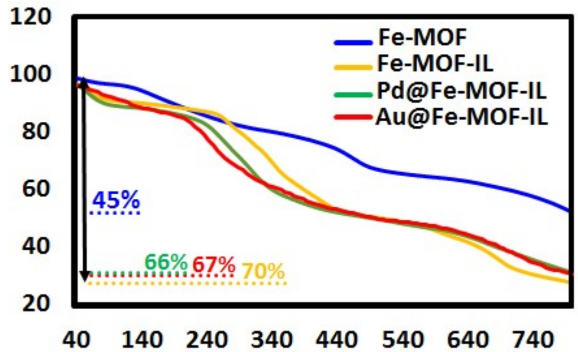


Figure S 2. TGA analysis of Fe-MOF, Fe-MOF-IL, Au@Fe-MOF-IL, and Pd@Fe-MOF-IL.

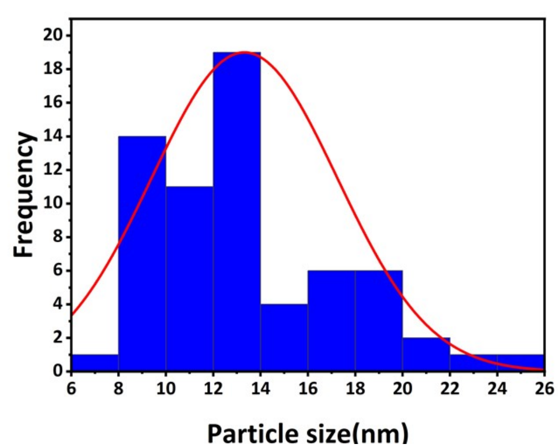


Figure S 3. Statistical analysis of the size distribution of Au NPs in Au@ Fe-MOF-IL catalyst.

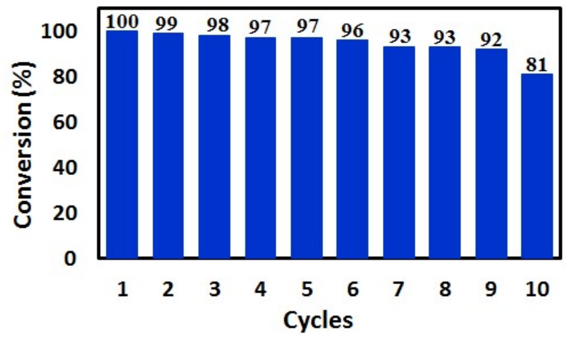
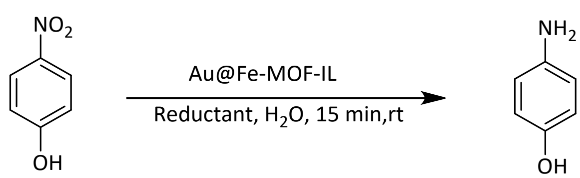


Figure S 4. Recycling of Au@Fe-MOF-IL in *p*-nitrophenol reduction.

1. Optimization tables and kinetic results

Table S 1. Optimization of 4-NP reduction reactions by different reducing agents in the presence of Au@Fe-MOF-IL catalyst[a].



Entry	Reductant	Yield (%)
1	Glycerol	7
2	Hydrazine	13
3	Formic acid	5
4	$NaBH_4$	99

[a]Reaction condition: 4-Nitro phenol (0.2 mmol), $NaBH_4$ (1 mmol), catalyst (6 mg Au@Fe-MOF-IL containing 0.033 mol% Au) in H_2O (1.5 mL) at room temperature.

Table S 2. Kinetic information of nitrophenol isomers reduction reactions calculated of UV-Vis spectrum (e.g. Conversion, reaction time, K_{app} and K_{nor}).

Entry	Sample	Conversion (%)	K_{app} (s^{-1})	K_{nor} ($g^{-1}s^{-1}$)	t (s)
1	*p*-nitrophenol	100	5.4×10^{-3}	5.4	120
2	*m*-nitrophenol	96	3.3×10^{-3}	3.3	30
3	*o*-nitrophenol	97	1.6×10^{-3}	1.6	120

Table S 3. Kinetic information of organic dyes (MB, MO, and MR) reduction reactions calculated of UV-Vis spectrum (e.g. Conversion, reaction time, K_{app} and K_{nor}).

Entry	Sample	Conversion (%)	K_{app} (s^{-1})	K_{nor} ($g^{-1}s^{-1}$)	t (s)
1	Methylene blue	92	1.46×10^{-2}	14.6	30
2	Methyl orange	90	5.6×10^{-3}	5.6	45
3	Methyl red	100	7×10^{-3}	7	300

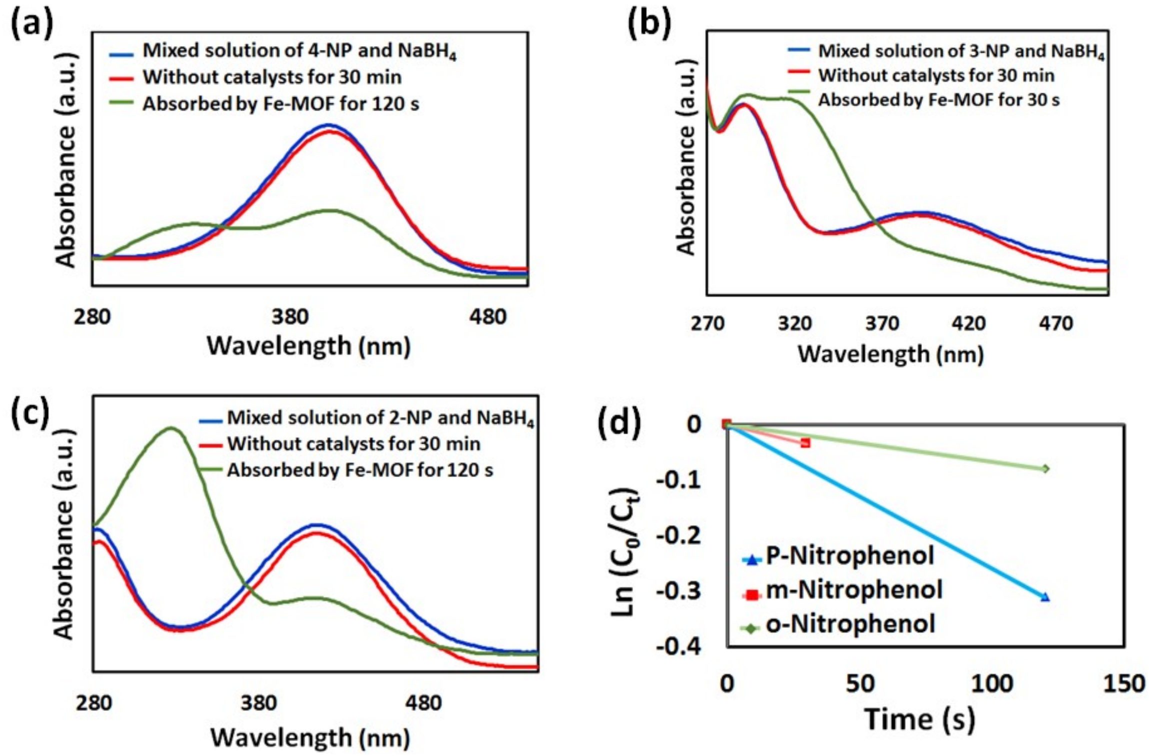


Figure S 5. UV–Vis spectra of original nitrophenol isomer solutions, and their spectra after adsorption by $NaBH_4$ for 30 min and after adsorption by 1.0 mg of Fe-MOF-IL for 120 s.

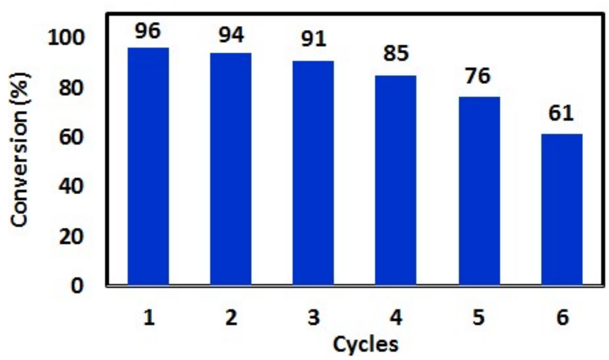


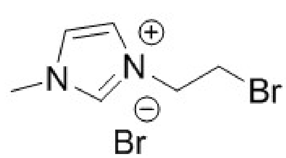
Figure S 6. Recycling of Pd@Fe-MOF-IL in Sonogashira-Hagihara cross-coupling reaction.

Table S 4. Non-exhaustive survey of catalytic performance of some Au-based catalysts reported for 4-NP reduction reaction with $NaBH_4$.

Catalyst	K_{app} ($\times$ 10^{-3} s^{-1})	Time (s)	Ref.
Au@Fe-MOF-IL	5.4	120	This work
Fe_3O_4@COF-Au	3.70	960	J. Mater. Chem. A, 2019 [99]
YC7@AuNPBump	3.50	660	Biomacromolecules, Lee2018 [100]
YC7@AuNPPhed	4.20	420	Biomacromolecules, Lee2018 [100]
p(AAm-co-TMT)@Au	2.30	660	Applied Catalysis B: Environmental, 2019 [101]
Au/OMS composite	0.97	3600	J. Am. Chem. Soc., 2011 [102]
Au-PDA/RGO	2.00	960	Applied Catalysis B: Environmental, 2016 [103]
Au10-JP	1.17	1080	ChemistrySelect, 2019 [104]

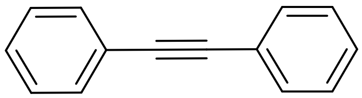
2. Compounds characterization

1-(2-bromoethyl)-3-methylimidazollium bromide ionic liquid (IL):



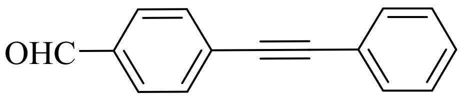
^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 9.42 (s, 1H), 7.96 (s, 1H), 7.85 (s, 1H), 4.68 (t, *J*= 5.8 Hz, 2H), 4.00 (t, *J*= 5.8 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm): 137.60, 137.44, 124.24, 124.13, 122.89, 122.83, 50.53, 36.56, 36.30, 32.16.

1,2-Diphenylethyne [1]:



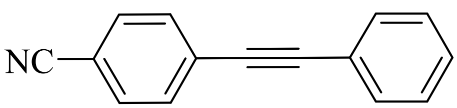
^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm): 7.63-7.58 (m, 4H), 7.45-7.37 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ(ppm): 131.75, 131.61, 128.34, 123.31, 89.45.

4-(Phenylethynyl)benzaldehyde [2]:



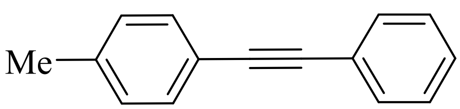
^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm): 10.06 (s, 1H), 7.90 (d, *J*= 8.3 Hz, 2H), 7.71 (d, *J*= 8.3 Hz, 2H), 7.62-7.57 (m, 2H), 7.43-7.40 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ(ppm): 191.49, 135.43, 132.19, 132.09, 131.90, 131.76, 129.65, 128.45, 122.52, 93.49, 88.55.

4-(Phenylethynyl)benzonitrile [3]:



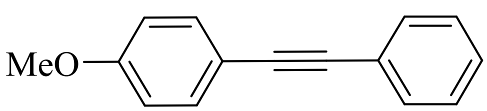
^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm): 7.68-7.62 (m, 4H), 7.61-7.56 (m, 2H), 7.45-7.40 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ(ppm): 132.19, 132.11, 132.04, 131.92, 131.77, 128.27, 122.24, 118.62, 111.48, 93.83, 87.78.

1-Methyl-4-(phenylethynyl)benzene [1]:



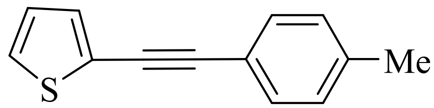
^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm): 7.61-7.57 (m, 2H), 7.49 (d, *J*= 8.1 Hz, 2H), 7.42-7.37 (m, 3H), 7.21 (d, *J*= 7.8 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ(ppm): 138.43, 131.64, 131.48, 129.25, 129.08, 128.27, 123.52, 120.23, 89.61, 88.77, 21.48.

1-Methoxy-4-(phenylethynyl)benzene [4]:



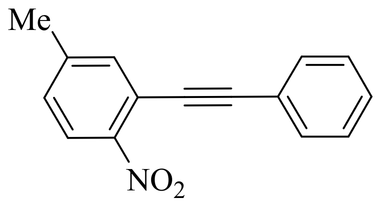
^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm): 7.57-7.55 (m, 2H), 7.52 (d, *J*= 8.9 Hz, 2H), 7.40-7.35 (m, 3H), 6.92 (d, *J*= 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) (ppm): δ 159.65, 133.16, 133.02, 131.41, 123.62, 115.41, 114.12, 113.94, 89.40, 88.10, 55.22.

2-(P-tolylethynyl)thiophene [5]:



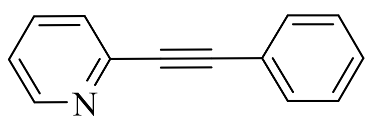
[1]H NMR (400 MHz, Chloroform-*d*) δ(ppm): 7.46 (d, *J*= 8.1 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.20 (d, *J*= 7.9 Hz, 2H), 7.07 – 7.03 (m, 1H), 2.41 (s, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ(ppm): 138.66, 131.70, 131.36, 129.20, 127.08, 127.02, 123.60, 119.87, 93.27, 81.98, 21.58.

4-Methyl-1-nitro-2-(phenylethynyl)benzene [6]:



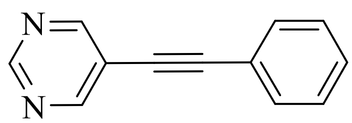
[1]H NMR (400 MHz, Chloroform-*d*) δ(ppm): 8.13 (s, 1H), 8.06 (d, *J*= 10.8 Hz, 1H), 7.64 (d, *J*= 8.5 Hz, 1H), 7.61-7.58 (m, 2H), 7.45-7.40 (m, 3H), 2.63 (s, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ(ppm): 146.87, 141.74, 132.36, 131.87, 131.72, 130.07, 128.52, 124.31, 122.38, 120.90, 98.57, 86.70, 20.82.

2-(Phenylethynyl)pyridine [2]:



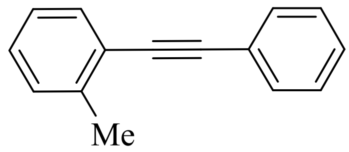
[1]H NMR (400 MHz, Chloroform-*d*) δ(ppm): 8.65 (dd, *J*= 4.9, 2.8 Hz, 1H), 7.73-7.68 (m, 1H), 7.65-7.62 (m, 2H), 7.56 (dd, *J*= 7.9, 1.1 Hz, 1H), 7.41-7.38 (m, 3H), 7.29-7.25 (m, 1H). [13]C NMR (100 MHz, Chloroform-*d*) δ(ppm): 150.05, 143.51, 136.24, 132.15, 132.02, 128.34, 127.13, 122.70, 122.29, 89.24, 88.65.

5-(Phenylethynyl)pyrimidine [7]:



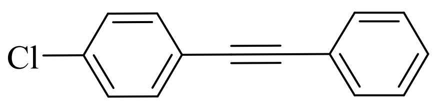
[1]H NMR (400 MHz, Chloroform-*d*) δ (ppm): 9.28 (s, 1H), 8.86 (s, 2H), 7.61-7.58 (m, 2H), 7.45-7.41 (m, 3H). [13]C NMR (100 MHz, Chloroform-*d*) δ(ppm): 158.67, 156.71, 131.82, 129.42, 128.60, 121.88, 121.77, 96.37, 82.64.

1-Methyl-2-(phenylethynyl)benzene [2]:



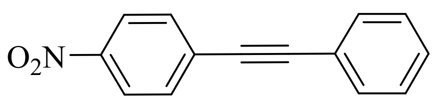
^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm): 7.63-7.61 (m, 3H), 7.46-7.39 (m, 3H), 7.32-7.24 (m, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ(ppm): 140.27, 132.60, 131.93, 131.60,129.57, 129.31, 128.55, 128.41, 125.69, 121.87, 93.45, 88.47, 20.85.

1-Chloro-4-(phenylethynyl)benzene [1]:



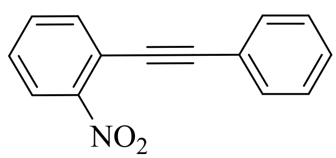
^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm): 7.58-7.55 (m, 2H), 7.50 (d, *J*= 8.7 Hz, 2H), 7.41-7.38 (m, 3H), 7.36 (d, *J*= 8.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm): 134.29, 132.84, 131.64, 128.73, 128.53, 128.43, 122.96, 121.81, 90.36, 88.27.

1-Nitro-4-(phenylethynyl)benzene [8]:



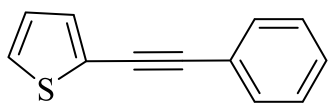
^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm): 8.26 (d, *J*= 16.1, 2H), 7.72 (d, *J*= 12.7 Hz, 2H), 7.61-7.59 (m, 2H), 7.44-7.42 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ(ppm): 147.01, 132.31, 131.88, 130.30, 129.32, 128.58, 123.68, 122.12, 94.74, 87.57.

1-Nitro-2-(phenylethynyl)benzene [8]:



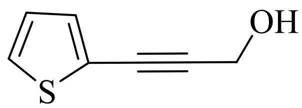
^{1}H NMR (400 MHz, Chloroform-*d*) δ(ppm): 8.13 (d, *J*= 7.8 Hz, 1H), 7.75 (d, *J*= 8.6 Hz, 1H), 7.65-7.62 (m, 3H), 7.50 (t, *J*= 7.8 Hz, 1H), 7.44-7.40 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ(ppm): 149.55, 134.52, 132.77, 131.98, 129.20, 128.48, 128.42, 124.69, 122.33, 118.73, 97.09, 84.72.

2-(Phenylethynyl)thiophene [8]:



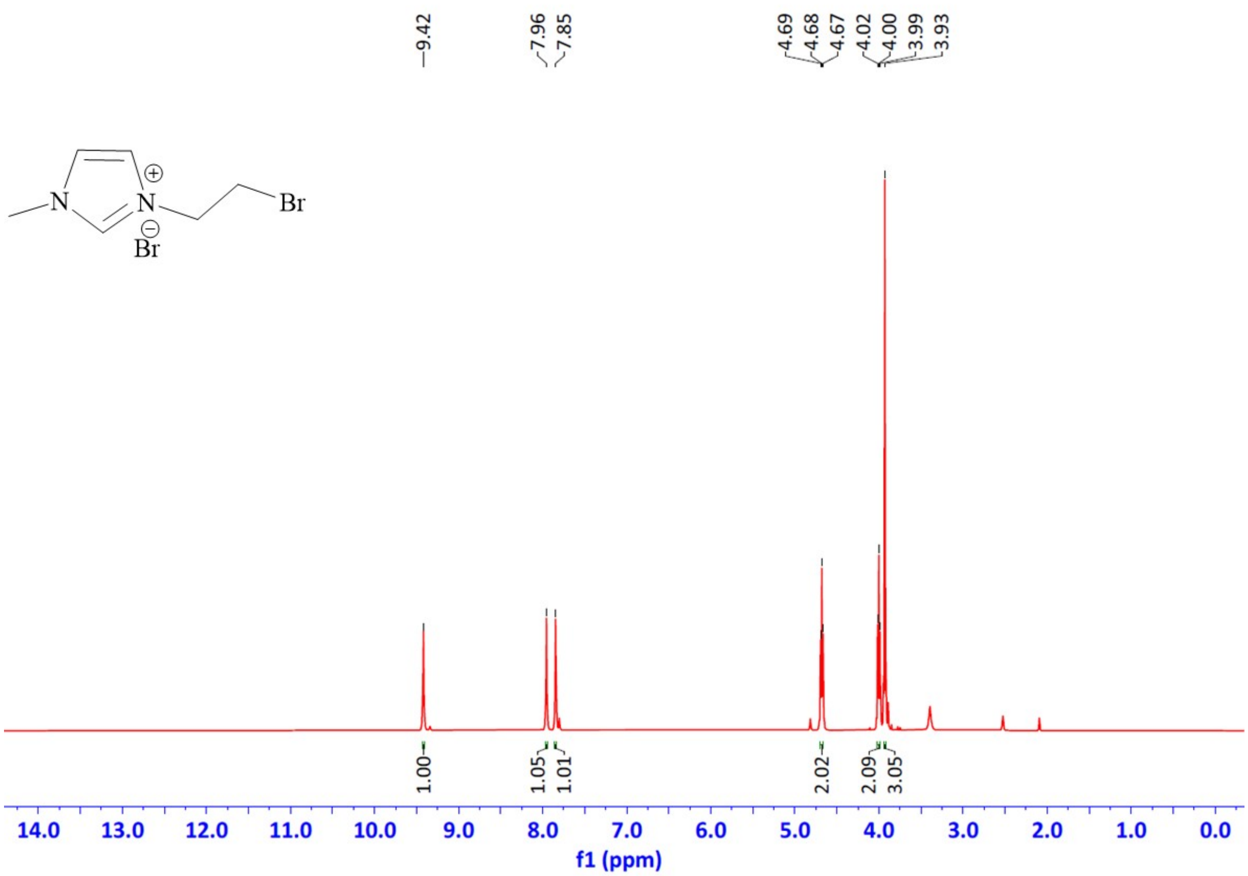
^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm): 7.59-7.55 (m, 2H), 7.42-7.38 (m, 3H), 7.34-7.32 (m, 2H), 7.06 (dd, *J*= 4.9, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm): 132.52, 131.90, 131.35, 129.25, 128.46, 128.41, 127.29, 127.14, 93.07, 82.64.

3-(Thiophen-2-yl)prop-2-yn-1-ol [9]:

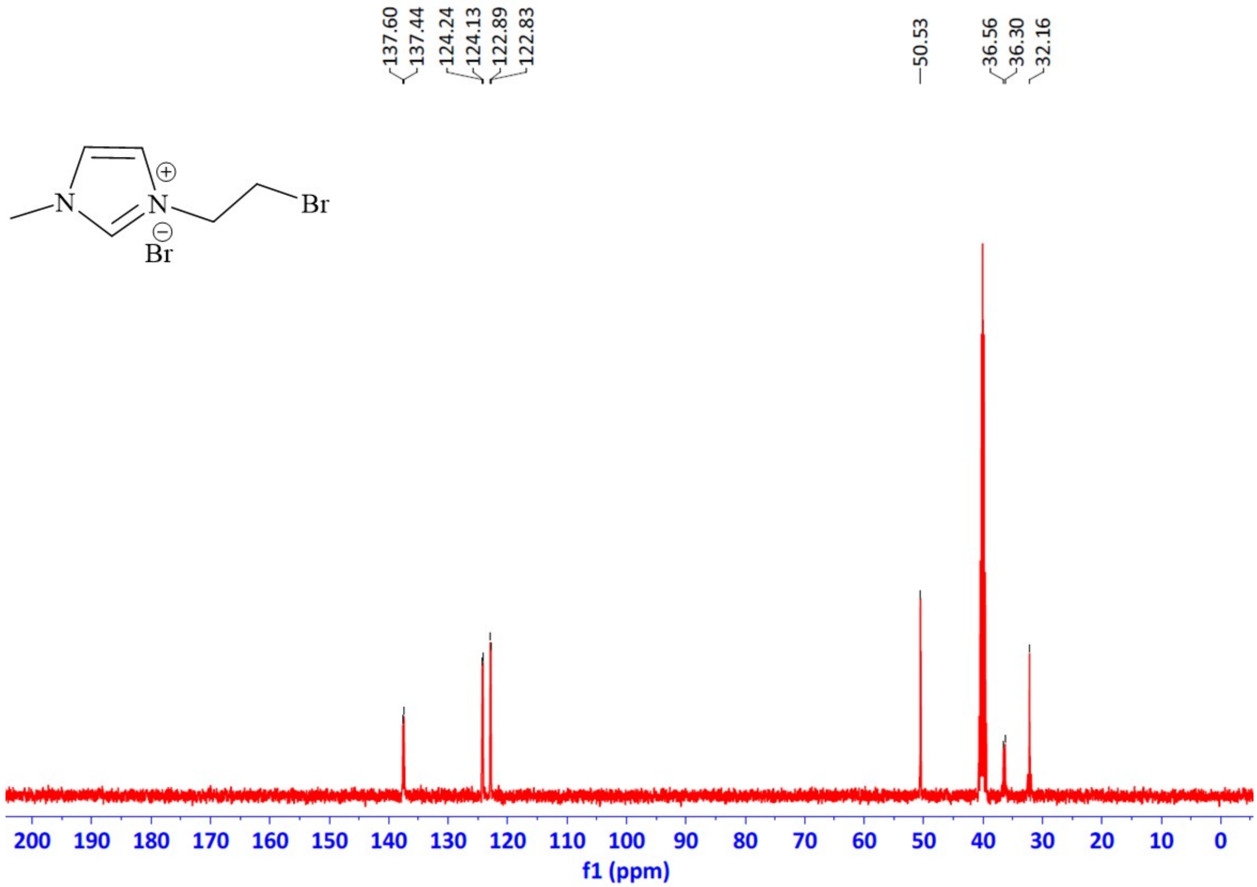


[1]H NMR (400 MHz, Chloroform-*d*) δ (ppm): 7.30 (dd, *J*= 5.2, 1.2 Hz, 1H), 7.25 (dd, *J*= 3.7, 1.2 Hz, 1H), 7.01 (dd, *J*= 5.2, 3.6 Hz, 1H), 4.54 (s, 2H), 1.85 (s, 1H). [13]C NMR (100 MHz, Chloroform-*d*) δ (ppm): 132.44, 127.50, 127.01, 122.42, 91.13, 79.10, 51.78.

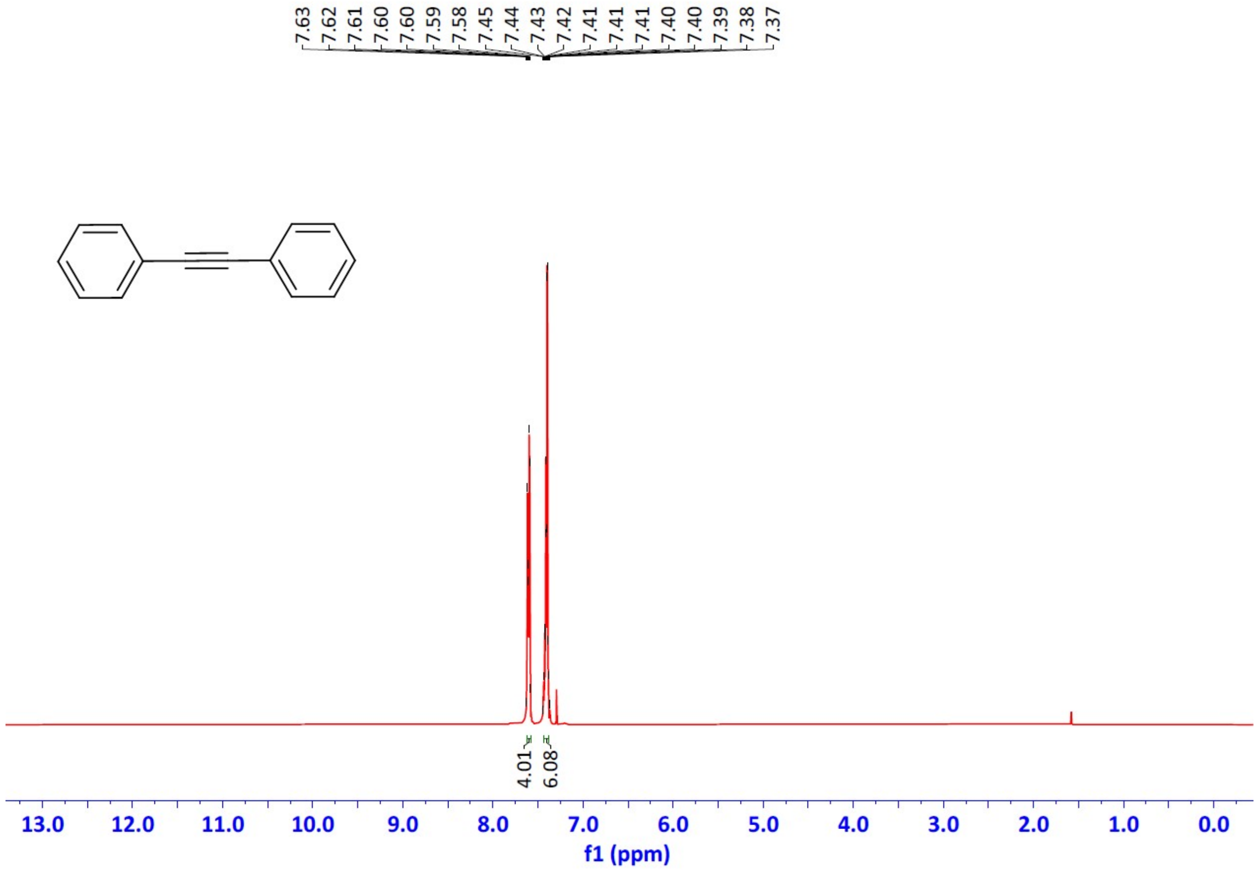
3. Copy of Original [1] H NMR and [13] C NMR spectra



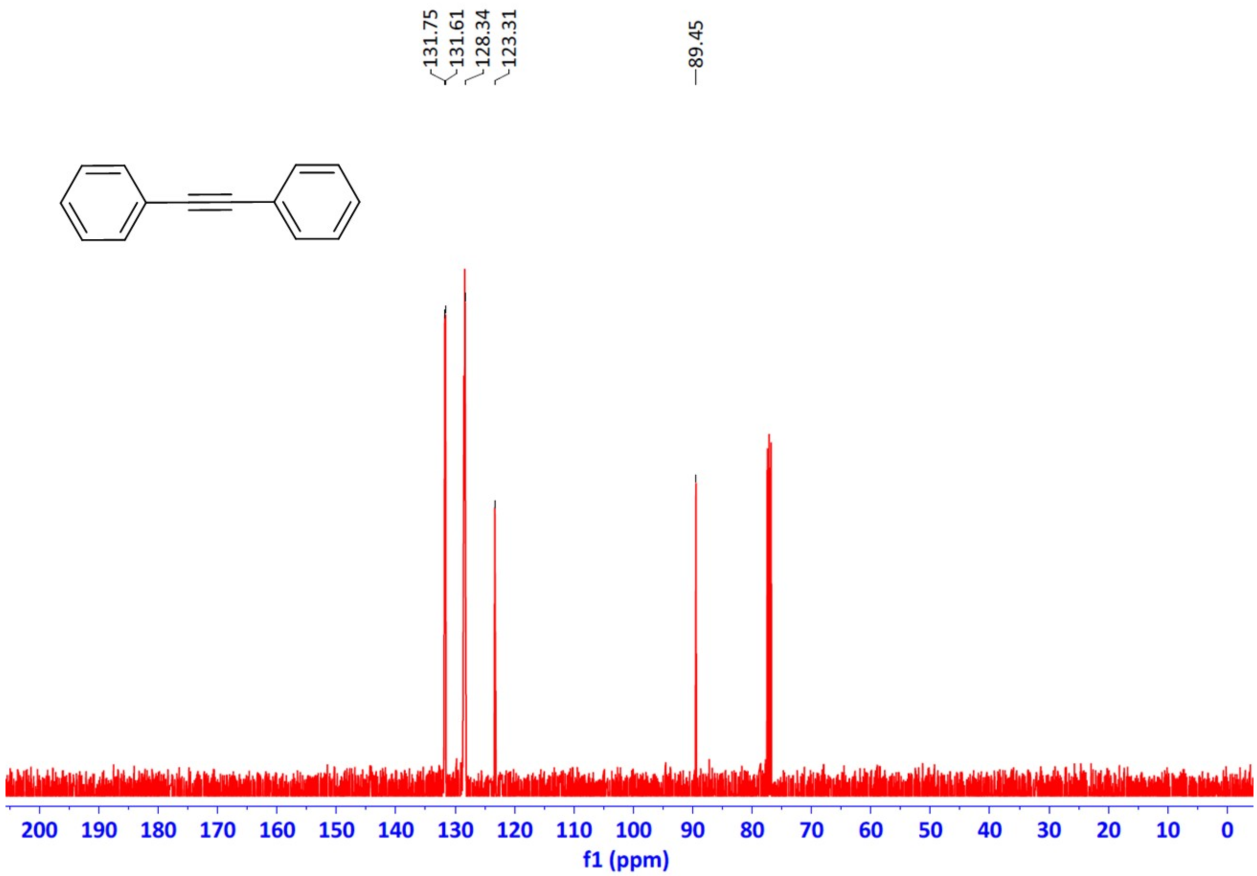
[1]H NMR of 1-(2-bromoethyl)-3-methylimidazollium bromide ionic liquid (IL)



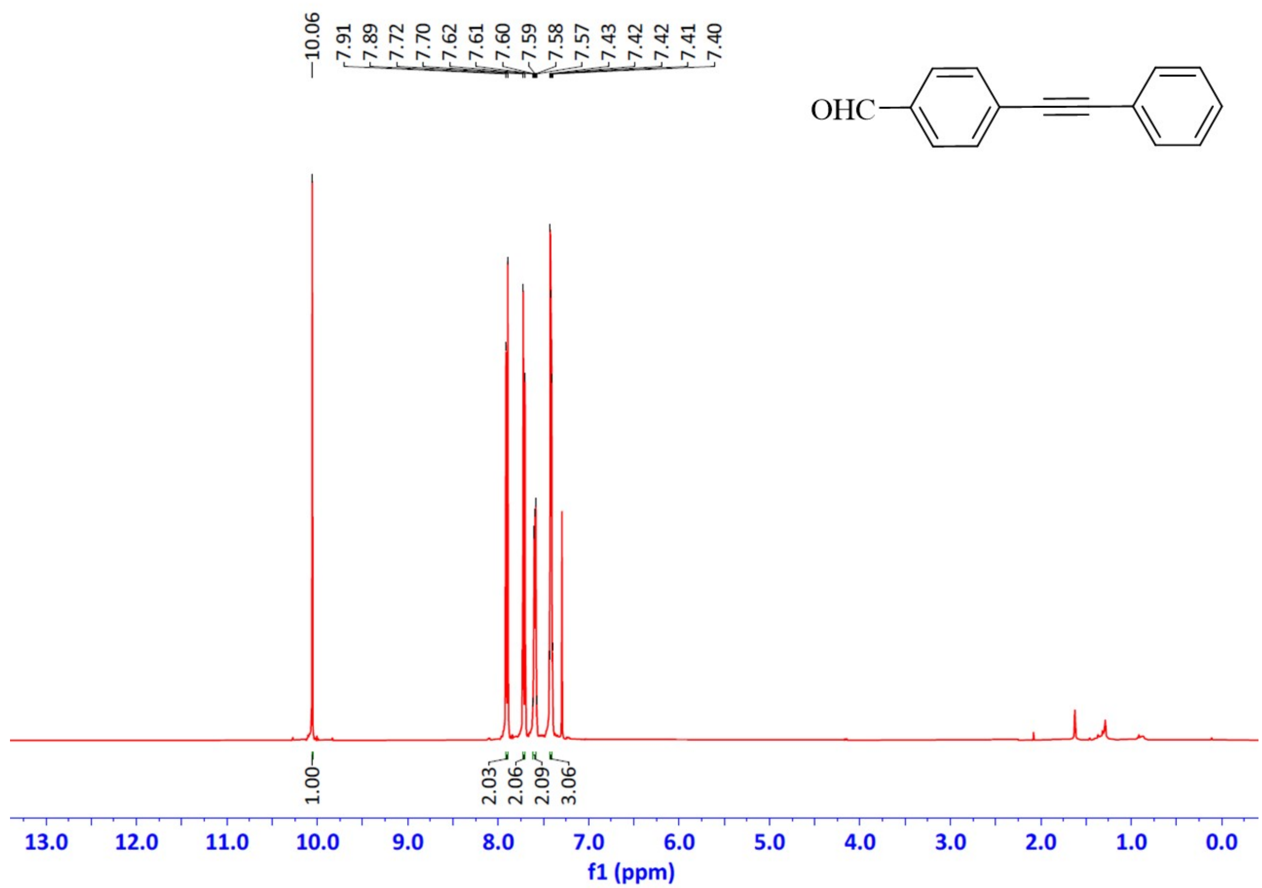
^{13}C NMR of 1-(2-bromoethyl)-3-methylimidazollium bromide ionic liquid (IL)



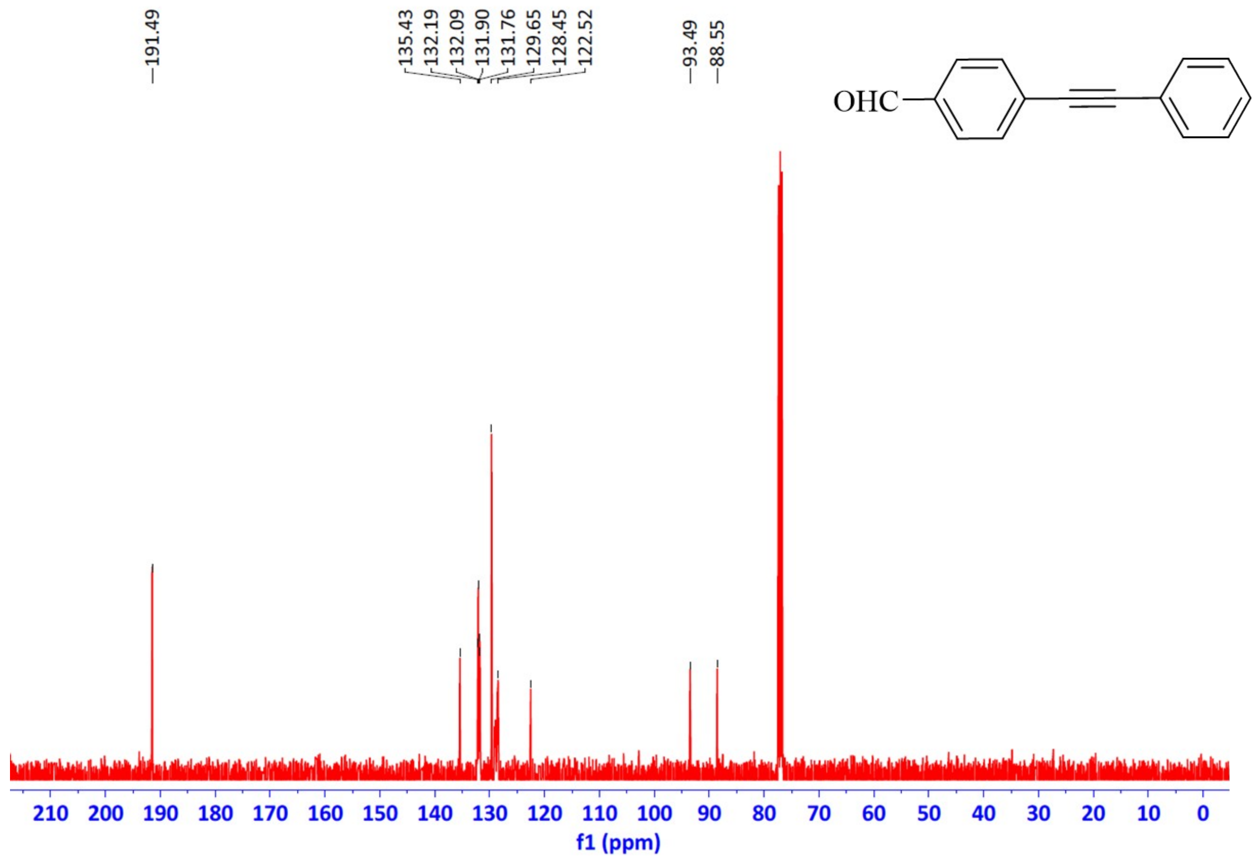
^{1}H NMR of 1,2-diphenylethyne



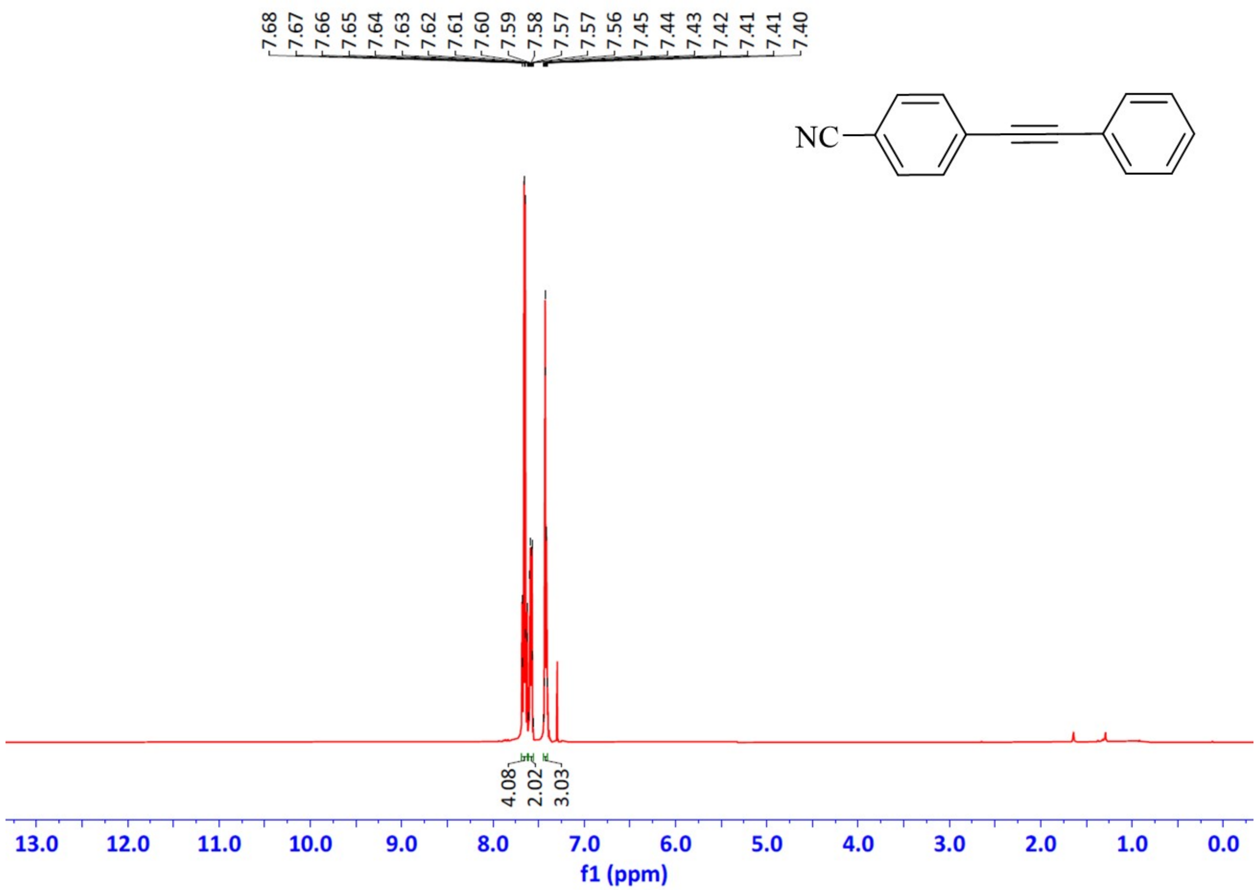
^{13}C NMR of 1,2-diphenylethyne



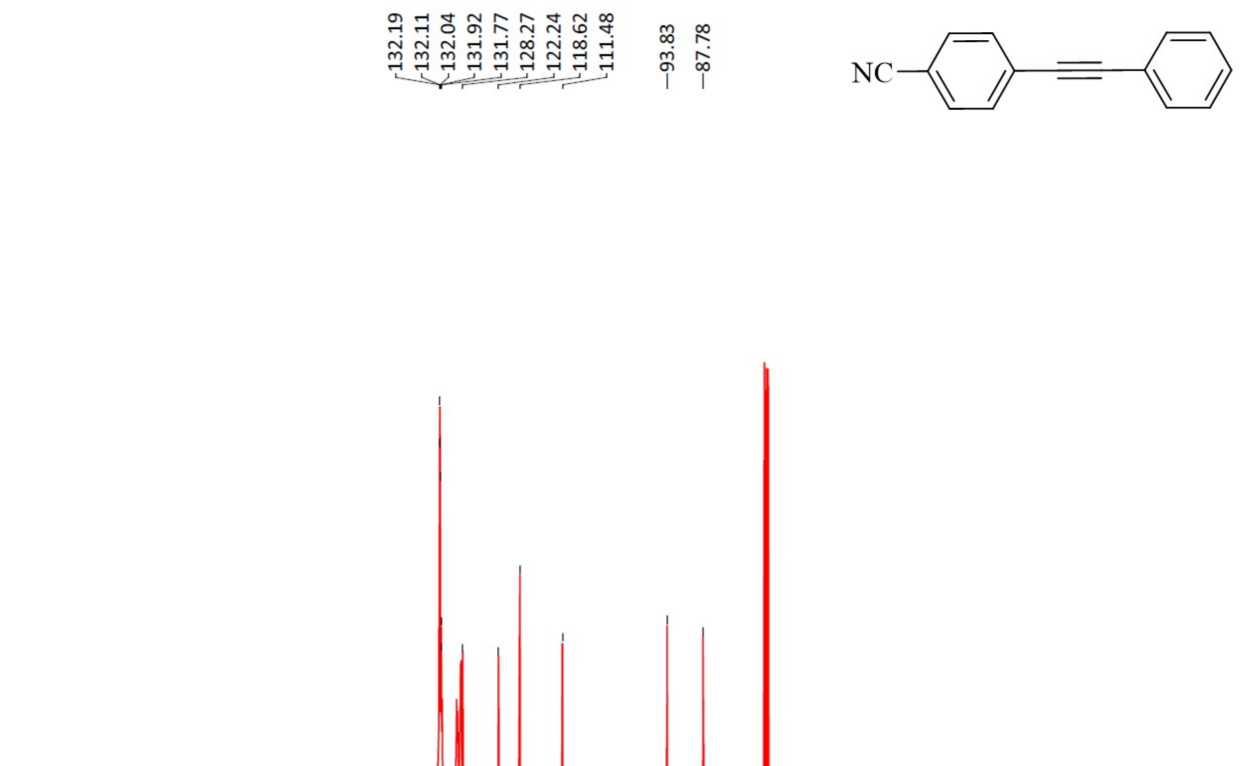
^1H NMR of 4-(phenylethynyl)benzaldehyde



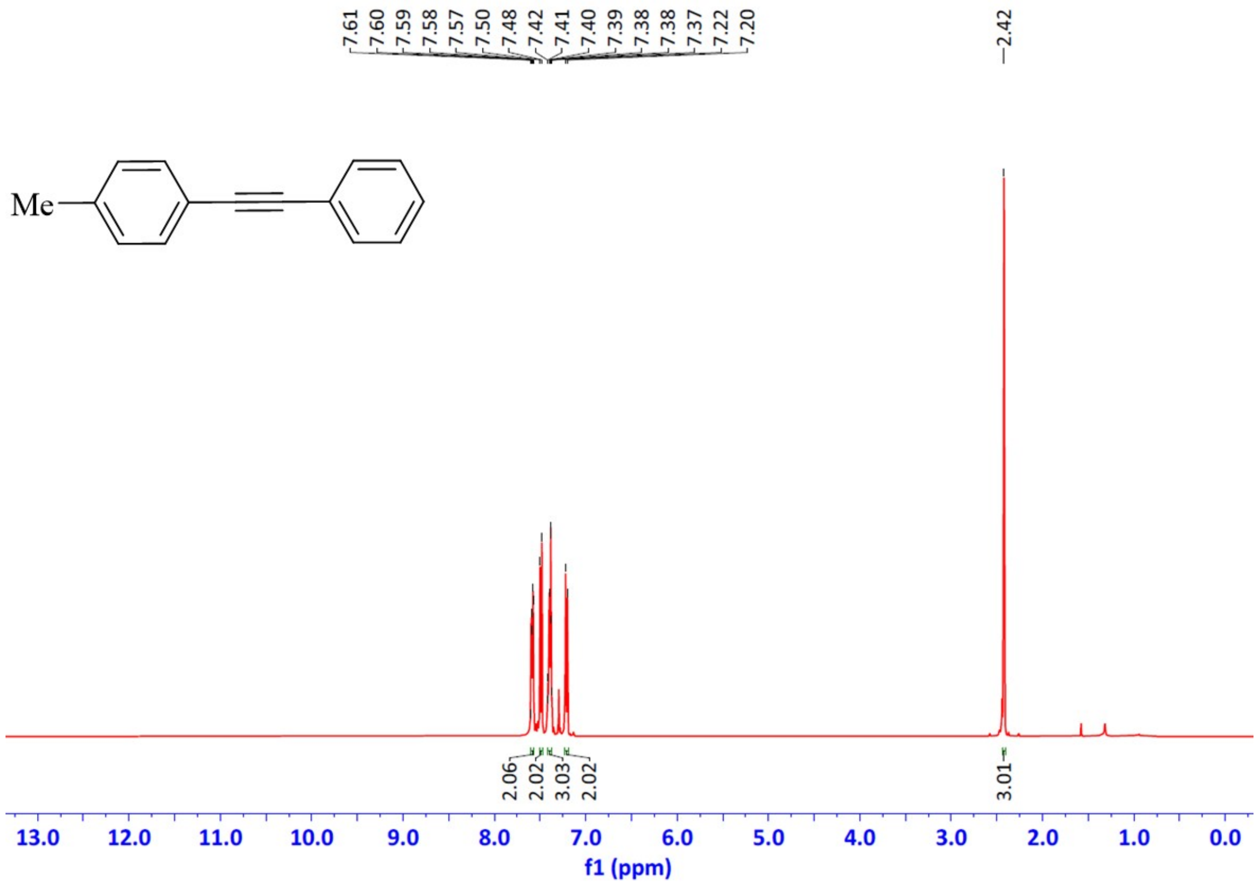
^{13}C NMR of 4-(phenylethynyl)benzaldehyde



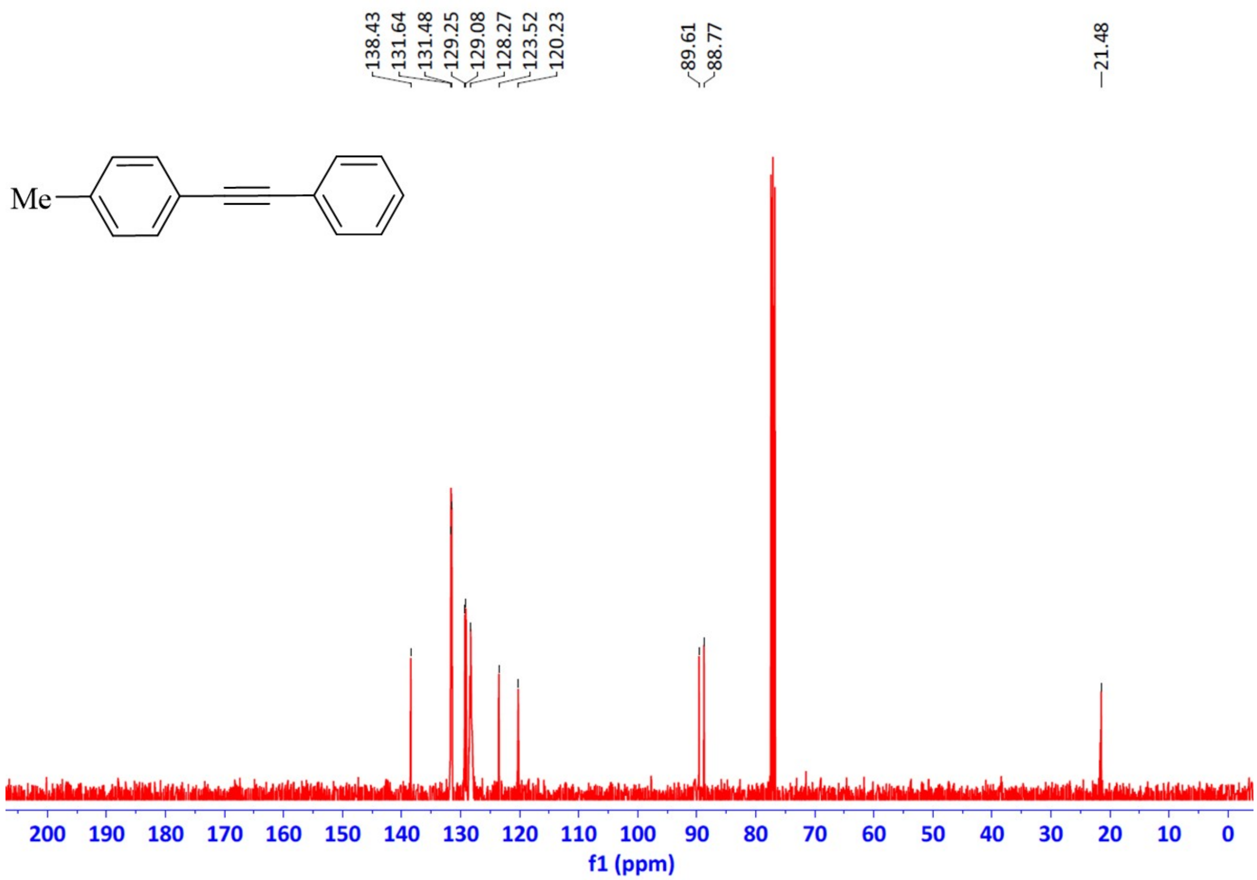
^{1}H NMR of 4-(phenylethynyl)benzonitrile



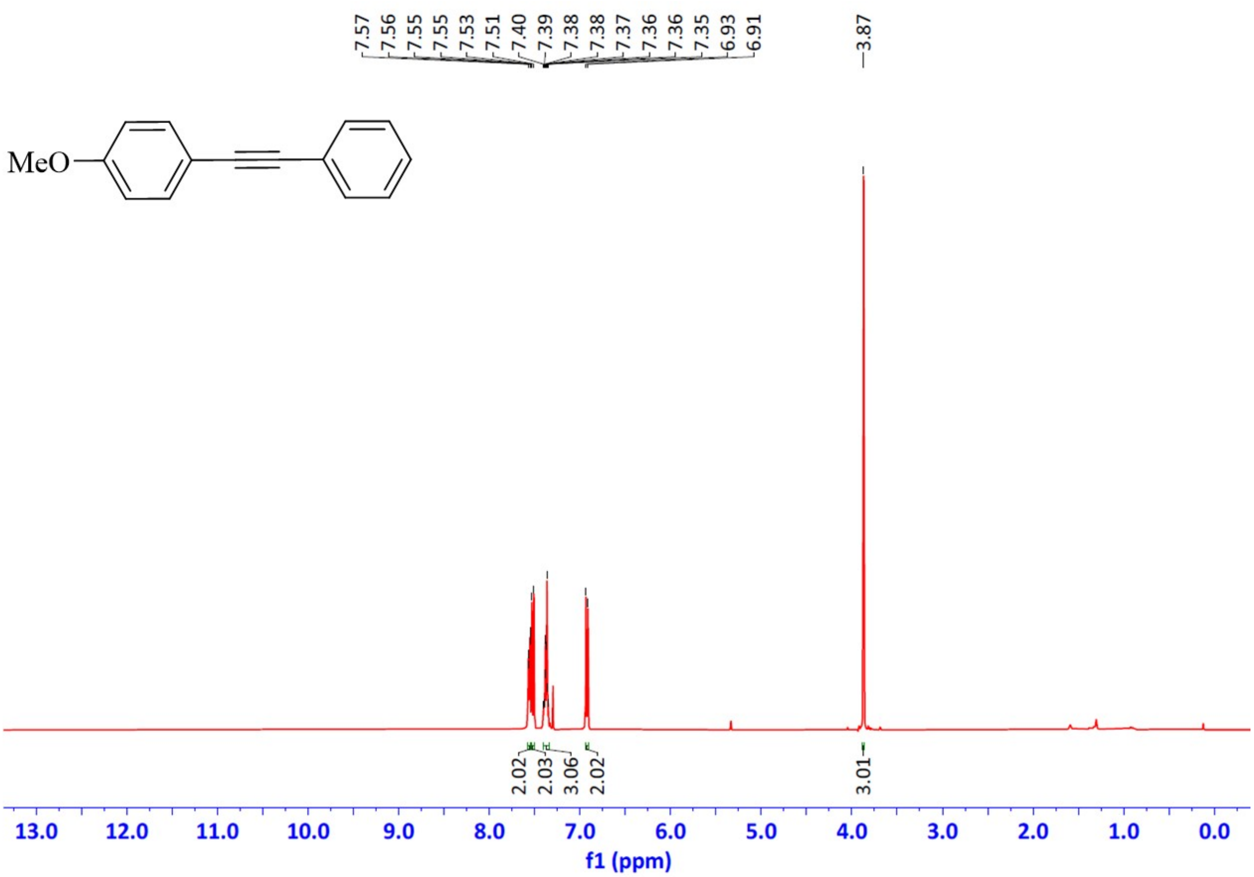
^{13}C NMR of 4-(phenylethynyl)benzonitrile



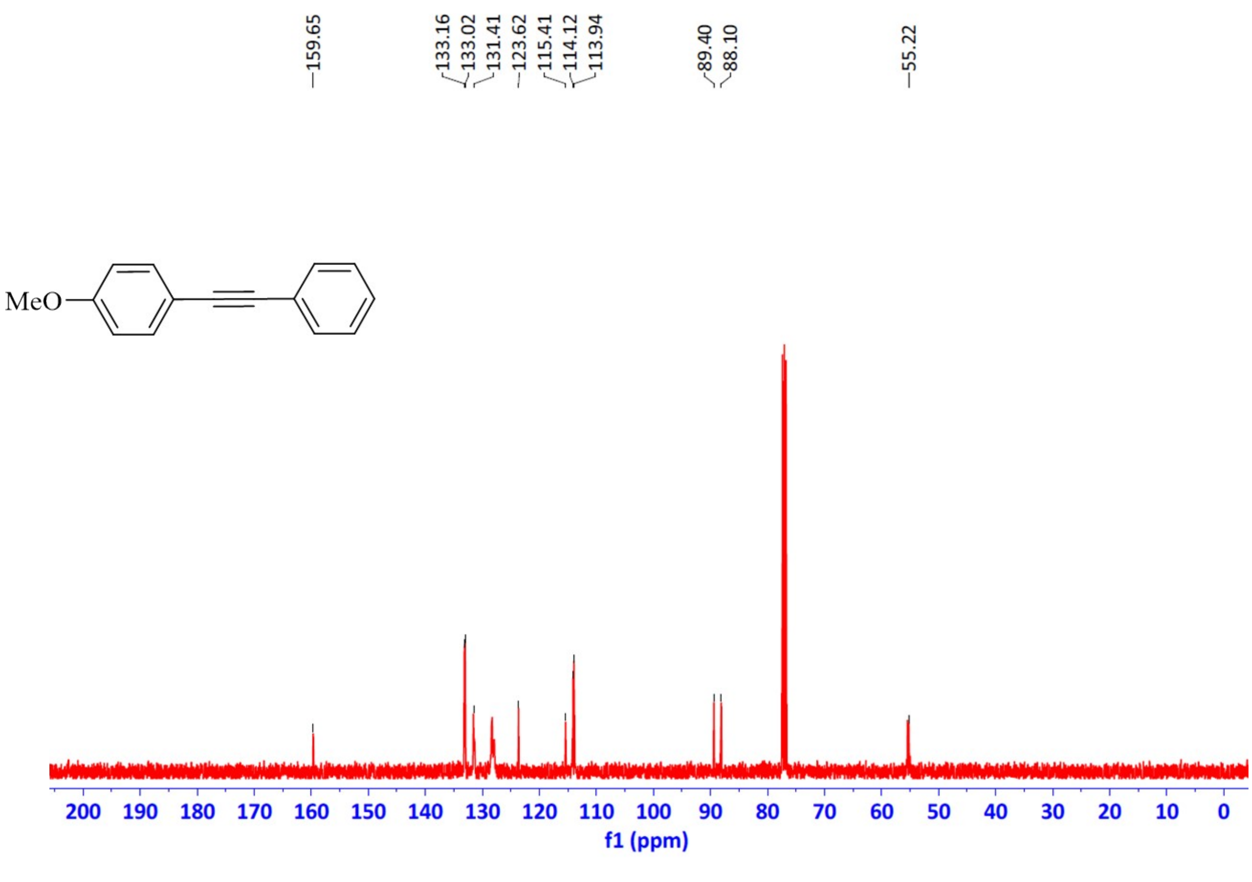
^1H NMR of 1-methyl-4-(phenylethynyl)benzene



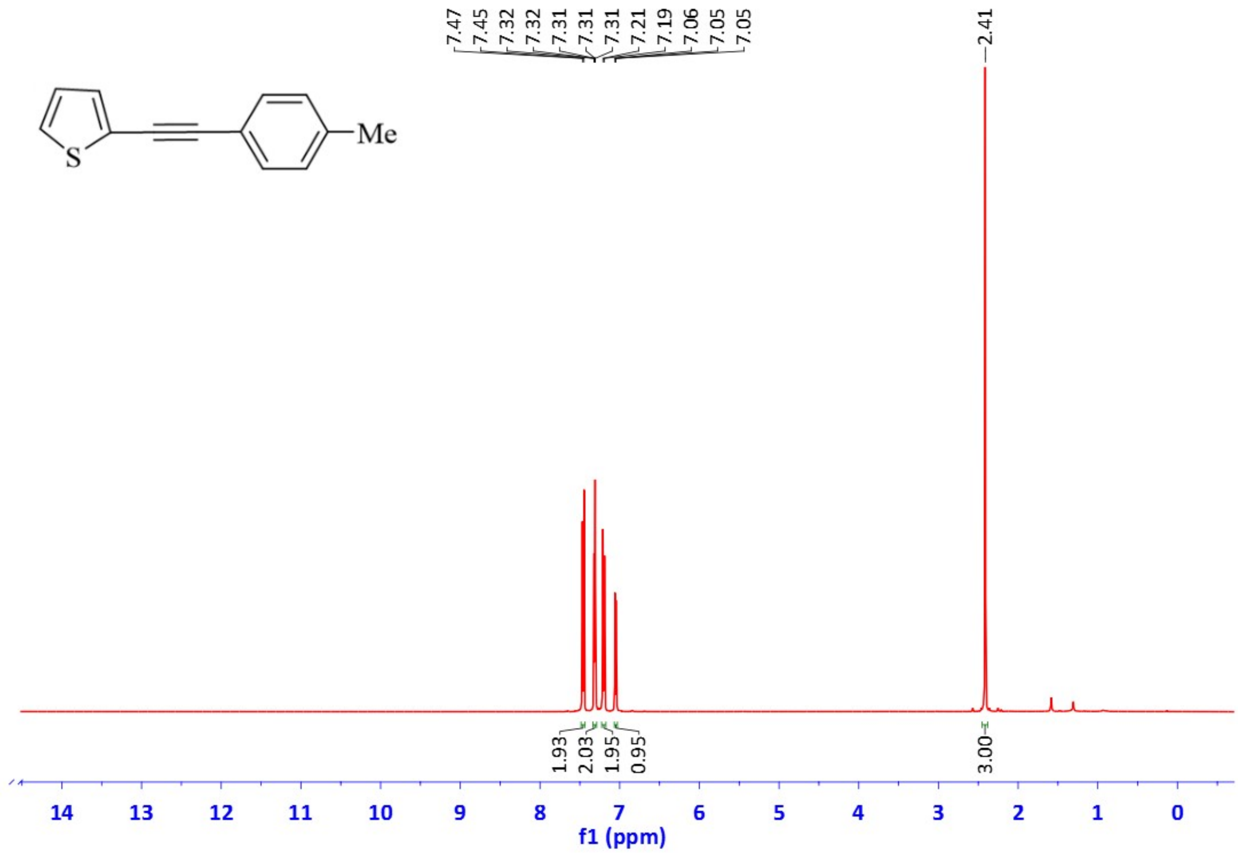
^{13}C NMR of 1-methyl-4-(phenylethynyl)benzene



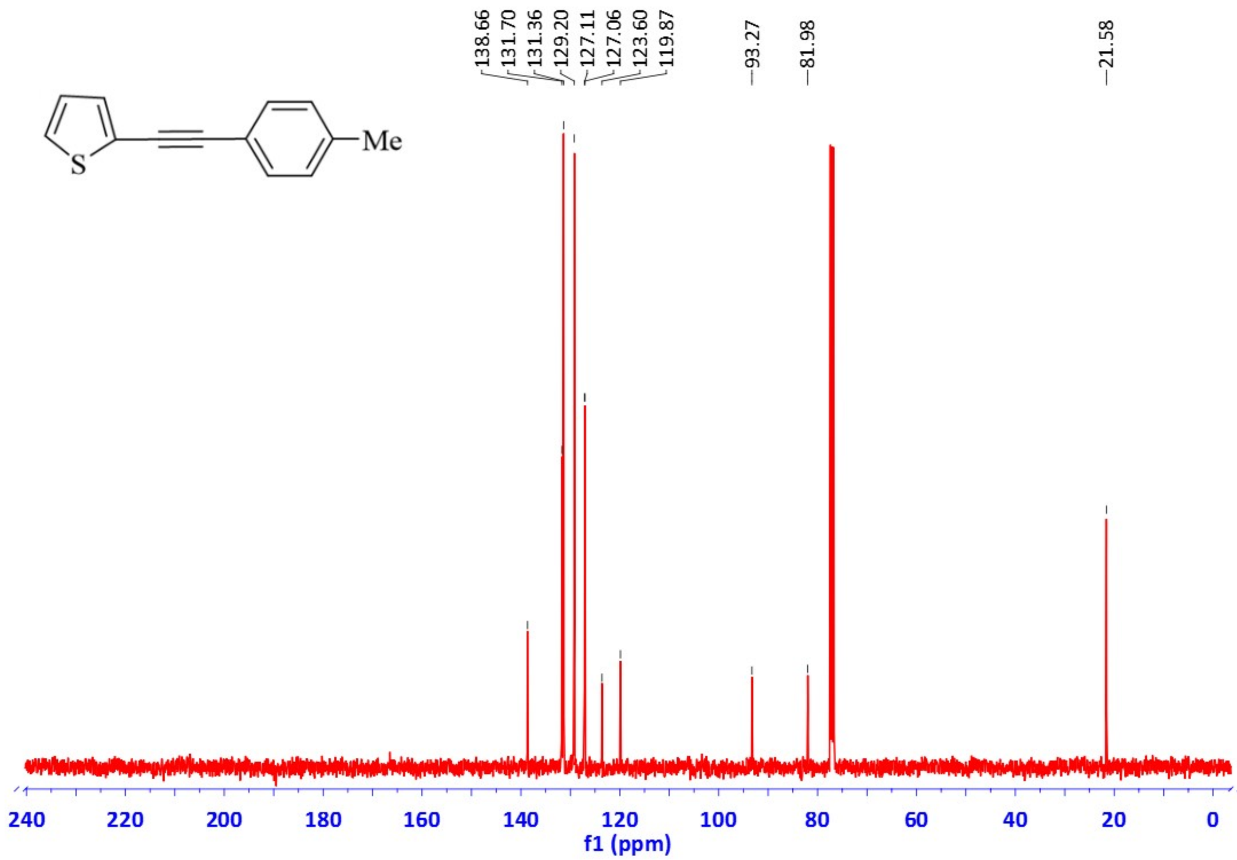
^{1}H NMR of 1-methoxy-4-(phenylethynyl)benzene



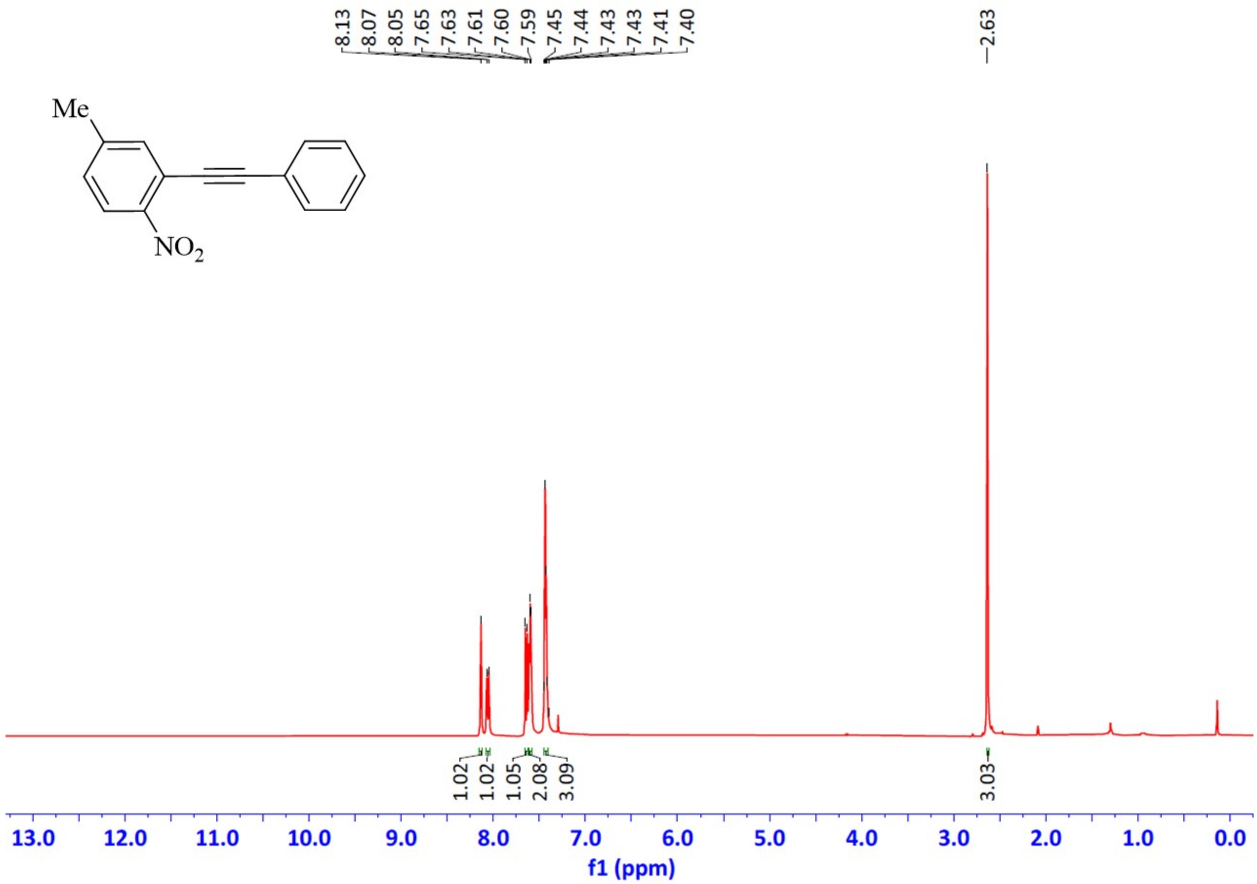
^{13}C NMR of 1-methoxy-4-(phenylethynyl)benzene



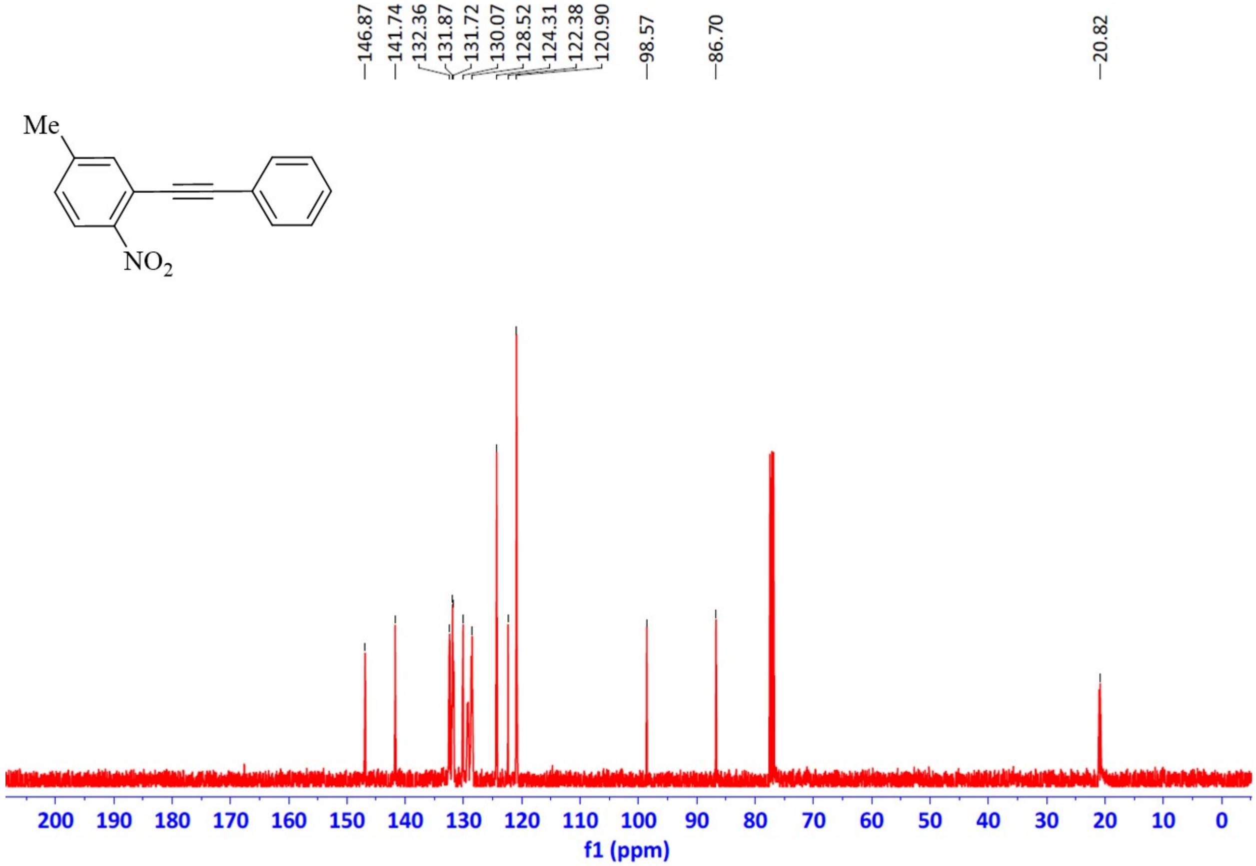
^{1}H NMR of 2-(p-tolylethynyl)thiophene



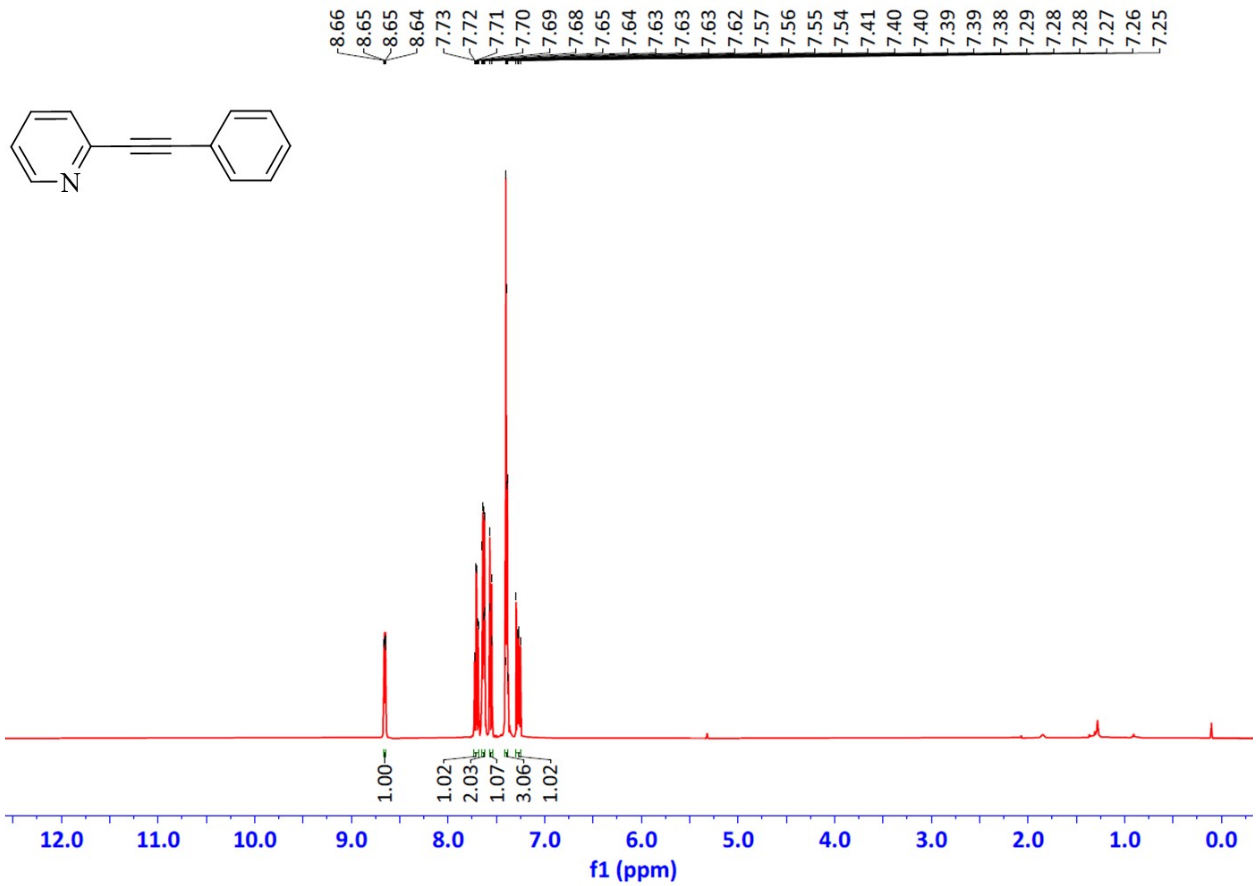
^{13}C NMR of 2-(p-tolylethynyl)thiophene



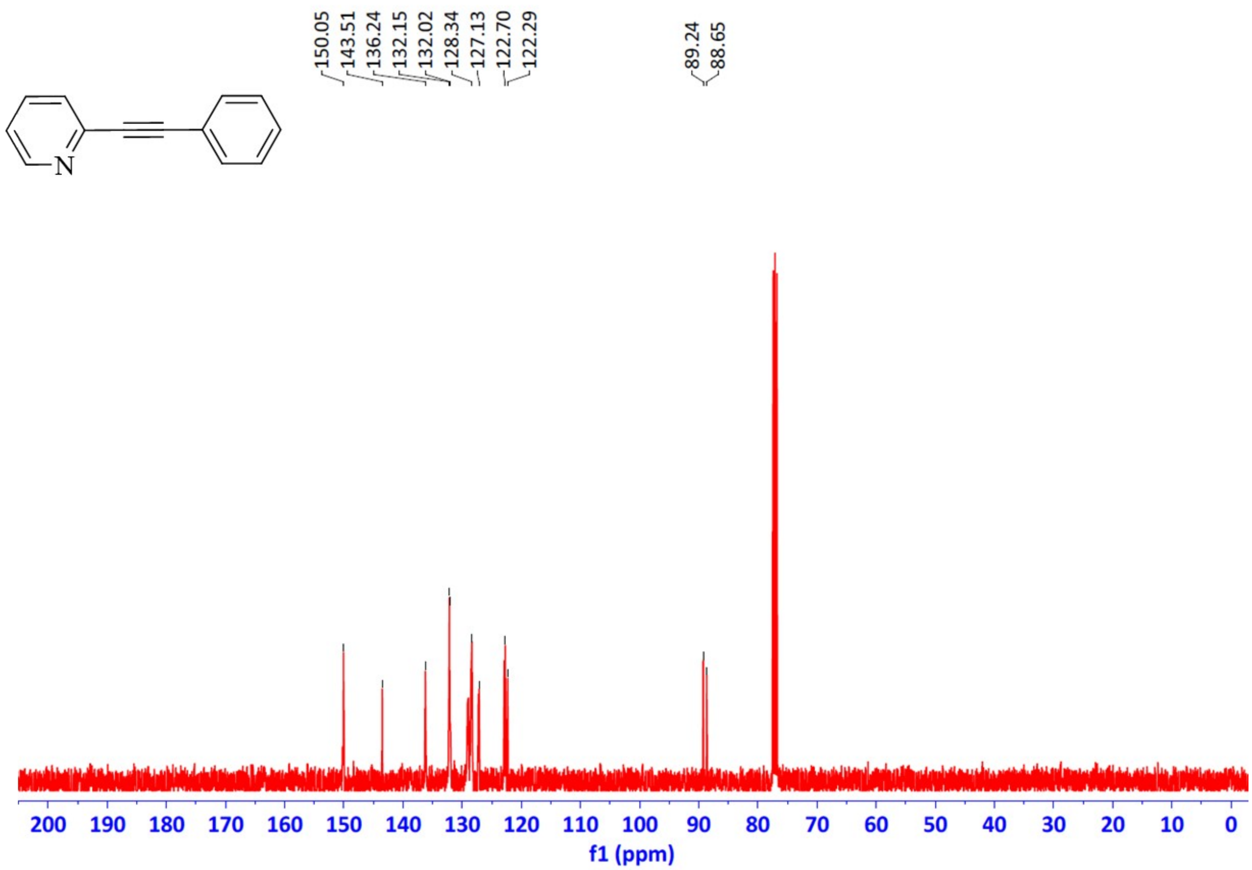
[1]H NMR of 4-methyl-1-nitro-2-(phenylethynyl)benzene



^{13}C NMR of 4-methyl-1-nitro-2-(phenylethynyl)benzene



^{1}H NMR of 2-(phenylethynyl)pyridine



^{13}C NMR of 2-(phenylethynyl)pyridine

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