Support Information

A Co-Cu bimetallic magnetic nanocatalyst with synergistic and bi-functional performance for the base-free Suzuki, Sonogashira, and C-N cross-coupling reactions in water

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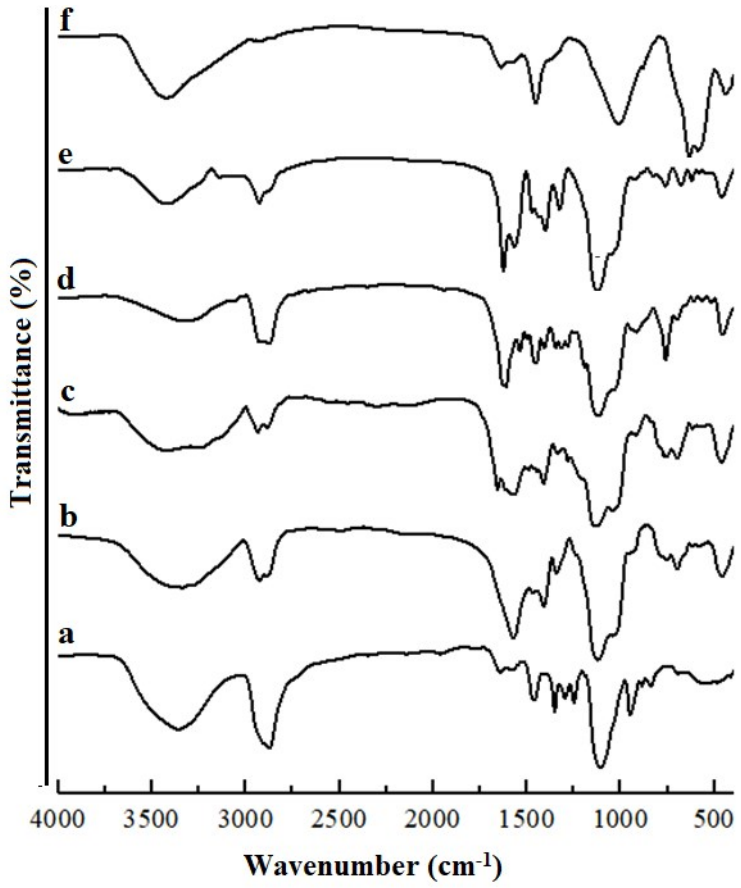


Figure S1. FT-IR spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6** compound

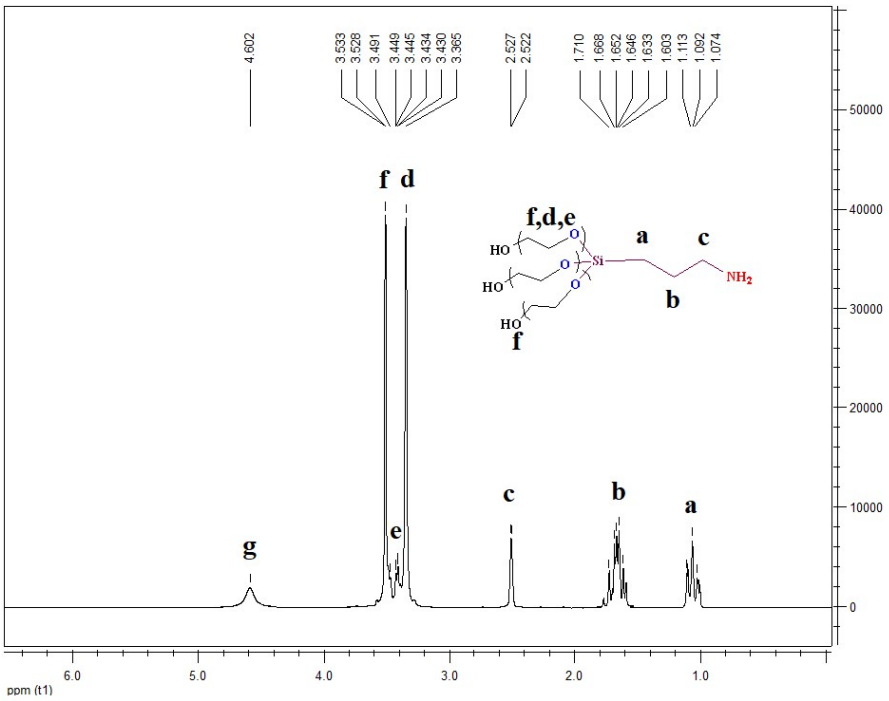


Figure S2. [1]HNMR spectrum of **1** (DMSO-d_6, 300 MHz)

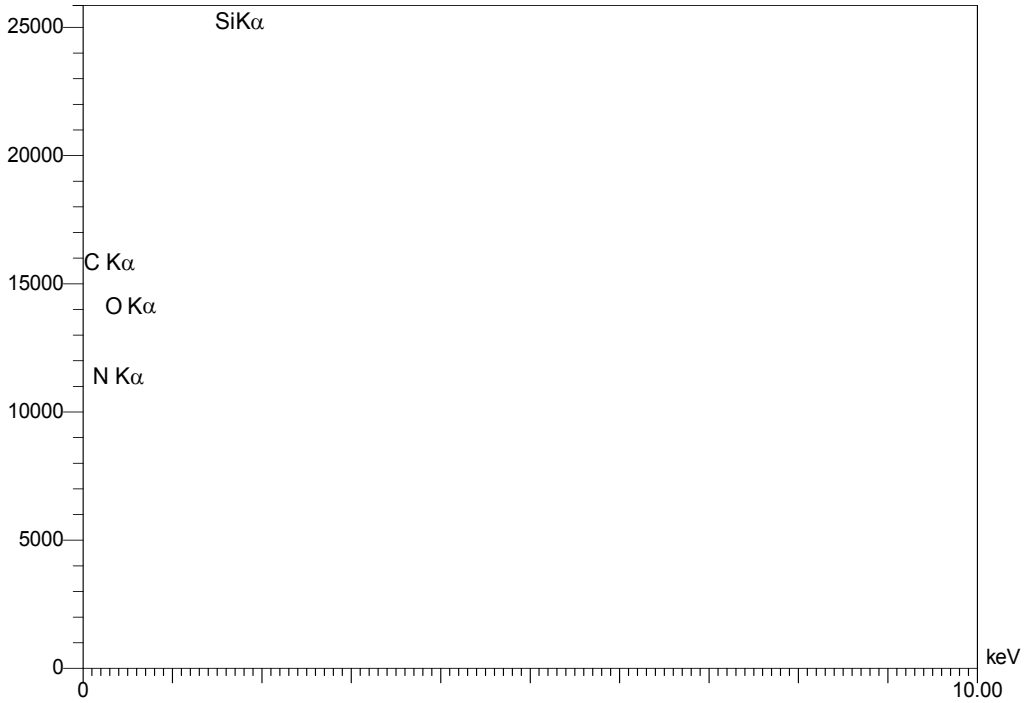


Figure S3. EDX analysis of PEG-APTES (**1**)

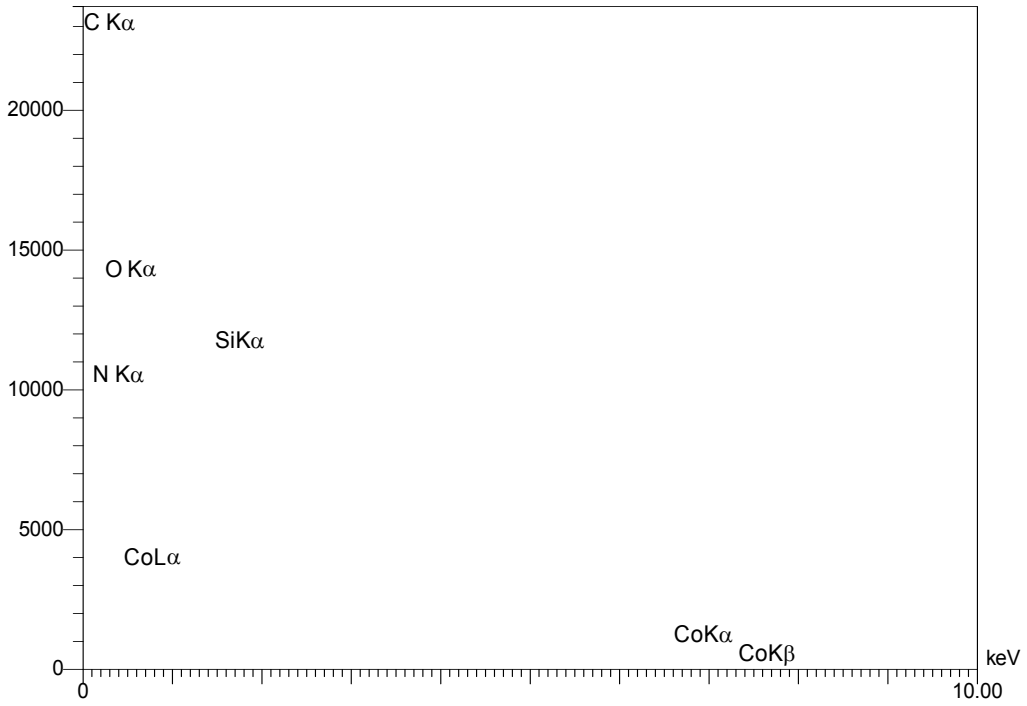


Figure S4. EDX analysis of PEG-APTES/Co (**2**)

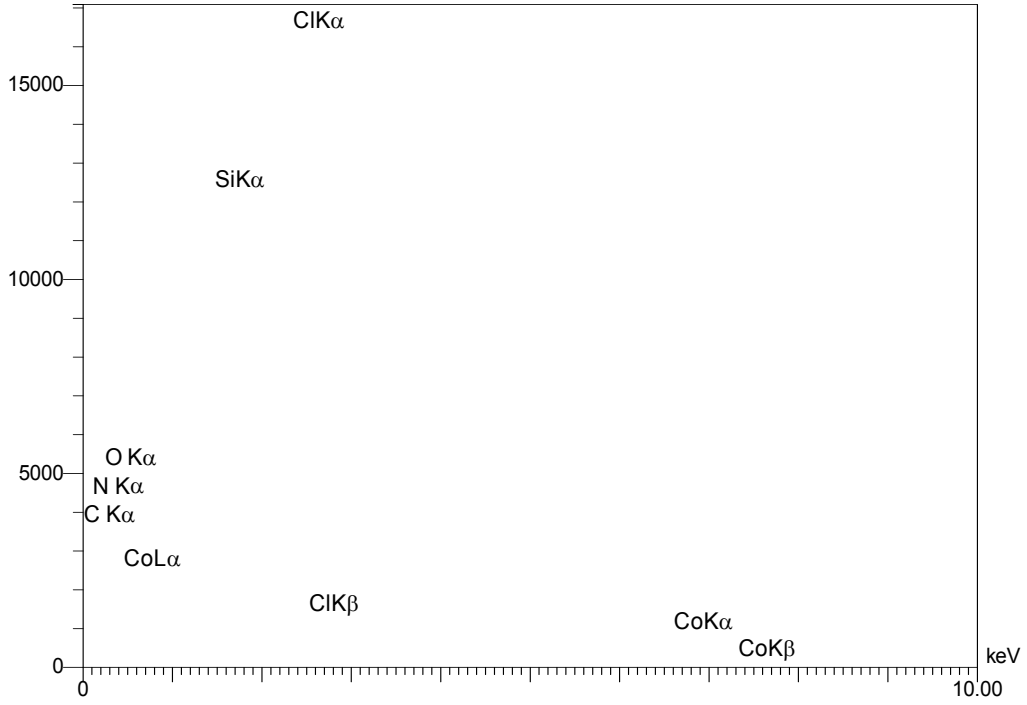


Figure S5. EDX analysis of PEG-APTES-Schiff base/Co (**3**)

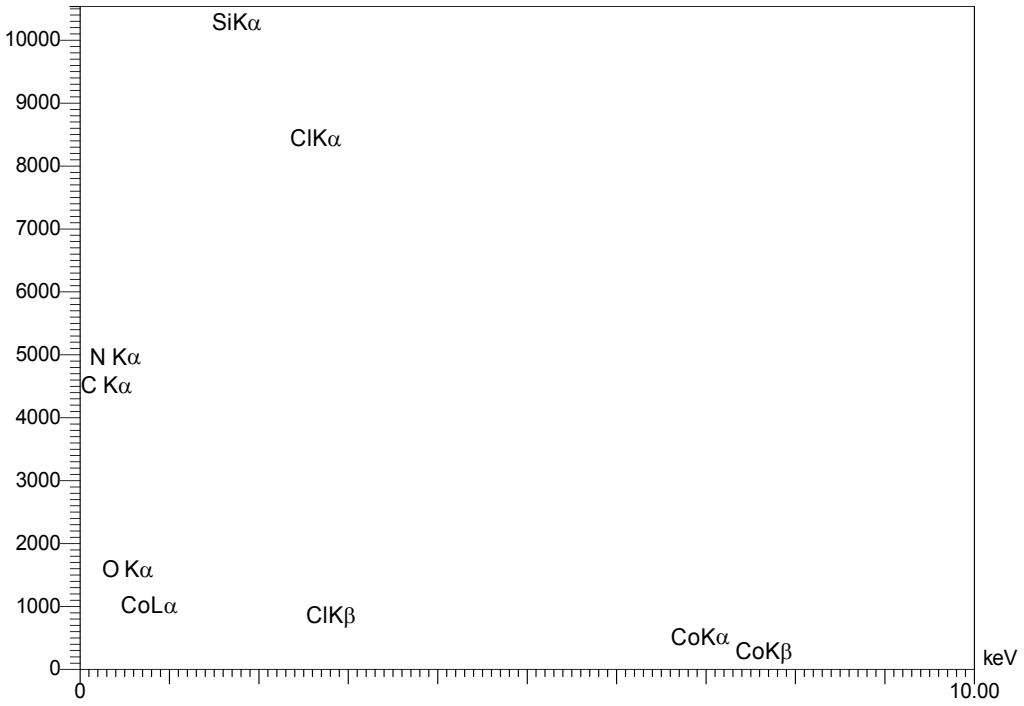


Figure S6. EDX analysis of Co complex-Schiff base-IL (**4**)

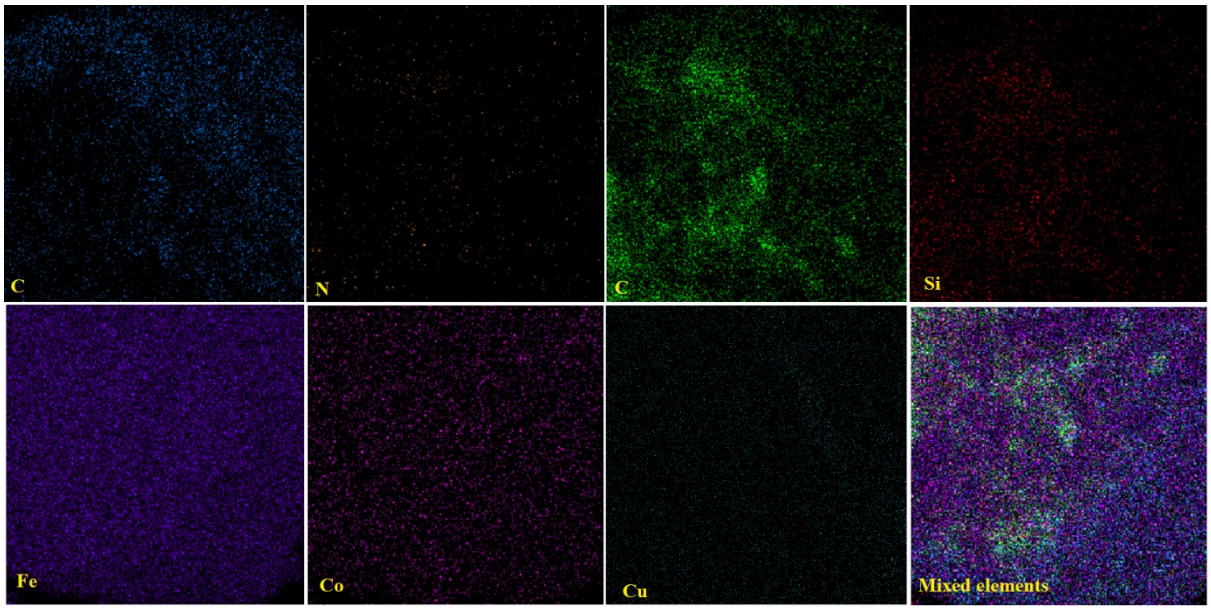


Figure S7. EDX mapping of Fe_3O_4@PEG/Cu-Co catalyst **6**

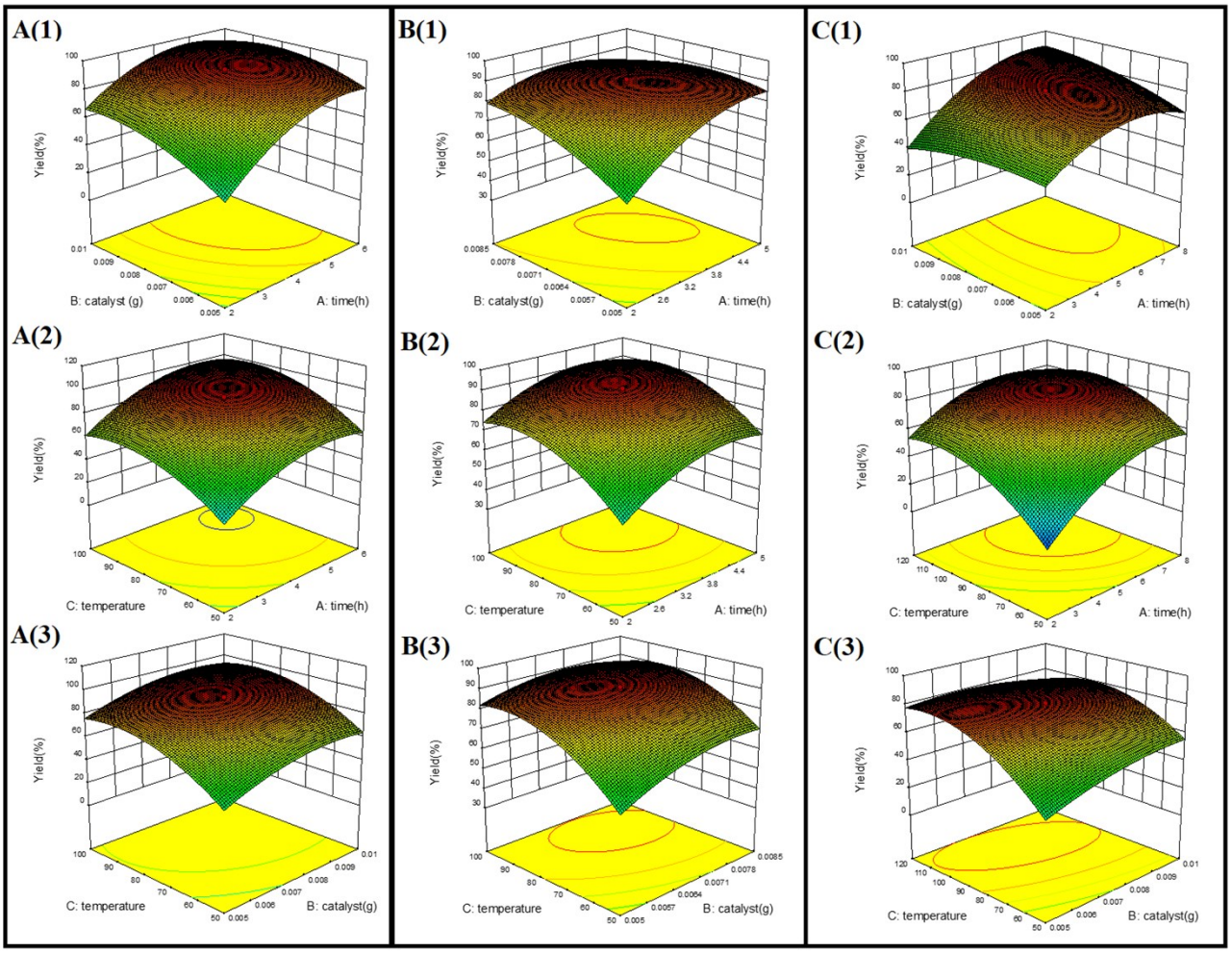


Figure S8. The 3D central design curves for foundation of optimization ranges for maximum response in (A) Sonogashira reaction model, (B) Suzuki reaction model, and (C) C-N cross coupling reaction model.

The model F-value of 535.95, 754.48, and 1465.52 for A, B, and C reactions, respectively indicate that the Quadratic model is significant. Values of "Prob>F" less than 0.0500 indicated that the model terms are significant. The "Lack of Fit F-value" of 2.59, 0.60, and 0.98 for A, B, and C reactions respectively, imply the Lack of Fit is not significant, which the Quadratic model to fit.

Table S1. ANOVA for Response Surface Quadratic Model in Sonogashira cross coupling [analysis of variance table]

Source	Sum of Squares	df	Mean Squares	F-Value	p-value Prob > F	significance
Model	14472.66	7	2067.52	535.95	< 0.0001	significant
C.V. %= 1.96 R^2= 0.9968 Adj R^2= 0.9950 Pred R^2= 0.9888 Adeq Precisior= 67.673						
A-time	3870.40	1	3870.40	1003.30	< 0.0001	
B-amount of catalyst	1247.00	1	1247.00	323.25	< 0.0001	

C-temperature	3275.40	1	3275.40	849.07	< 0.0001	
AB	190.12	1	190.12	49.29	< 0.0001	
AC	3.13	1	3.13	0.95	0.3537	
BC	10.13	1	10.13	3.06	0.1106	
A^2	2956.31	1	2956.31	766.35	< 0.0001	
B^2	1126.84	1	1126.84	292.10	< 0.0001	
C^2	2883.78	1	2883.78	747.55	< 0.0001	
Residual	46.29	12	3.86			
Lack of Fit	36.29	7	5.18	2.59	0.1559	not significant
Pure Error	10.00	5	2.00			
Cor Total	14518.95	19				

Table S2. ANOVA for Response Surface Quadratic Model in Suzuki cross coupling [analysis of variance table]

Source	Sum of Squares	df	Mean Squares	F-Value	p-value Prob > F	significance
Model	5989.98	9	665.55	754.48	< 0.0001	significant
C.V. %= 1.29						
R^2= 0.9985						
Adj R^2= 0.9972						
Pred R^2= 0.9945						
Adeq Precisior= 90.066						
A-time	865.61	1	865.61	981.27	< 0.0001	
B-amount of catalyst	354.61	1	354.61	401.99	< 0.0001	
C-temperature	1630.57	1	1630.57	1848.44	< 0.0001	
AB	378.12	1	378.12	428.65	< 0.0001	
AC	10.12	1	10.12	11.48	0.0069	
BC	78.12	1	78.12	88.56	< 0.0001	
A^2	1034.19	1	1034.19	1172.37	< 0.0001	
B^2	430.58	1	430.58	488.11	< 0.0001	
C^2	1671.41	1	1671.41	1894.74	< 0.0001	
Residual	8.82	10	0.88			
Lack of Fit	3.32	5	0.66	0.60	0.7033	not significant
Pure Error	5.50	5	1.10			
Cor Total	5998.80	19				

Table S3. ANOVA for Response Surface Quadratic Model in C-N cross coupling [analysis of variance table]

Source	Sum of Squares	df	Mean Squares	F-Value	p-value Prob > F	significance
Model	14371.65	9	1596.85	1465.52	< 0.0001	significant
C.V. %= 1.87						
R^2= 0.9992						
Adj R^2= 0.9986						
Pred R^2= 0.9966						
Adeq Precisior= 99.173						
A-time	3663.12	1	3663.12	3361.84	< 0.0001	
B-amount of catalyst	170.00	1	170.00	156.01	< 0.0001	
C-temperature	2974.51	1	2974.51	2729.87	< 0.0001	
AB	512.00	1	512.00	469.89	< 0.0001	
AC	220.50	1	220.50	202.36	< 0.0001	
BC	338.00	1	338.00	310.20	< 0.0001	
A^2	3472.86	1	3472.86	3187.23	< 0.0001	
B^2	370.36	1	370.36	339.90	< 0.0001	
C^2	3791.69	1	3791.69	3479.84	< 0.0001	
Residual	10.90	10	1.09			

Lack of Fit	5.40	5	1.08	0.98	0.5081	not significant
Pure Error	5.50	5	1.10			
Cor Total	14382.55	19				

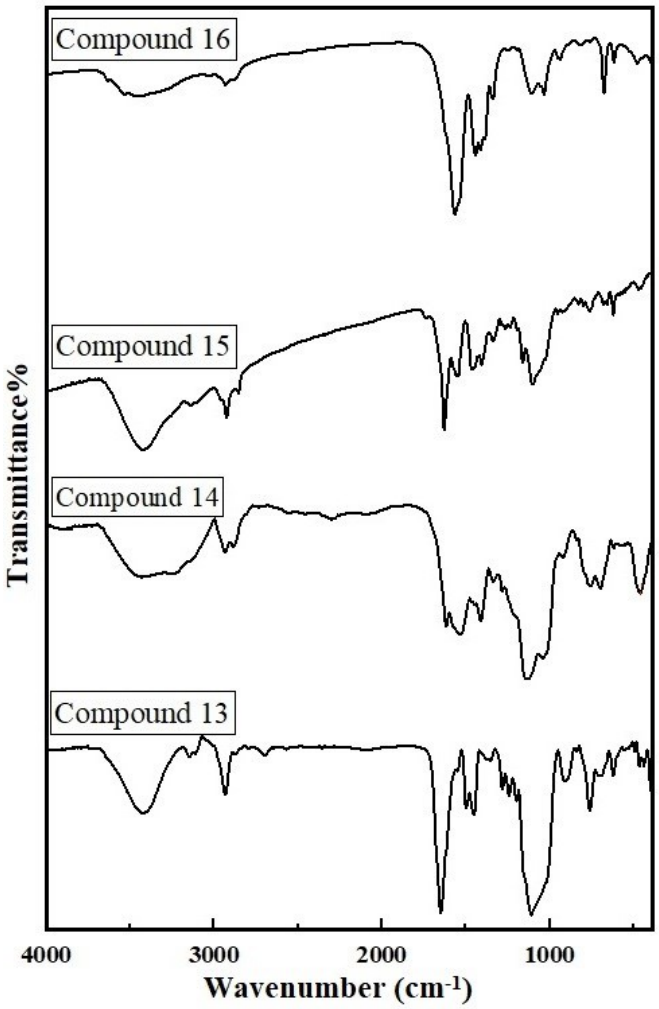


Fig. S9 FTIR spectra of compounds **13**, **14**, **15**, and **16**

Characterization data for compound 13

FTIR analysis ν (cm^{-1}): 1103 (Si-O-Si), 1485 (C=C), 1555 (C=C), 1683 (C=N), 3403 (O-H). EXD analysis (mean average of 5 point): wt% = C 56.76, Cl 1.39, N 1.96, O 37.58, Si 2.31.

Characterization data for compound 14

FTIR analysis ν (cm^{-1}): 1111 (Si-O-Si), 1410 (C=C), 1570 (C=C), 1668 (C=N), 3423 (O-H), 486 (Co-O). EXD analysis (mean average of 5 point): wt% = C 55.63, Cl 1.34, N 1.94, O 37.53, Si 2.26, Co 1.30. ICP analysis: Co wt% 1.37.

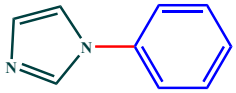
Characterization data for compound 15

FTIR analysis ν (cm^{-1}): 1100 (Si-O-Si), 1410 (C=C), 1493 (C=C), 1670 (C=N), 3406 (O-H), 484 (Cu-O), 622 (Cu-N). EXD analysis (mean average of 5 point): wt% = C 55.13, Cl 1.22, N 1.94, O 37.53, Si 2.26, Cu 1.92. ICP analysis: Cu wt% 1.95.

Characterization data for compound 16

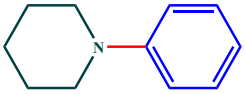
FTIR analysis ν (cm^{-1}): 1114 (Si-O-Si), 1408 (C=C), 1484 (C=C), 1610 (C=N), 34019 (O-H), 490 (Co-O), 622 (Co-N), 460 (Cu-O). EXD analysis (mean average of 5 point): wt% = C 56.09, Cl 1.34, N 1.44, O 36.53, Si 2.24, Cu 1.19, Co 2.07. ICP analysis: Cu wt% 1.23, Co 2.00 wt% .

1-phenyl-1H-imidazole (Table 1, 9a)



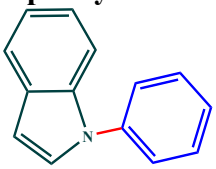
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 80% (115.33 mg) as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.15-7.45 (m, 6H), 7.80 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 118.2, 121.5, 127.5, 130.0, 130.3, 135.5, 137.4.

1-phenylpiperidine (Table 1, 9b)



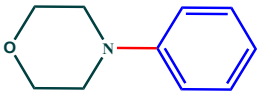
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 75% (120.93 mg) as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 1.62 (m, 6H), 3.73 (d, J=5.0 Hz, 4H), 6.73-6.80 (m, 3H), 7.07-7.17 (m, 2H), 6.93 (m, 2H), 7.22-7.25 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 24.6, 25.6, 54.1, 114.4, 123.6, 129.1, 150.5.

1-phenyl-1H-indole (Table 1, 9c)



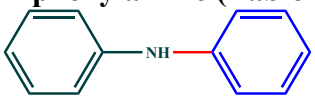
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 68% (131.40 mg) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 6.60 (m, 1H), 7.20 (m, 2H), 7.32 (m, 2H), 7.41-7.65 (m, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 103.5, 110.6, 120.4, 121.1, 122.3, 124.3, 126.5, 128.0, 129.3, 129.6, 135.8, 139.8.

4-phenylmorpholine (Table 1, 9d)



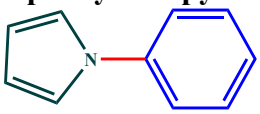
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 73% (119.15 mg) as a pale yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 3.14 (t, J_1=4.0 Hz, J_2=7.5 Hz, 4H), 3.30 (t, J_1=4.0 Hz, J_2=7.5 Hz, 4H), 6.60 (m, 3H), 7.27 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 49.2, 66.8, 115.6, 119.9, 129.1, 151.2.

Diphenylamine (Table 1, 9e)



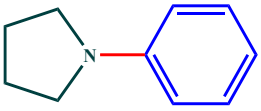
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 65% (109.99 mg) as a yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 5.64 (s, br, 1H), 6.95 (m, 2H), 7.10 (m, 4H), 7.26 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 117.8, 121.0, 130.0, 145.9.

1-phenyl-1H-pyrrole (Table 1, 9f)



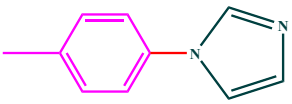
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 80% (114.55 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 6.27 (t, J_1=2.25 Hz, J_2=4.5 Hz, 2H), 7.00 (m, 2H), 7.12-7.18 (m, 1H), 7.28-7.33 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 110.4, 120.5, 121.2, 126.9, 130.5, 140.7.

1-phenylpyrrolidine (Table 1, 9g)



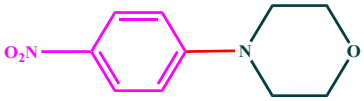
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 78% (114.83 mg) as a pale yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 2.05 (t, J_1= 5.0 Hz, J_2=7.5 Hz, 4H), 3.27 (t, J_1= 5.0 Hz, J_2=7.5 Hz, 4H), 6.55-6.60 (m, 3H), 7.20 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 25.3, 51.3, 114.7, 121.8, 130.0, 150.7.

1-(p-tolyl)-1H-imidazole (Table 1, 9h)



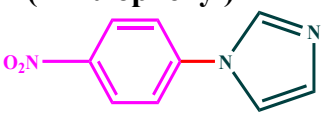
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 70% (110.74 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 2.51 (s, 3H). 6.90 (d, J=7.5 Hz, 2H), 7.12 (d, J=7.5 Hz, 2H), 7.22 (d, J=7.5 Hz, 2H), 7.70 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 20.5, 118.0, 123.7, 130.2, 130.7, 134.4, 135.1, 138.8.

4-(4-nitrophenyl)morpholine (Table 1, 9i)



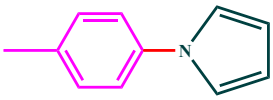
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 75% (156.15 mg) as a yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 3.38 (t, J_1=4.25 Hz, J_2=7.5 Hz, 4H), 3.47 (t, J_1=4.25 Hz, J_2=7.5 Hz, 4H), 6.80 (m, 1H), 7.20 (m, 1H), 8.14 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 54.3, 66.5, 112.6, 124.3, 136.9, 154.2.

1-(4-nitrophenyl)-1H-imidazole (Table 1, 9j)



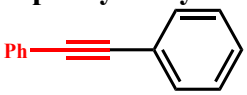
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 87% (164.57 mg) as a light brown solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.21 (d, *J*=7.7 Hz, 1 H), 7.32 (d, *J*=7.7 Hz, 1 H), 7.52 (d, *J*=7.5 Hz, 2 H), 7.93 (s, 1 H), 8.30 (m, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 118.6, 122.0, 125.0, 130.2, 136.2, 143.1, 147.9.

1-(p-Tolyl)-1H-pyrrole (Table 1, 9k)



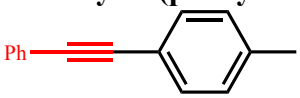
Prepared according to the general C-N coupling procedure on 1mmol scale and obtained an isolated yield of 70% (110.04 mg) as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 2.41 (s, 3H), 6.37 (m, 2H),), 7.10 (m, 2H), 7.26 (m, 2H), 7.30-7.33 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 20.9, 110.0, 119.4, 120.5, 130.0, 135.5, 138.6.

Diphenylacetylene (Table 2, 11a)



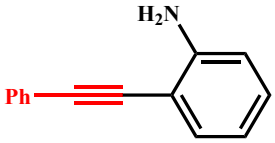
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 95% (169.31 mg) as a colorless solid. ^{1}H NMR (250 MHz, CDCl3); δ (ppm)= 6.93-7.29 (m, 5H), 7.44-7.98 (m, 5H), ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 89.5, 123.4, 126.5, 127.7, 128.3,128.5, 128.8, 129.3, 131.5.

1-methyl-4-(phenylethynyl)benzene (Table 2, 11b)



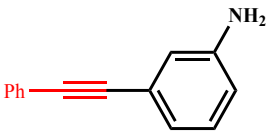
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 95% (182.63 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 2.22 (s, 3H), 6.71-7.16 (m, 3H), 7.19–7.71 (m, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 21.5, 88.7, 89.6, 120.2, 123.5, 128.0, 128.3, 129.1, 131.5, 131.6, 138.4.

2-(Phenylethynyl)aniline (Table 2, 11c)



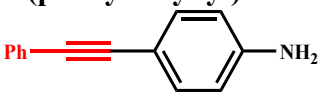
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 65% (125.60 mg) as a yellowish-brown solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 3.76 (s, 2 H), 6.75 (m, 2 H), 7.31-7.34 (m, 3 H), 7.46 - 7.54 (m, 4 H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 93.4, 108.0, 113.6, 118.8, 127.3, 127.9, 128.8, 129.0, 131.8, 133.3, 151.0.

3-(Phenylethynyl)aniline (Table 2, 11d)



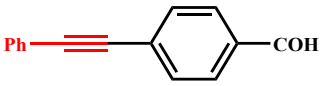
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 68% (131.40 mg) as a yellow pale oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm)= 3.79 (s, 2H), 7.25-7.37 (m, 6H), 7.52-7.54 (m, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm)= 74.0, 81.7, 121.9, 128.4, 128.5, 129.3, 132.6.

4-(phenylethynyl)aniline (Table 2, 11e)



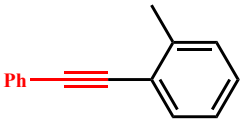
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 78% (150.72 mg) as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 3.63 (s, 2H, NH_2), 6.53 (m, 3H), 7.29-7.40 (m,5H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 87.4, 90.2, 112.6, 115.0, 124.0, 127.8, 128.3, 131.4, 133.0, 146.8.

4-(phenylethynyl)benzaldehyde (Table 2, 11f)



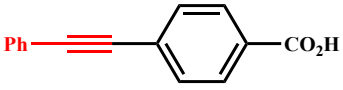
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 97% (200.05 mg) as a brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.28–7.34 (m, 7 H), 7.55 (m, 1 H), 7.96 (m, 1 H), 10.55 (s, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 126.6, 127.3, 128.0, 129.4, 1297, 129.8, 130.7, 133.3, 135.2, 135.4, 190.0.

1-methyl-2-(phenylethynyl)benzene (Table 2, 11g)



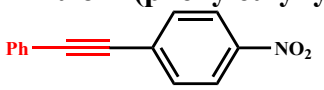
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 80% (153.80 mg) as a colerless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 2.75 (s, 3H), 7.10–7.23 (m, 1H), 7.28-7.33 (m, 2H), 7.30–7.40 (m, 3H), 7.49–7.60 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 20.8, 123.0, 125.6, 128.2, 128.3, 129.3, 129.5, 131.5, 131.8, 132.5, 140.1.

4-(Phenylethynyl)benzoic acid (Table 2, 11h)



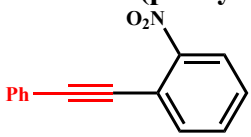
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 97% (215.56 mg) as a brown solid. ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm)= 7.49 (3H, m), 7.70-8.04 (6H, m), 12.98 (1H, s); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ (ppm)= 127.3, 127.5, 129.0, 129.6, 130.0, 130.5, 140.0, 145.1, 167.7.

1-nitro-4-(phenylethynyl)benzene (Table 2, 11i)



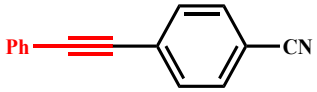
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 98% (218.76 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 6.66-7.41 (m, 3H), 7.54-7.69 (m, 4H), 8.22 (d, J=7.7 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 87.5, 94.8, 122.0, 123.6, 128.5, 129.3,130.2, 132.0, 132.3, 147.0.

1-Nitro-2-(phenylethynyl)benzene (Table 2, 11j)



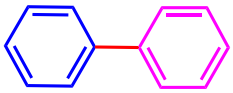
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 92% (205.37 mg) as a orange oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.35-7.41 (m, 5H), 7.55-7.57 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 74.0, 82.1, 121.7, 128.5, 129.2, 132.7.

4-(phenylethynyl)benzonitrile (Table 2, 11k)



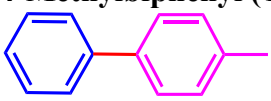
Prepared according to the general Sonogashira coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 95% (193.06 mg) as a pale yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.28-7.31 (m, 3H), 7.45-7.54 (m, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 87.7, 93.8, 11.4 118.6, 122.2, 128.2, 129.0, 129.5, 130.7, 132.0, 132.5.

Biphenyl (Table 3, 12a)



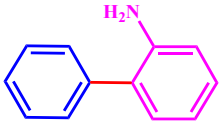
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 91% (140.33 mg) as a white solid. ^{1}H NMR (250MHz, $CDCl_3$): δ (ppm)= 7.34 (m, 2H), 7.44 (m, 4H), 7.58-7.60 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm)= 127.2, 127.3, 129.0, 141.3.

4-Methylbiphenyl (Table 3, 12b)



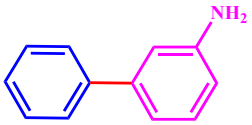
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 90% (151.40 mg) as a white solid. ^{1}H NMR (250MHz, $CDCl_3$): δ (ppm)= 2.44 (s, 3H), 7.28 (m, 2H), 7.36 (m, 1H), 7.45-54 (m, 4H), 7.62 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 21.1, 127.0, 127.1, 129.0, 129.6, 137.0, 137.1, 138.6, 141.2.

2-Aminobiphenyl (Table 3, 12c)



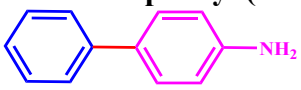
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 68% (115.06 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm)= 5.00 (s, br, 2H), 6.73-6.82 (m, 2H), 7.28-7.50 (m, 5H), 7.50-7.66 (m, 2H), 8.59 (m, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm)= 85.2, 94.8, 109.6, 115.1, 118.9, 122.9, 127.9, 128.0, 129.4, 131.1, 132.0, 145.7

3-Aminobiphenyl (Table 3, 12d)



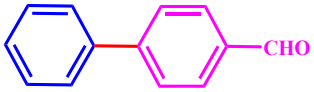
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 72% (121.83 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm)= 3.73 (s, 2H), 7.33-7.39 (m, 6H), 7.50-7.58 (m, 1H), 7.86-8.86 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm)= 114.4, 118.5, 118.6, 127.3, 127.5, 130.1, 140.0, 140.7, 149.8.

4-Aminobiphenyl (Table 3, 12e)



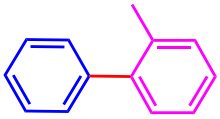
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 79% (133.68 mg) as a pale yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm)= 3.54 (s, 2H, NH_2), 6.66 (d, J=4.75 Hz, 2H), 7.32-7.36 (m, 5H), 7.37 (m, 2H), 7.59 (d, J = 7.80 Hz, Ar*H*); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm)= 87.4, 90.1, 112.7, 114.8, 124.0, 127.7, 128.3, 131.4, 133.0, 146.7.

4-Phenylbenzaldehyde (Table 3, 12f)



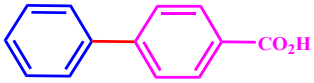
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 92% (167.64 mg) as a yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm)= 7.28 (m, 3H), 7.52 (m, 2H), 7.65 (m, 2H), 7.98(m, 2H), 10.08 (s, 1H), ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm)= 127.3, 127.7, 128.5, 130.0, 130.2, 135.3, 140.0, 147.2, 192.0.

2-Methylbiphenyl (Table 3, 12g)



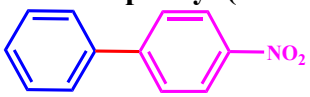
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 72% (121.12 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 2.26 (s, 3H), 7.28 (m, 3H), 7.38 (m, 3H), 7.48 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 20.6, 125.9, 126.9, 127.3, 128.2, 128.9, 129.3, 129.9, 130.4, 135.4, 142.1.

4-phenylbenzoic acid(Table 3, 12h)



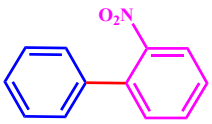
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 92% (182.36 mg) as a white solid. ^{1}H NMR (250 MHz, DMSO-d_6): δ(ppm)= 7.41 (m, 1H), 7.59 (m, 2H), 7.80 (m, 2H), 7.85 (d, 2H), 8.12 (d, J = 4.25 Hz, 2H), 13.20 (s, 1H); ^{13}C NMR (62.5 MHz, DMSO-d_6): δ(ppm)= 126.7, 127.0, 128.2, 129.0, 129.9, 130.6, 139.2, 143.6, 167.4.

4-Nitrobiphenyl (Table 3, 12i)



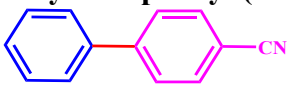
Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 93% (185.25 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.45-7.76 (m, 7H), 8.31 (m, 2H); ^{13}C NMR (62.5 MHz, CDCl3): δ (ppm)= 125.0, 127.6, 128.0, 128.9, 129.5, 129.7, 141.1, 147.9.

2-Nitrobiphenyl (Table 3, 12j)



Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 91% (181.27 mg) as a pale yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.43-7.52 (m, 3H), 7.58-7.64 (m, 3H), 7.91-8.44 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 121.9, 122.0, 127.2, 128.6, 129.2, 129.8, 133.0, 136.7, 142.9, 148.8.

4-Cyanobiphenyl (Table 3, 12k)



Prepared according to the general Suzuki coupling procedure on 1mmol aryl halide scale and obtained an isolated yield of 91% (163.09 mg) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.41-7.48 (m, 3H), 7.58-7.76 (m, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 110.9, 118.7, 127.4, 127.6, 128.8, 129.0, 129.3, 129.6, 130.0, 130.5, 132.2, 139.9, 146.2.

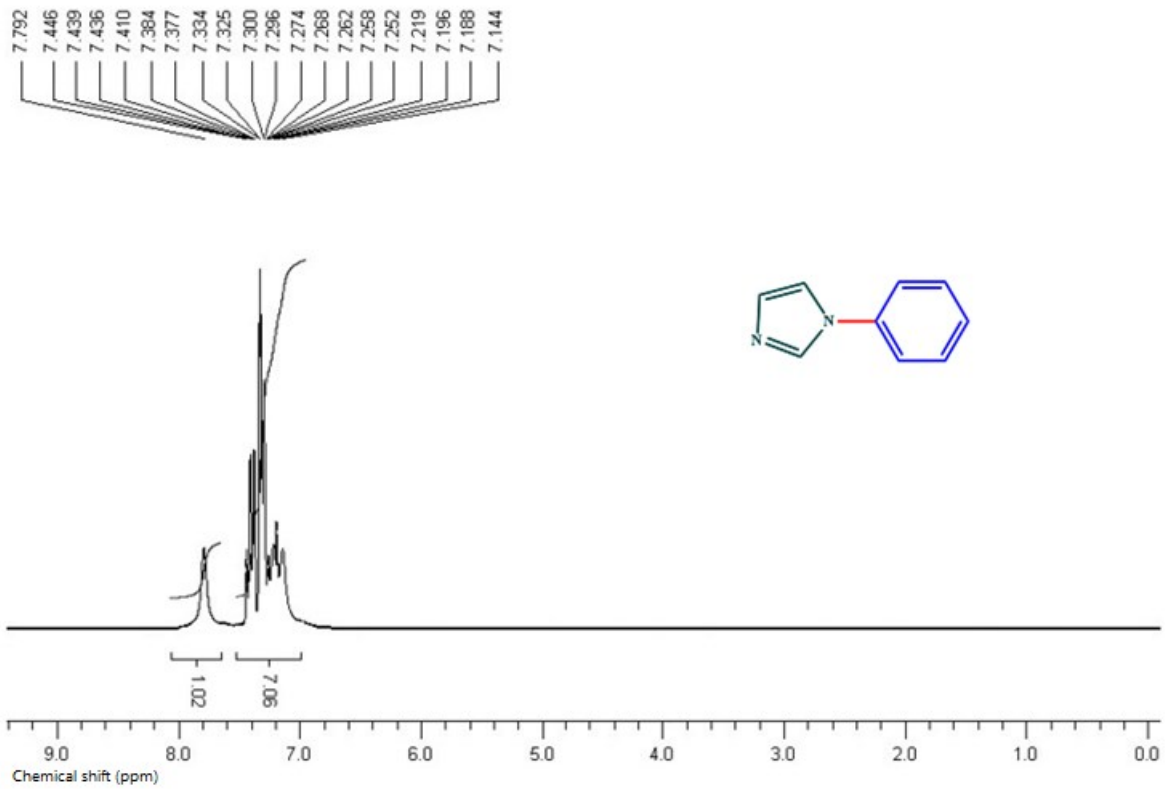


Figure S10. [1]HNMR spectrum of **9a**

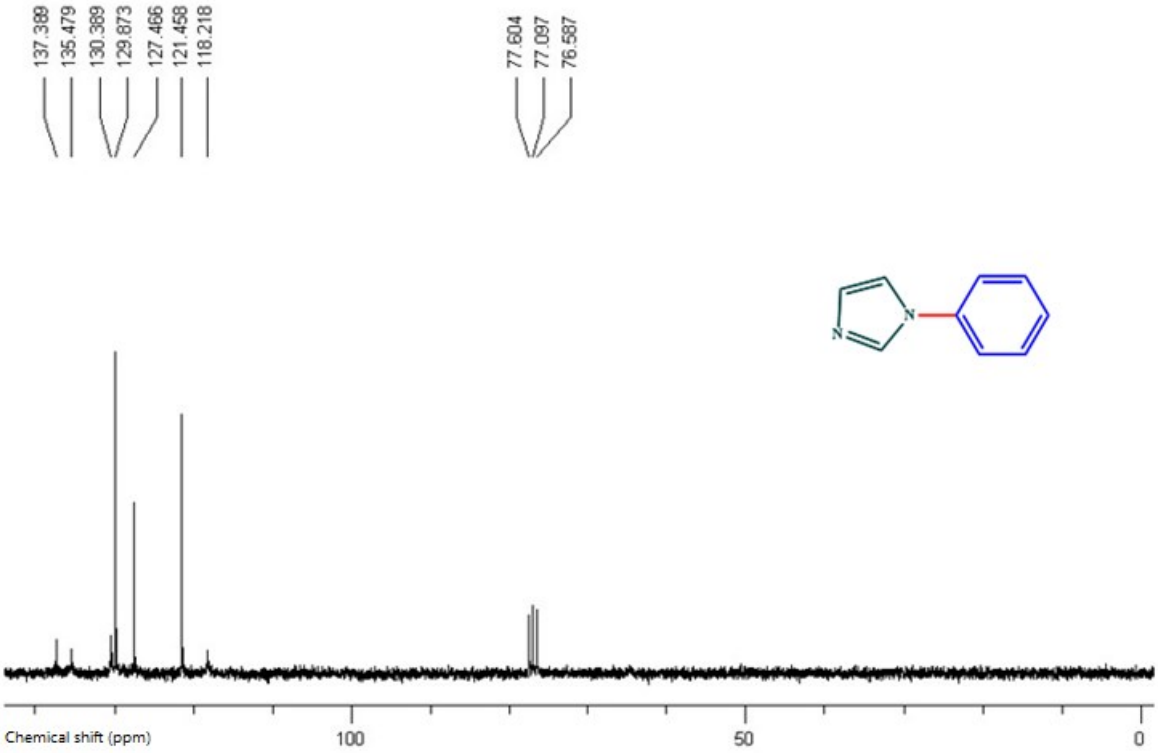


Figure S11. [13]CNMR spectrum of **9a**

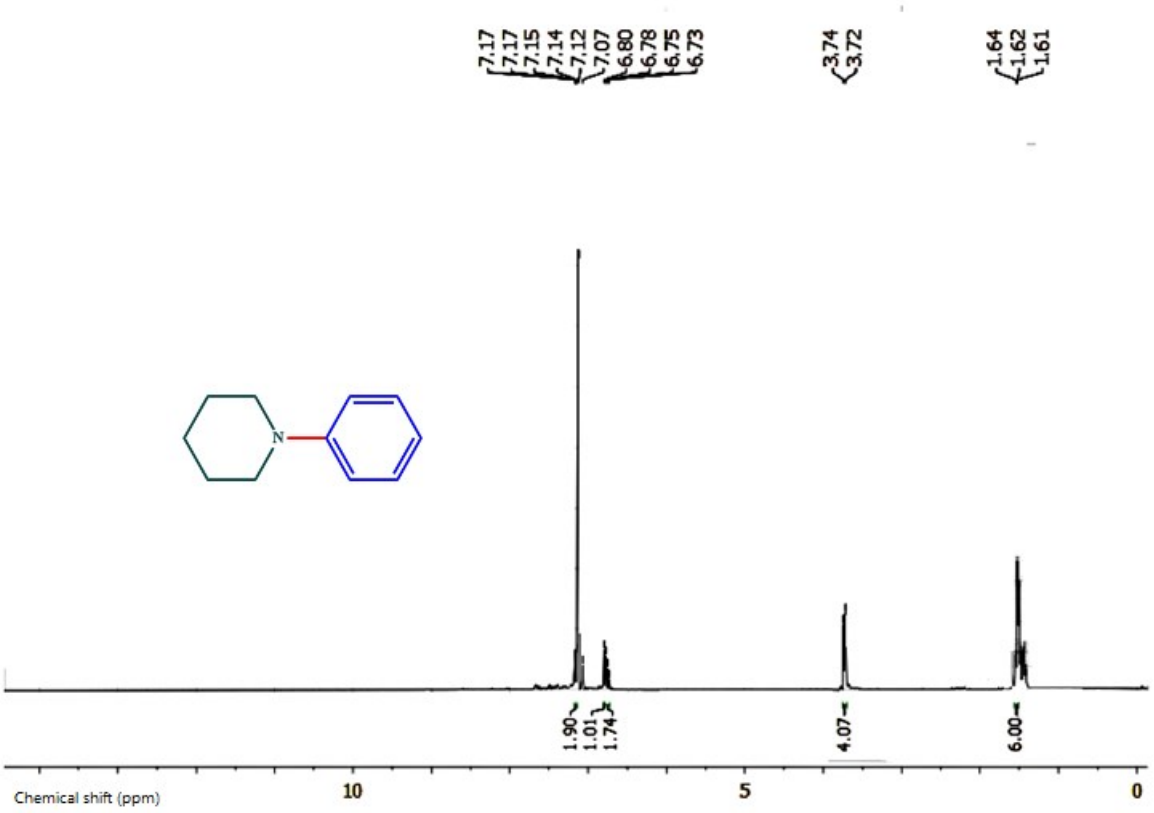


Figure S12. [1]HNMR spectrum of **9b**

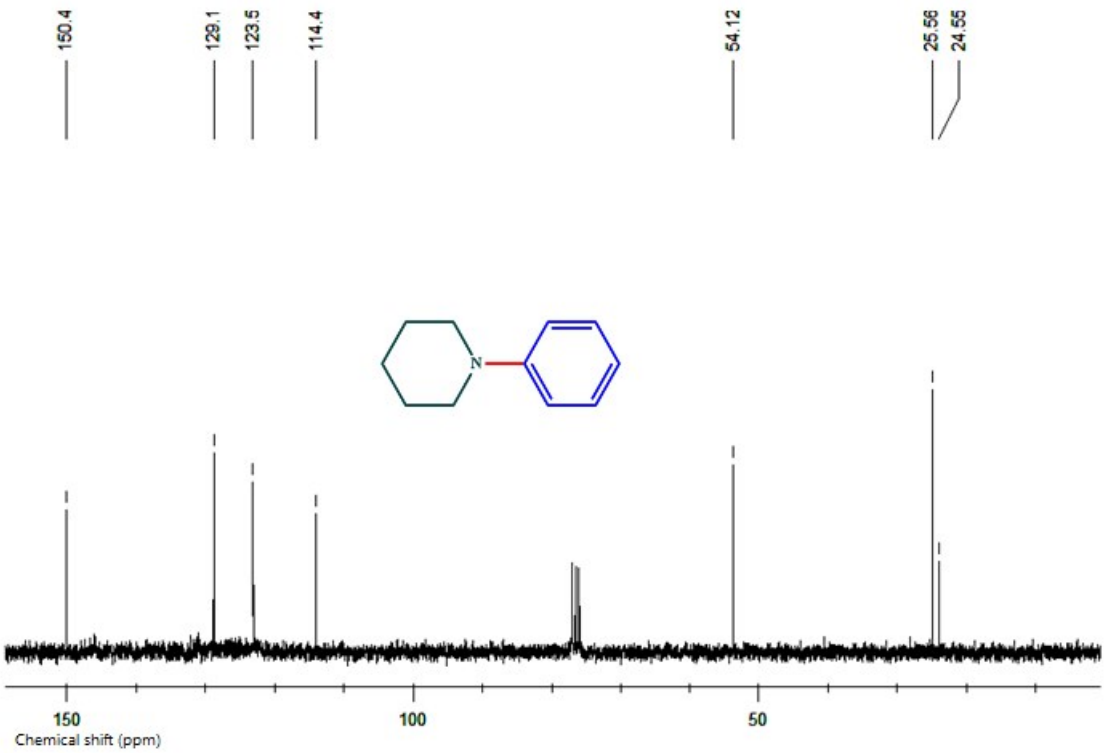


Figure S13. [13]CNMR spectrum of **9b**

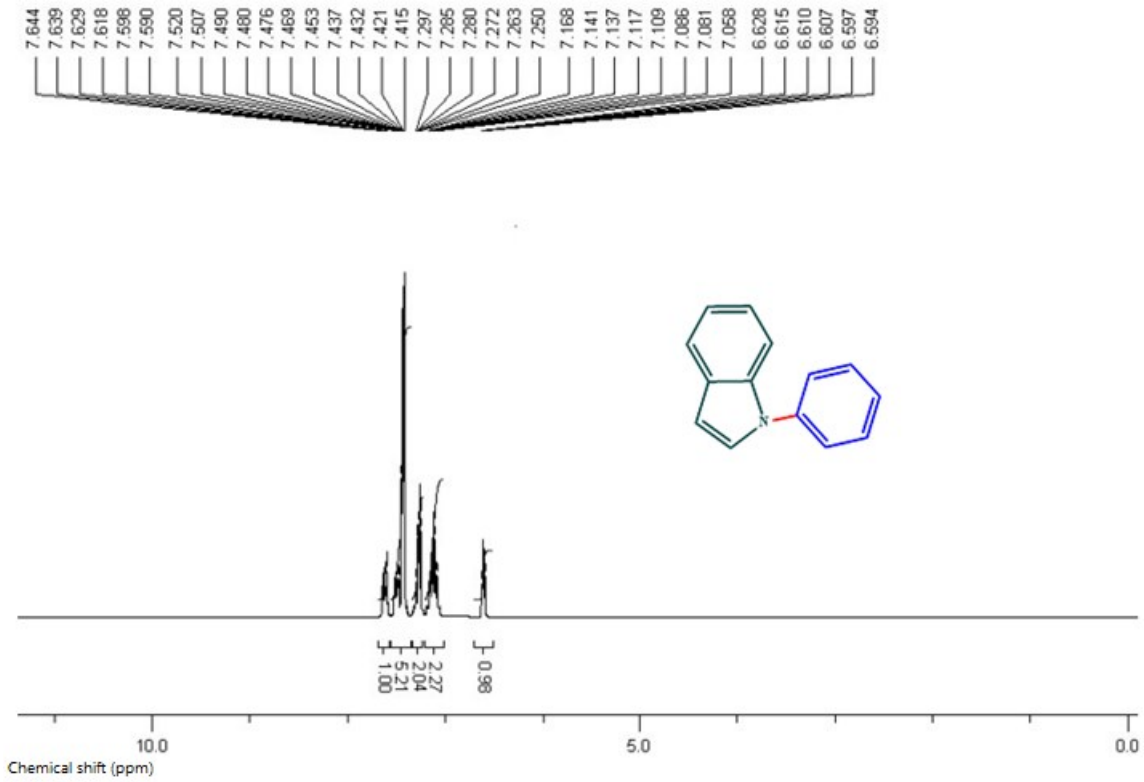


Figure S14. [1]HNMR spectrum of **9c**

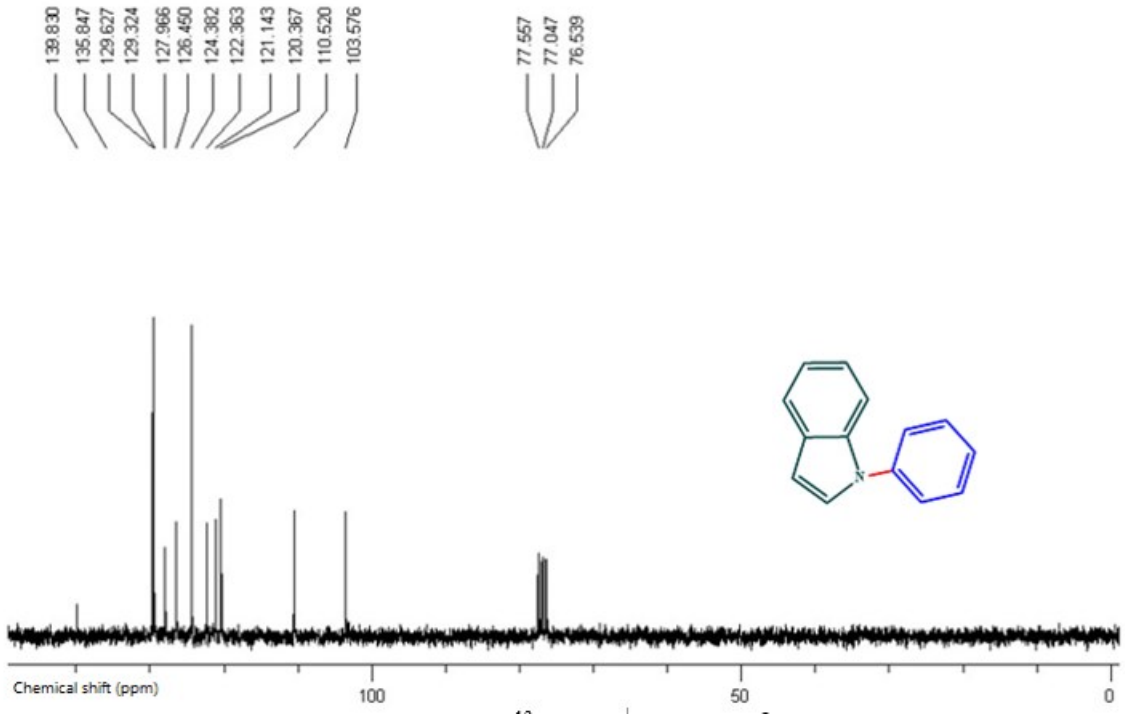


Figure S15. [13]CNMR spectrum of **9c**

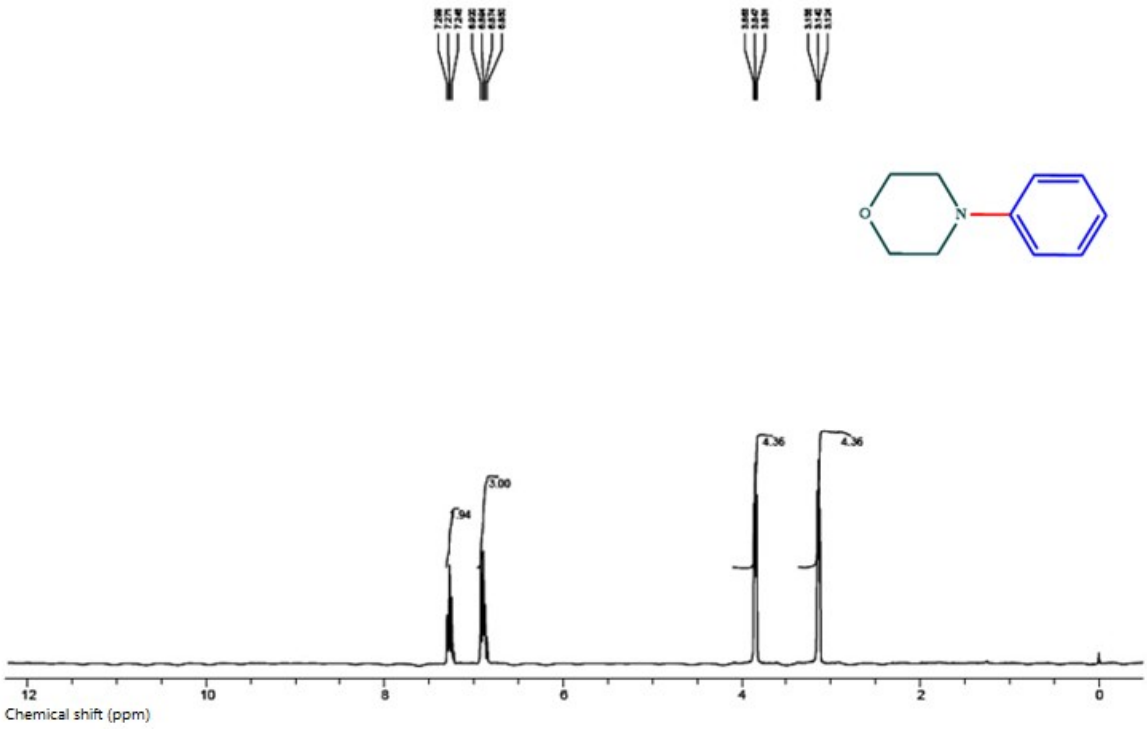


Figure S16. [1]HNMR spectrum of **9d**

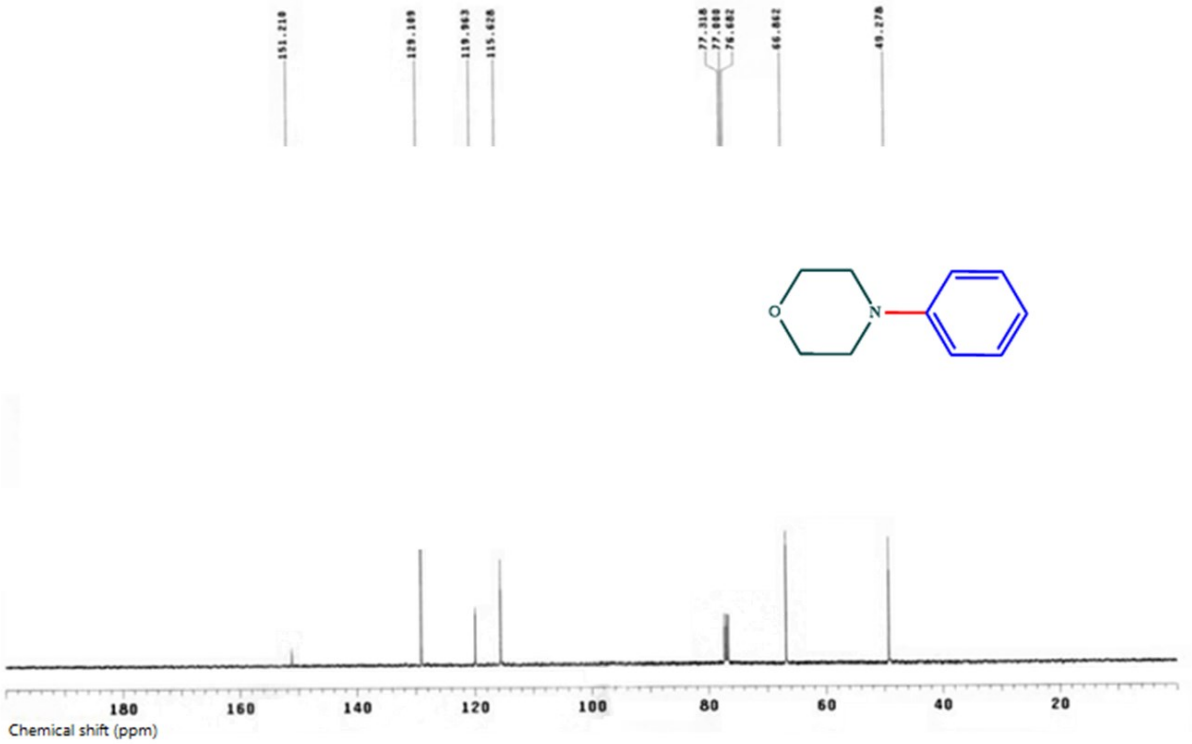


Figure S17. [13]CNMR spectrum of **9d**

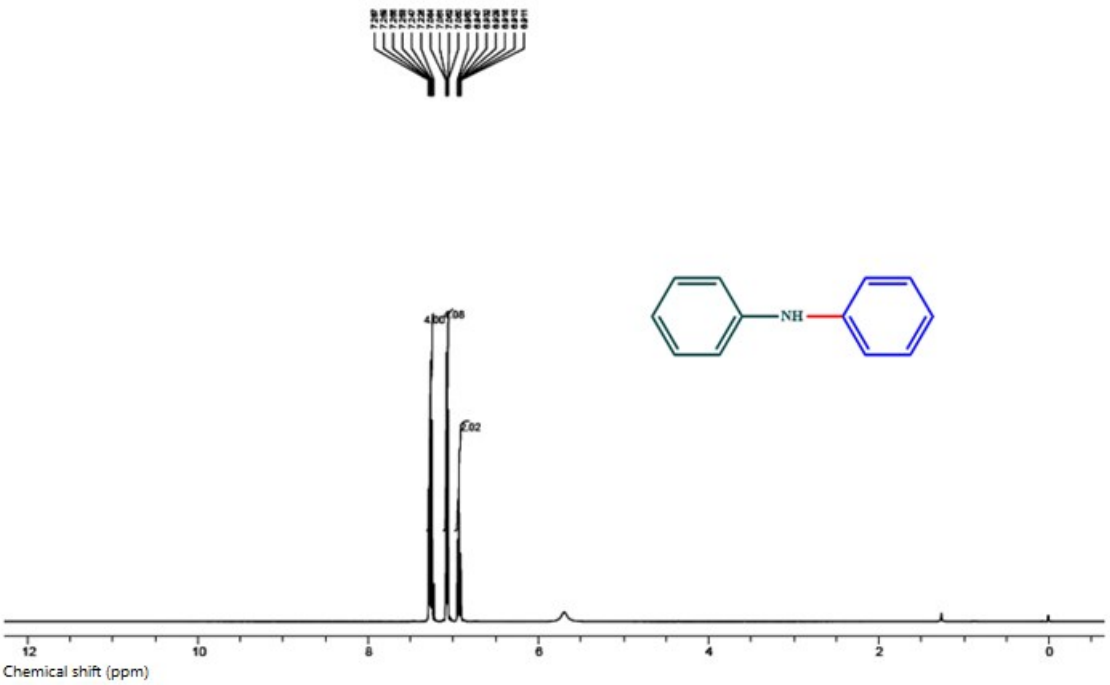


Figure S18. [1]HNMR spectrum of **9e**

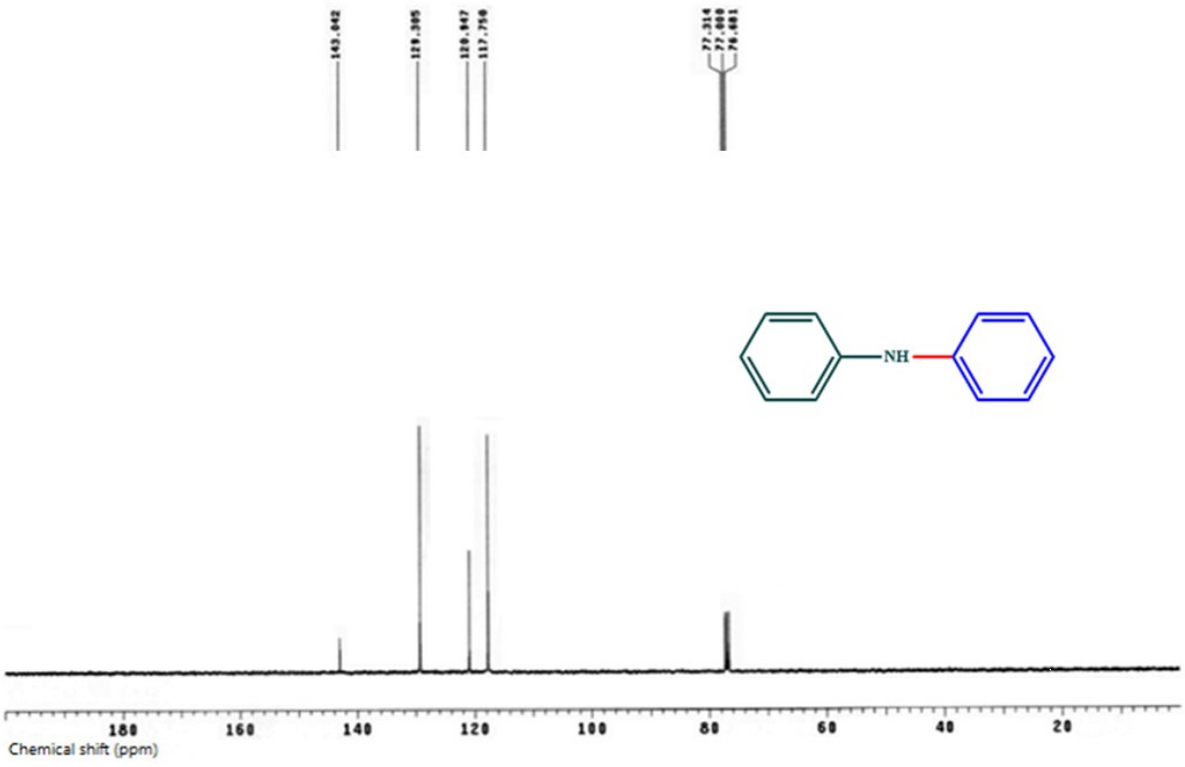


Figure S19. [13]CNMR spectrum of **9e**

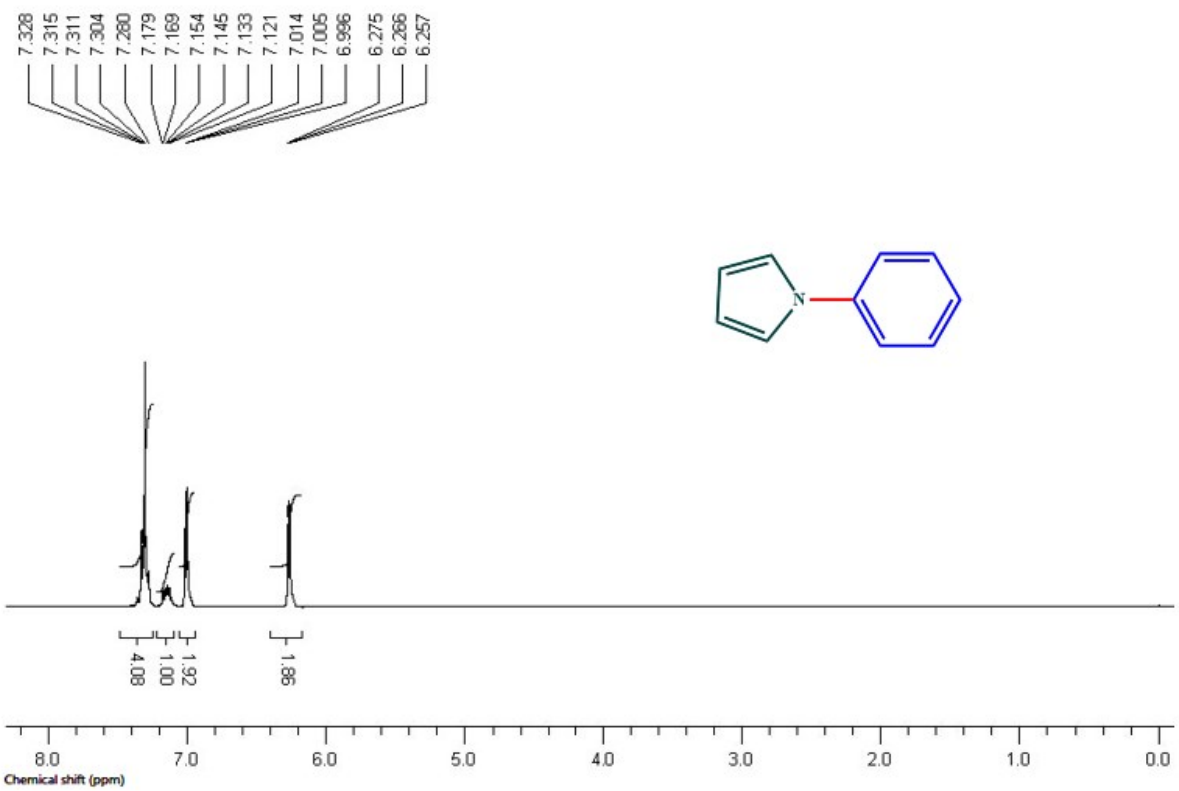


Figure S20. [1]HNMR spectrum of **9f**

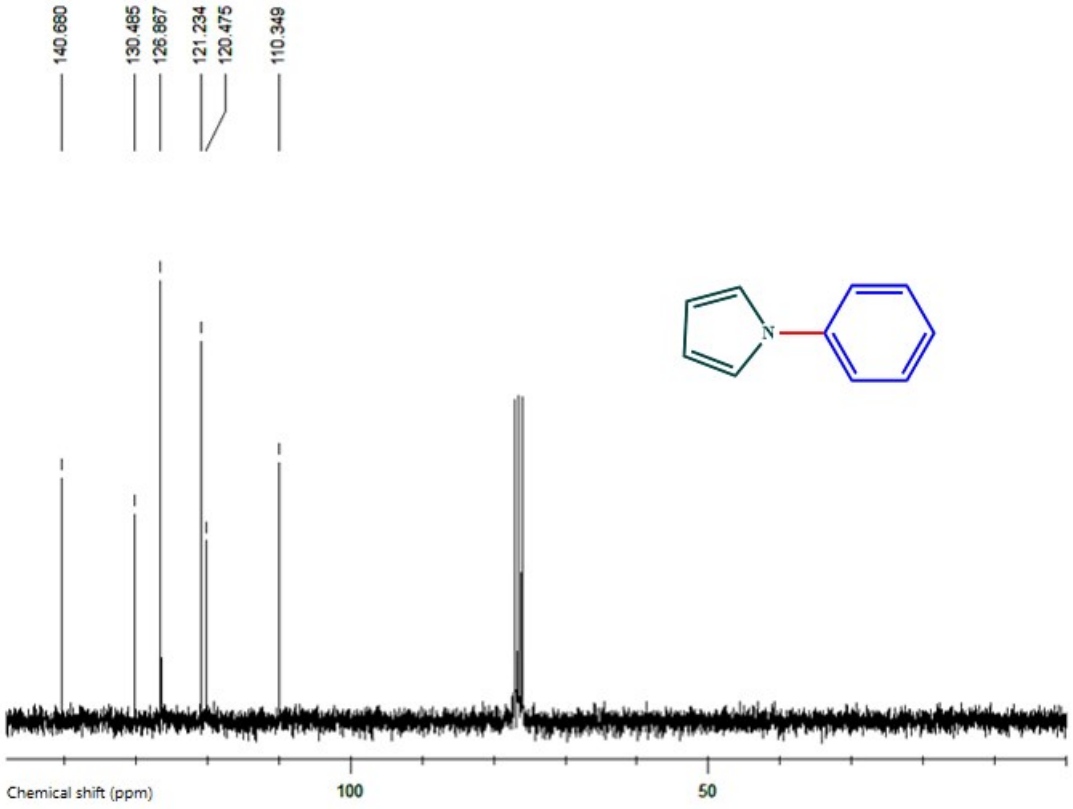


Figure S21. [13]CNMR spectrum of **9f**

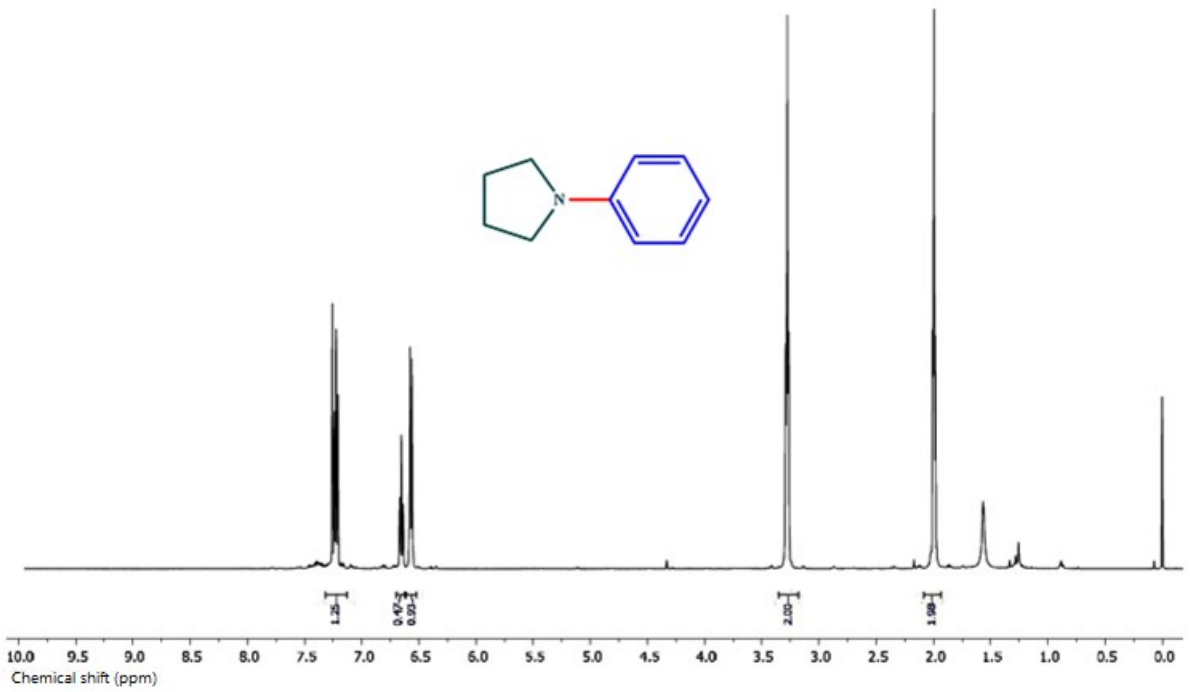


Figure S22. [1]HNMR spectrum of **9g**

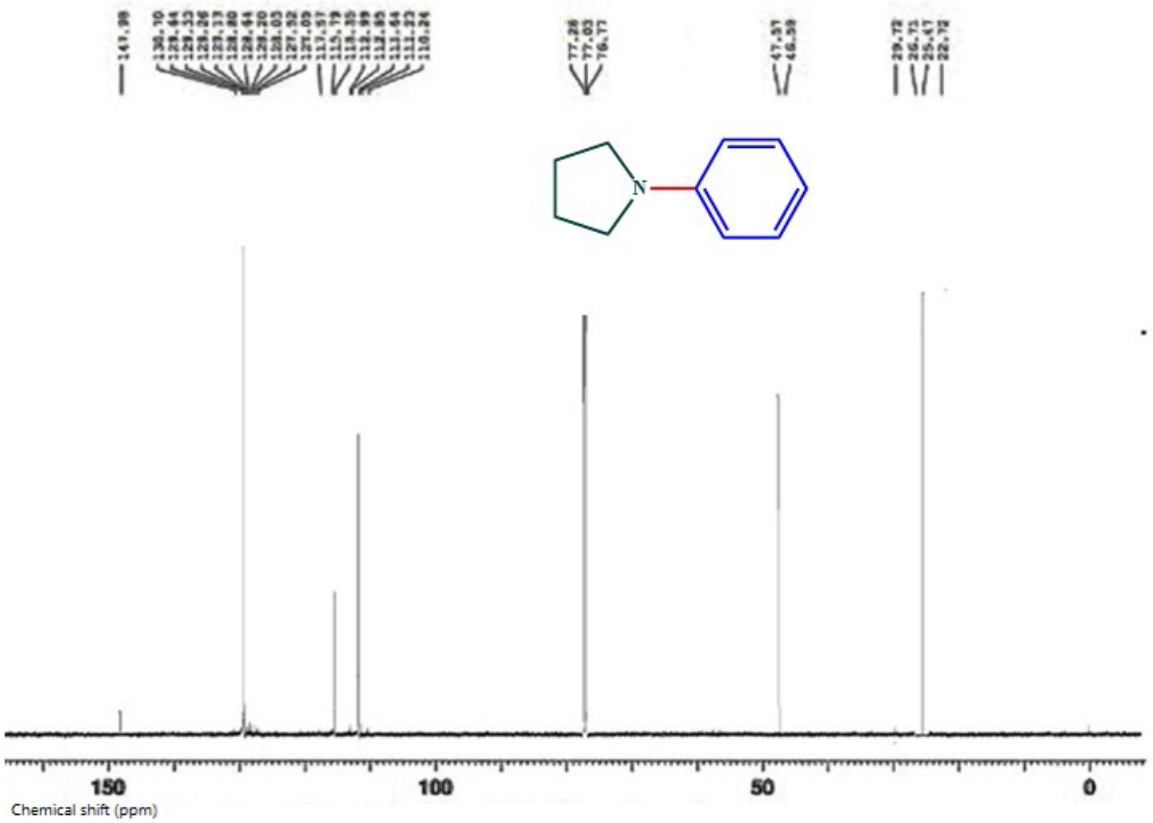


Figure S23. [13]CNMR spectrum of **9g**

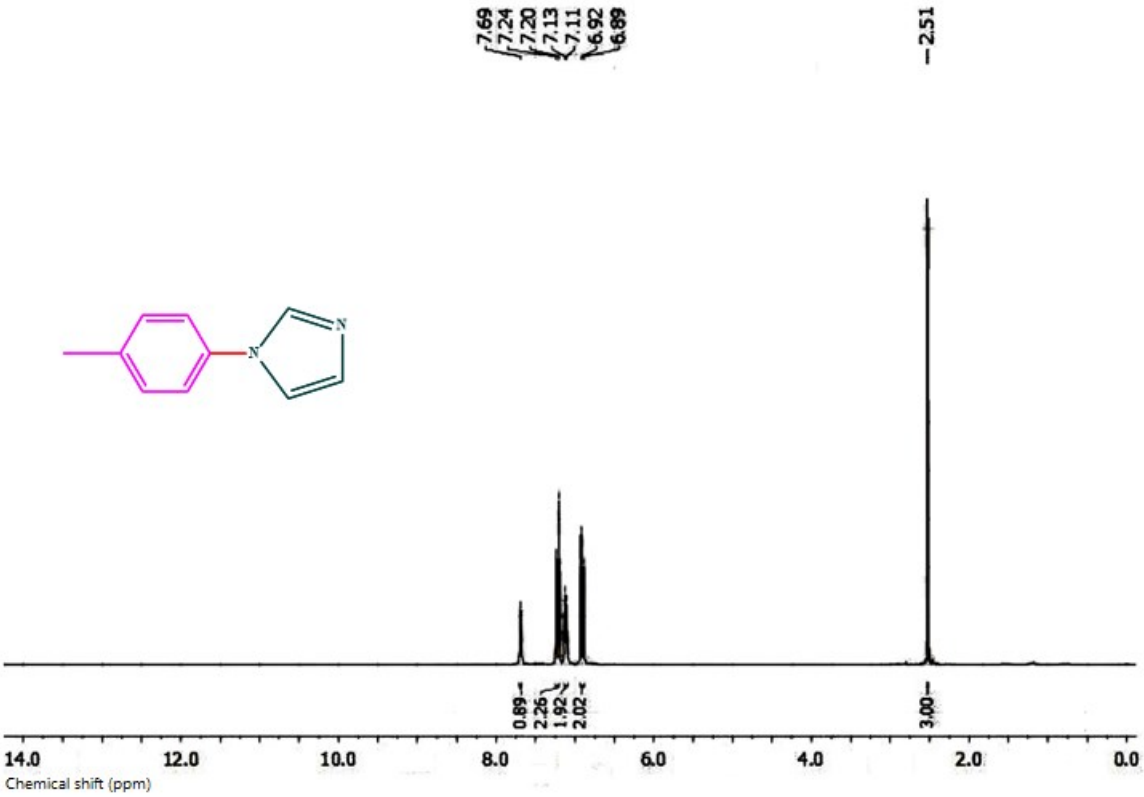


Figure S24. [1]HNMR spectrum of **9h**

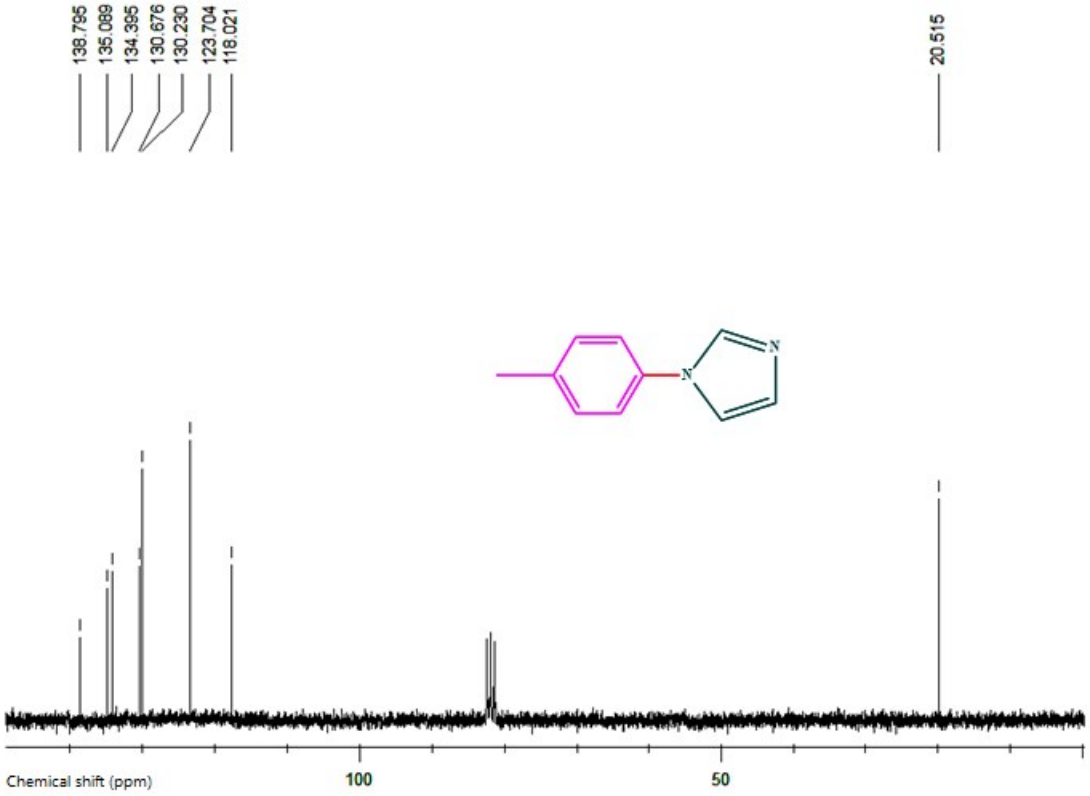


Figure S25. [13]CNMR spectrum of **9h**

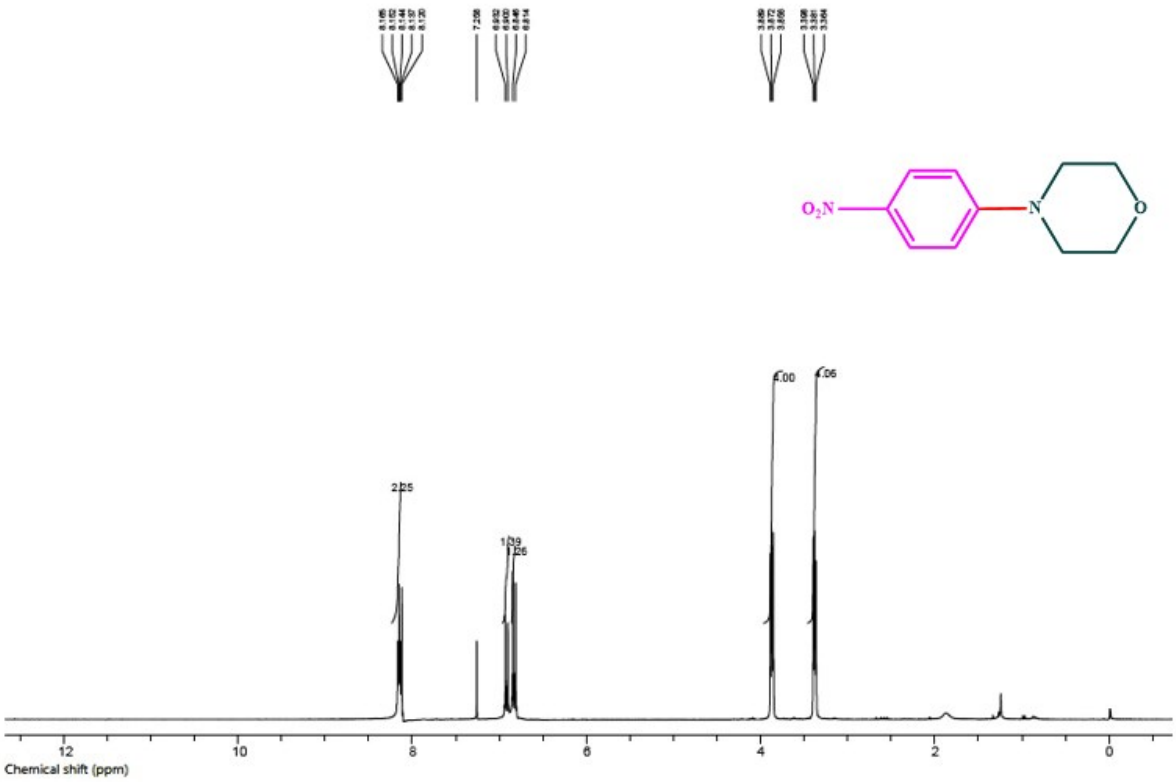


Figure S26. [1]HNMR spectrum of **9i**

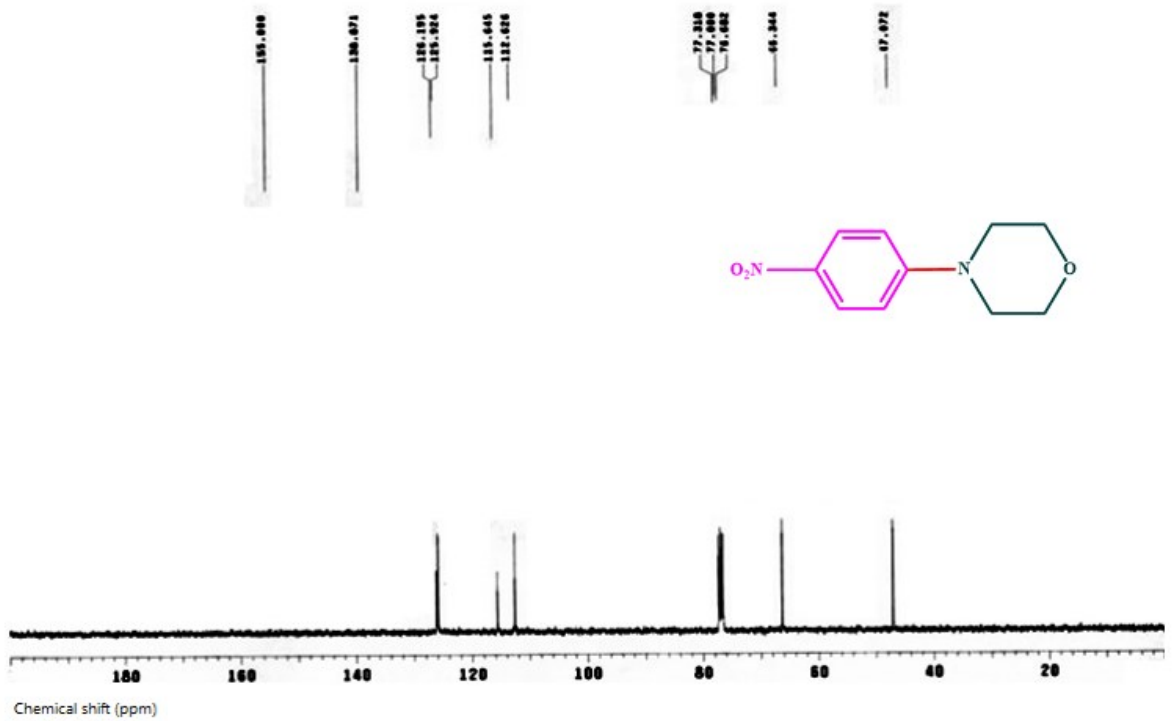


Figure S27. [13]CNMR spectrum of **9i**

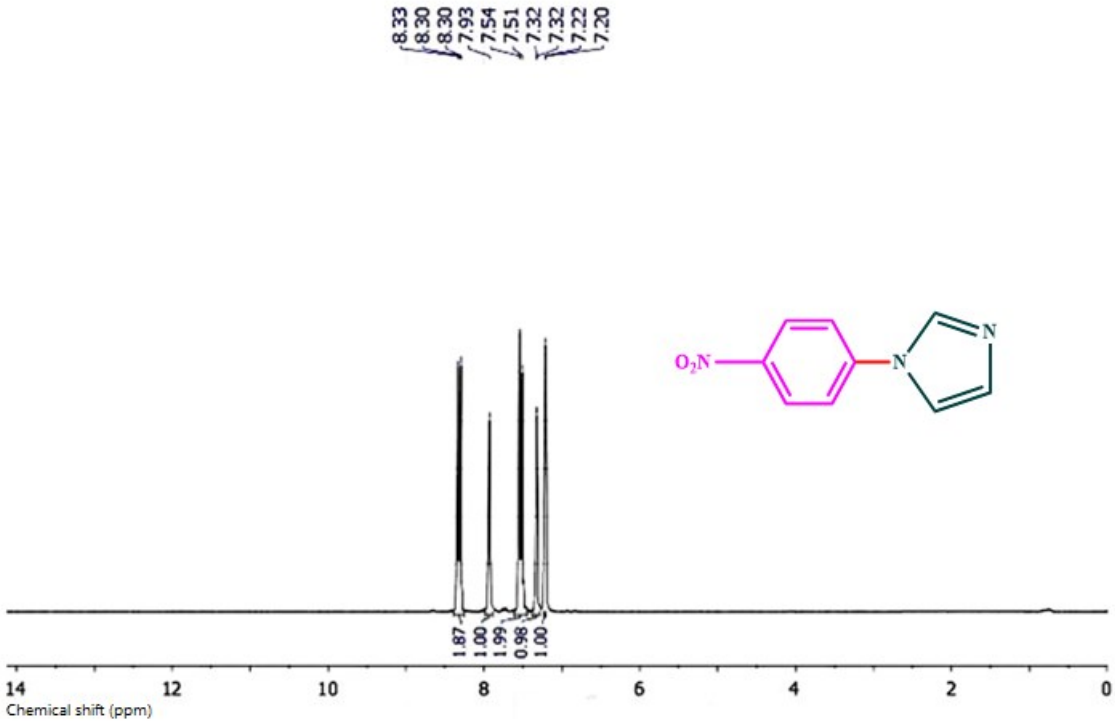


Figure S28. [1]HNMR spectrum of **9j**

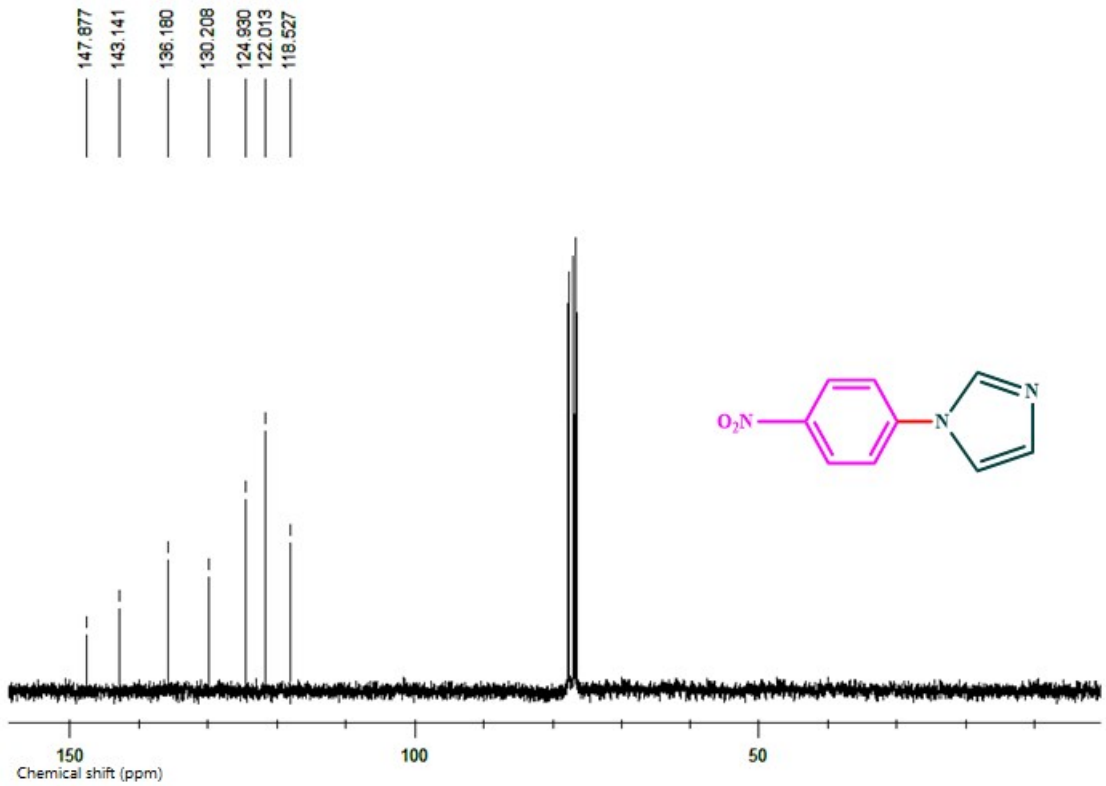


Figure S29. [13]CNMR spectrum of **9j**

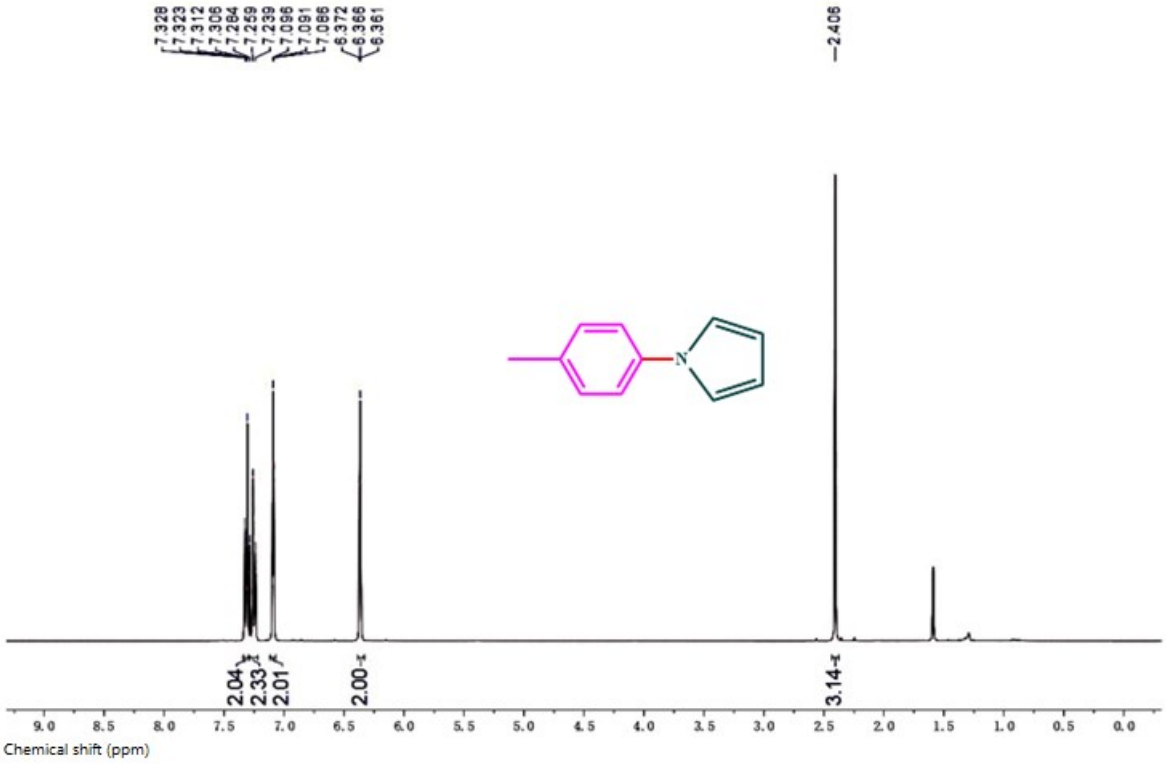


Figure S30. [1]HNMR spectrum of **9k**

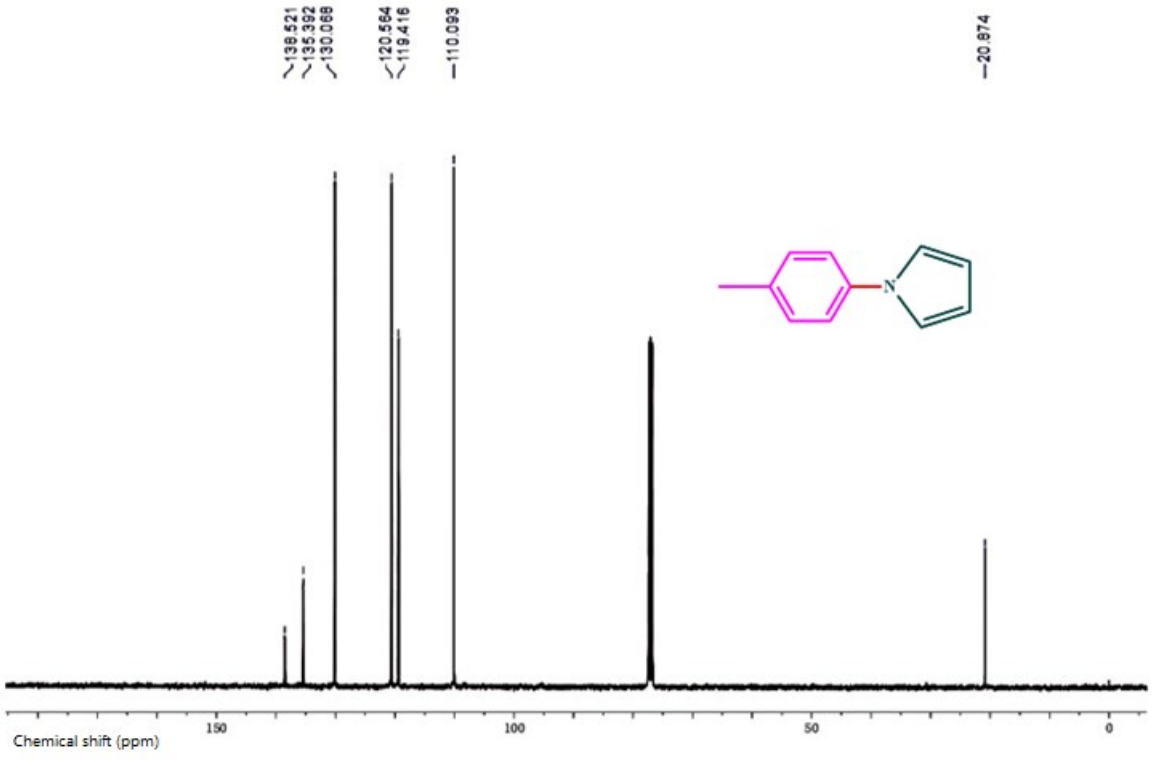


Figure S31. [13]CNMR spectrum of **9k**

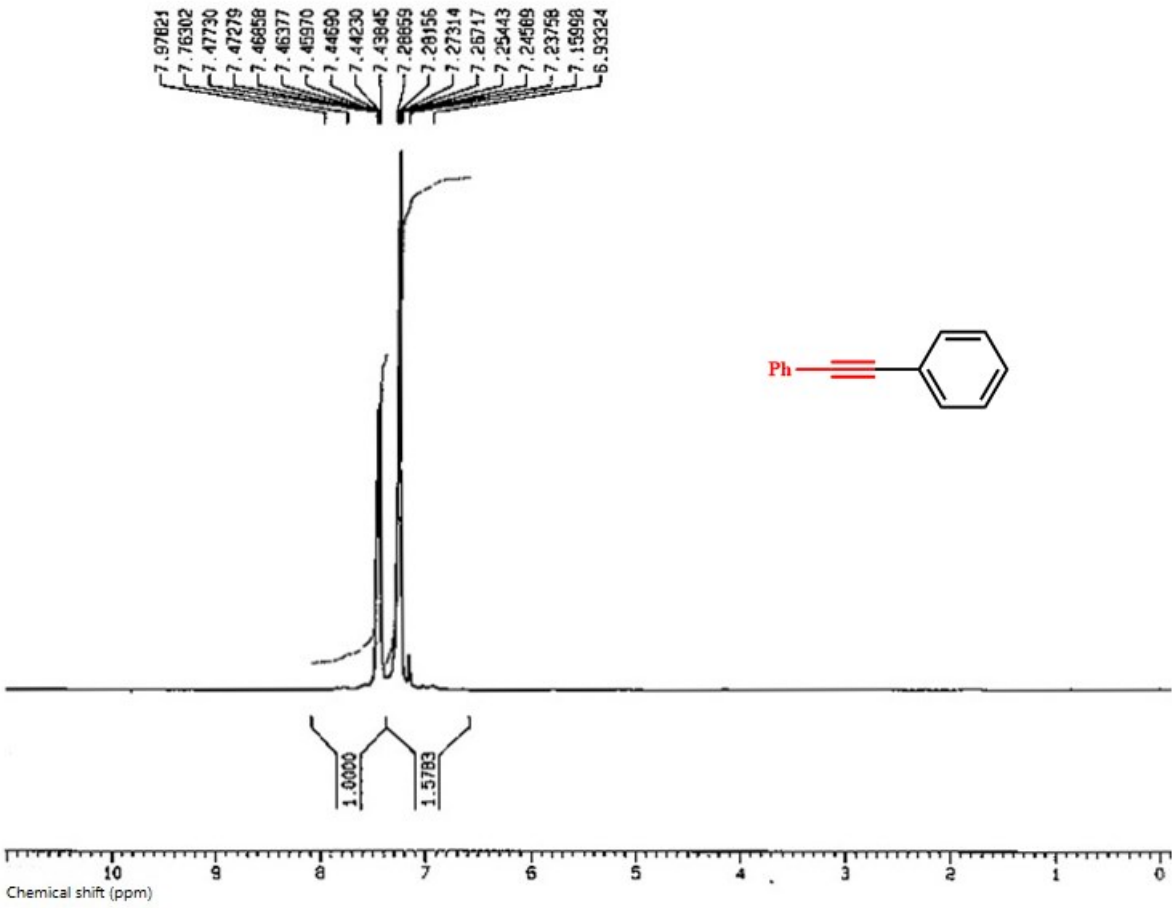


Figure S32. [1]HNMR spectrum of **11a**

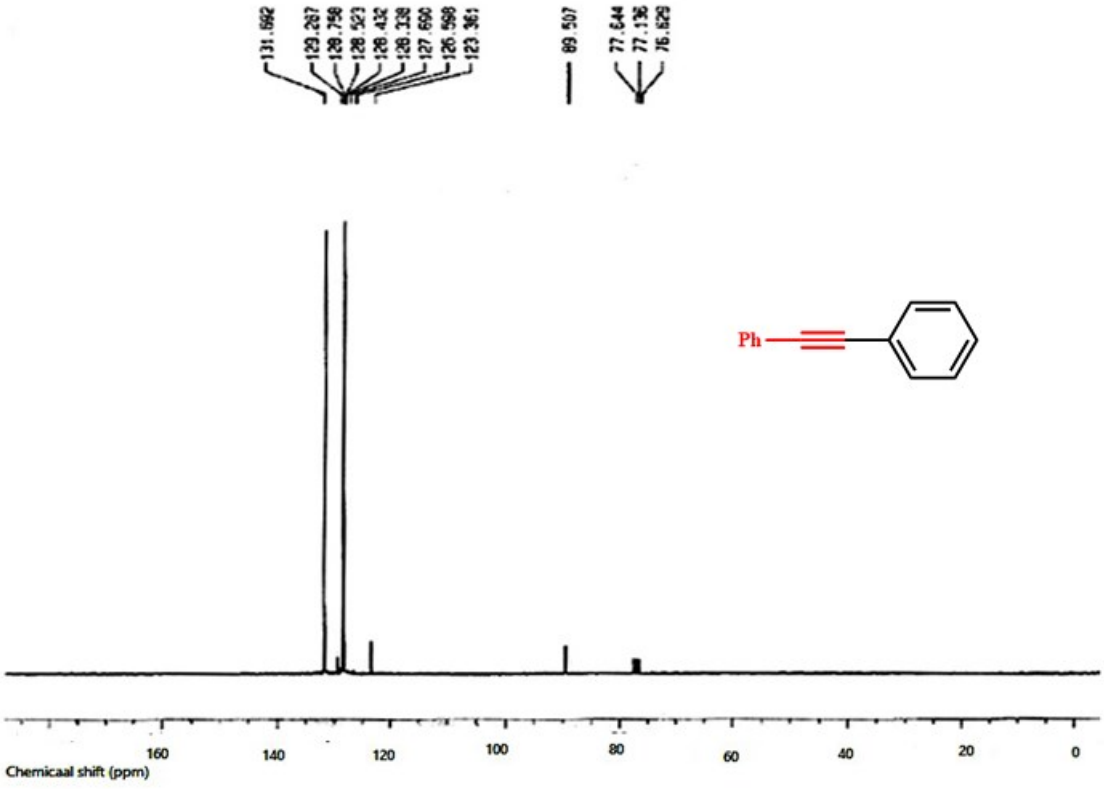


Figure S33. [13]CNMR spectrum of **11a**

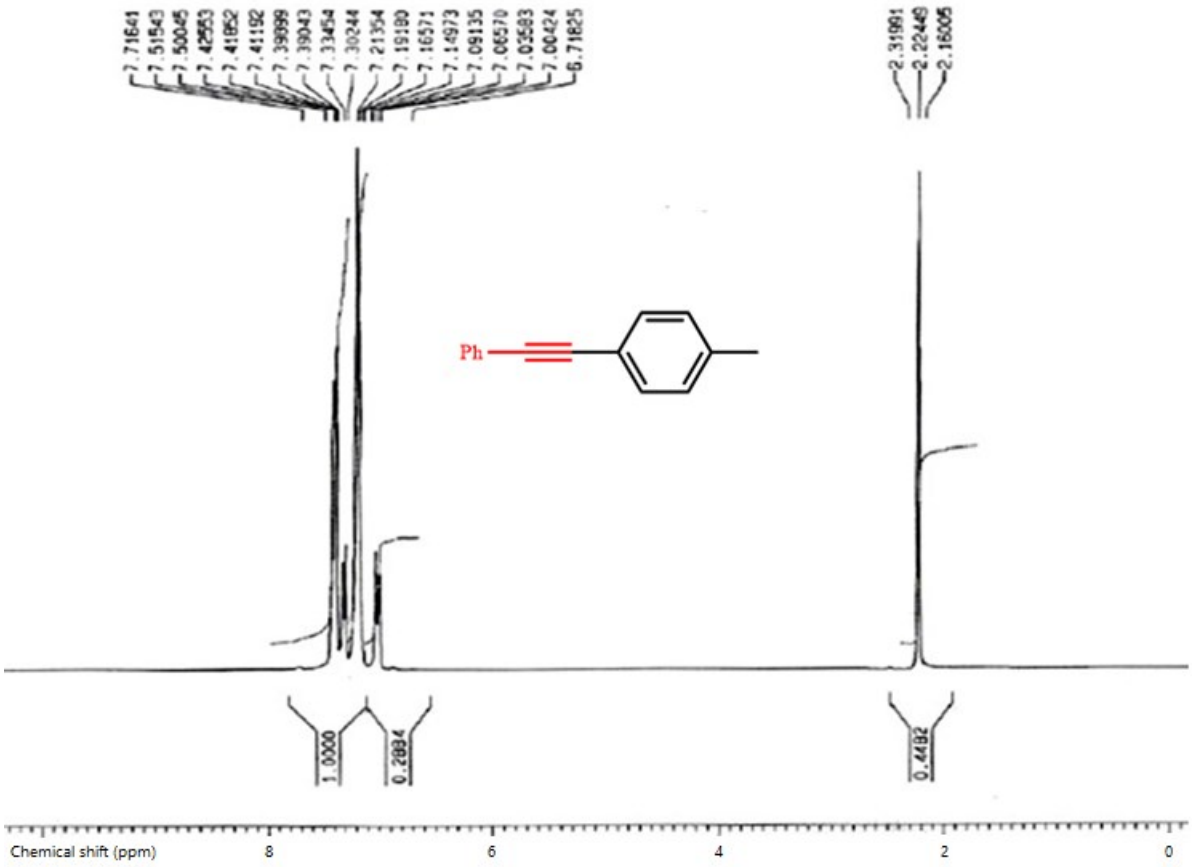


Figure S34. [1]HNMR spectrum of **11b**

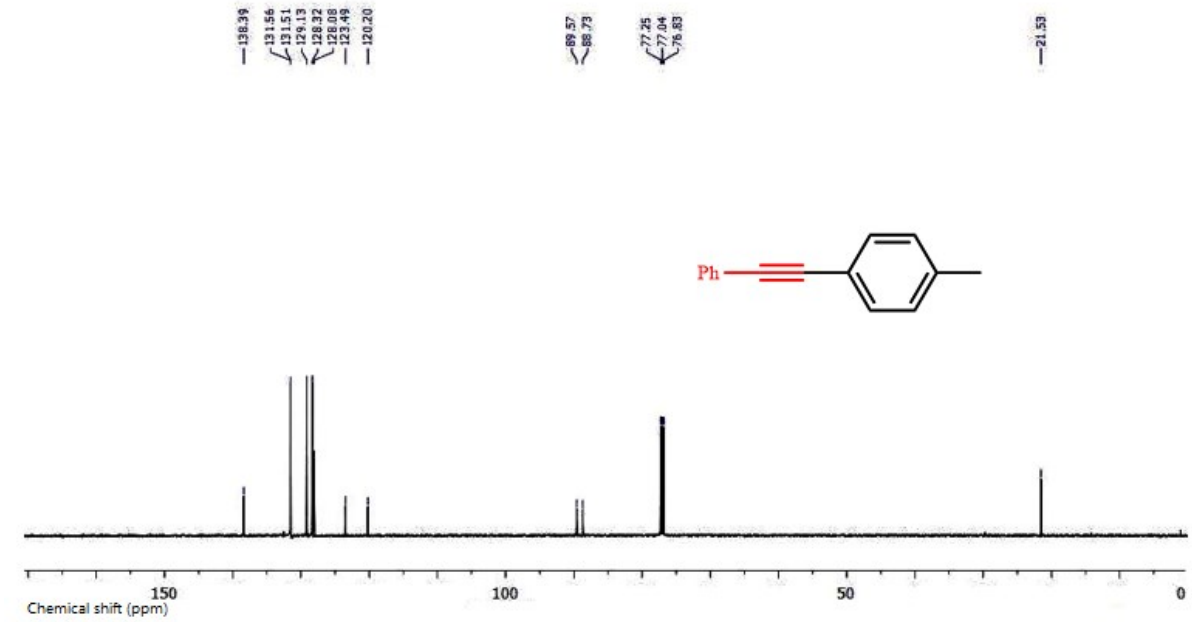


Figure S35. [13]CNMR spectrum of **11b**

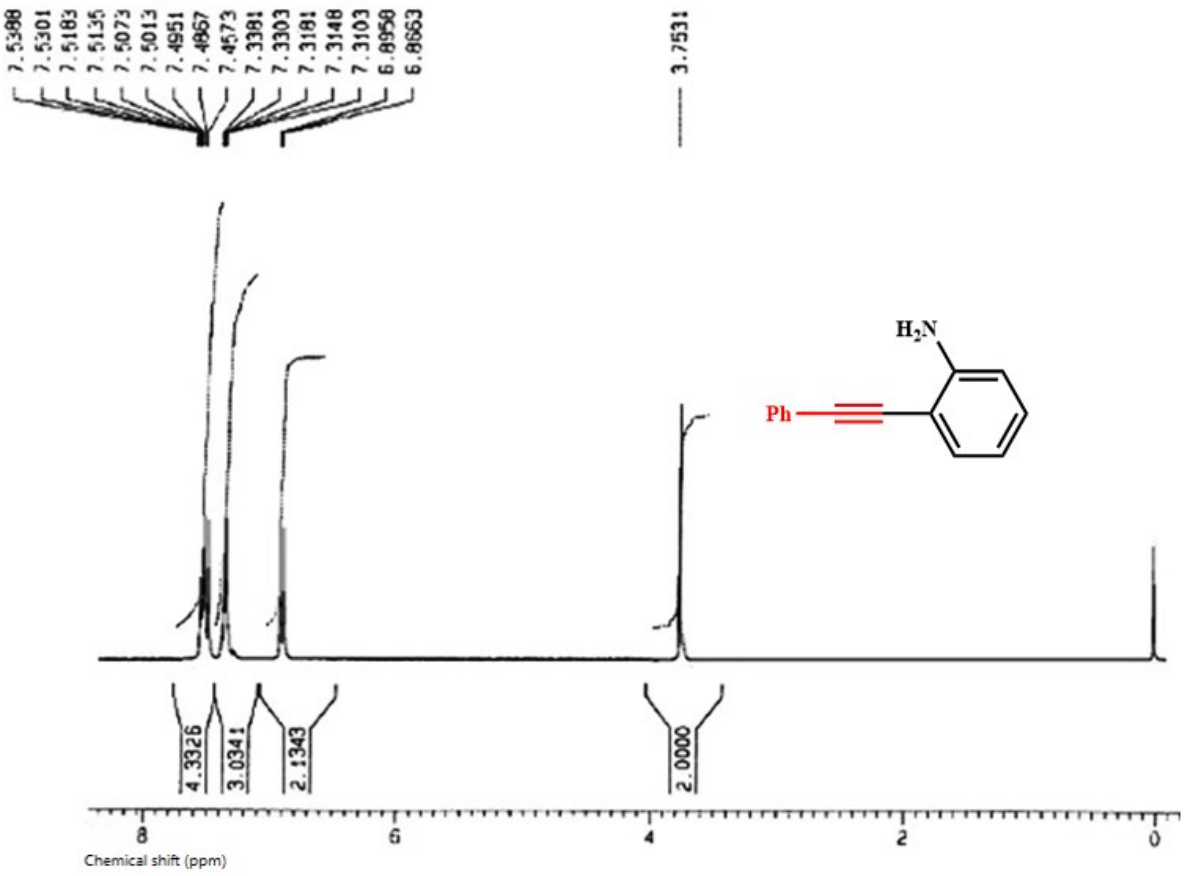


Figure S36. [1]HNMR spectrum of **11c**

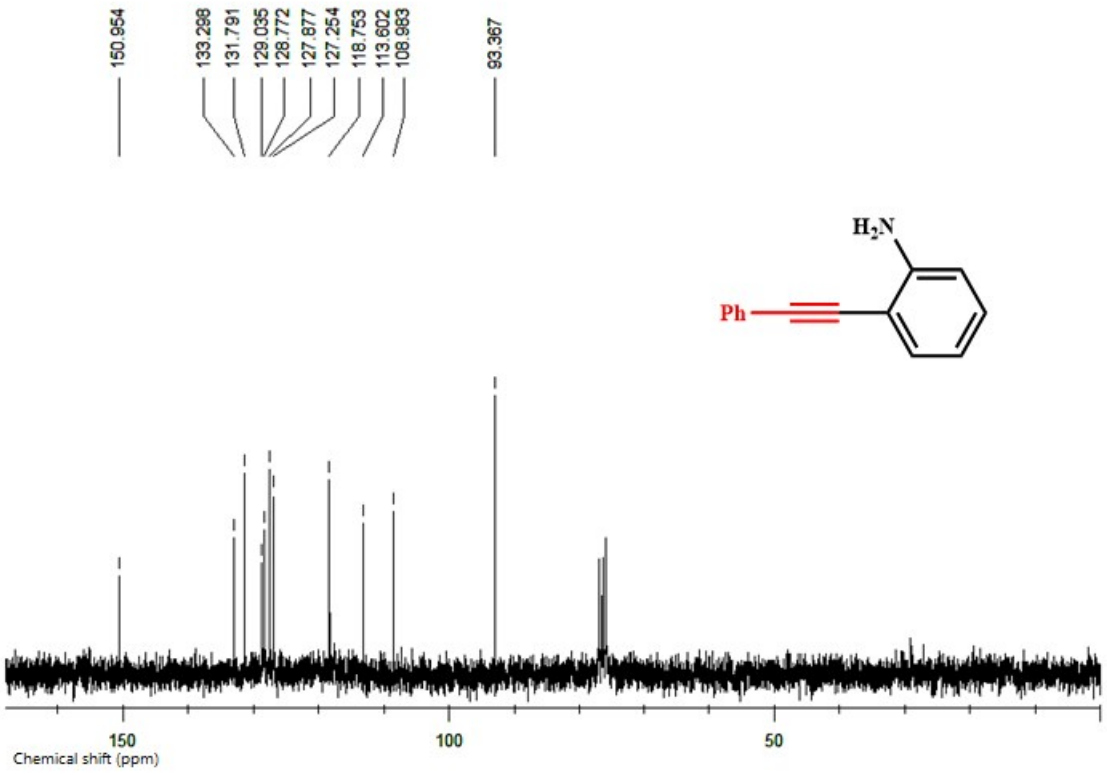


Figure S37. [13]CNMR spectrum of **11c**

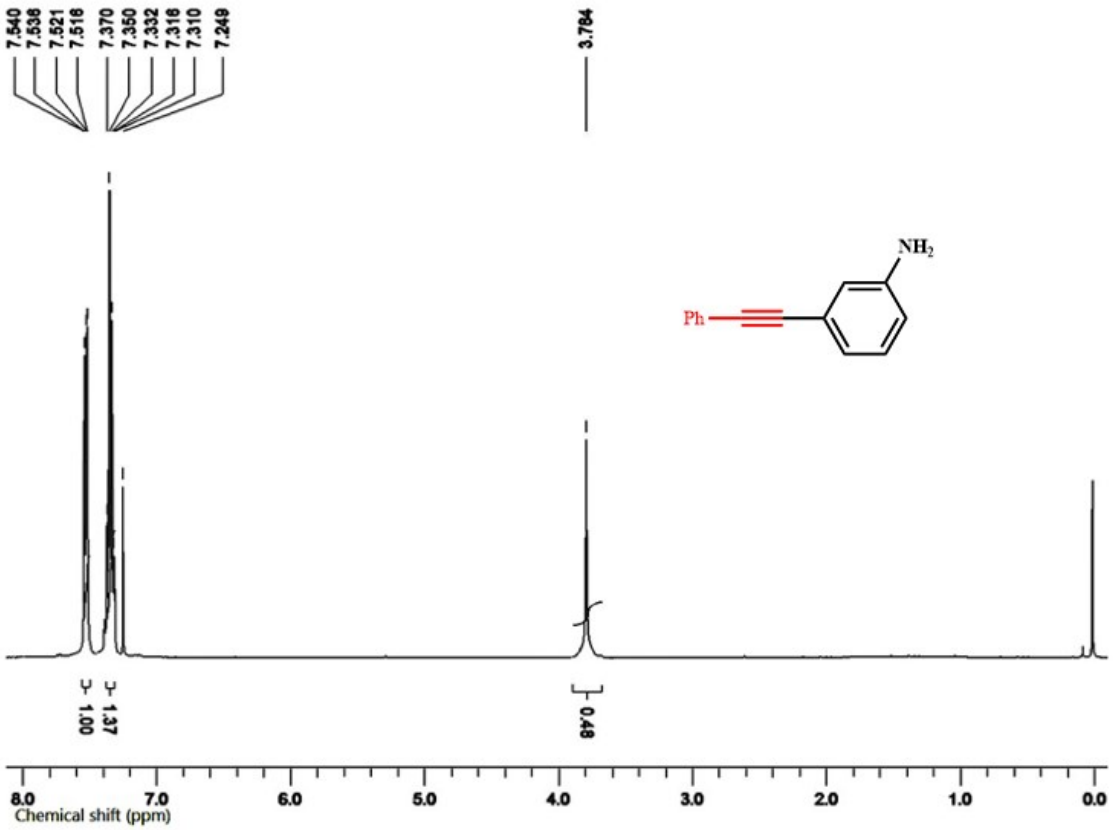


Figure S38. [1]HNMR spectrum of **11d**

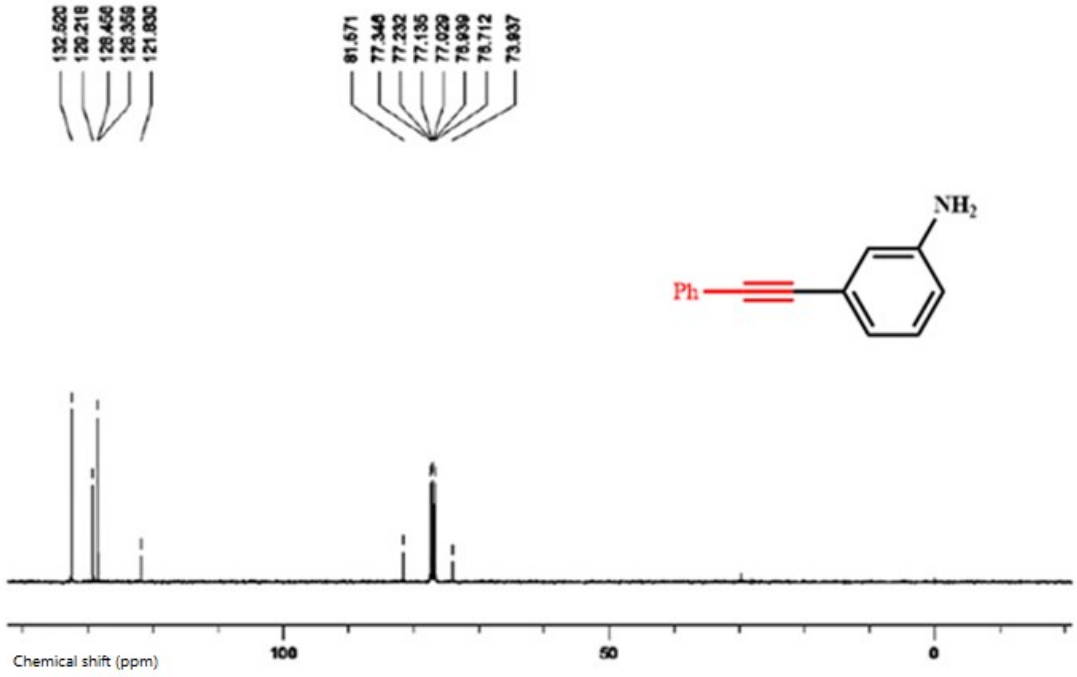


Figure S39. [13]CNMR spectrum of **11d**

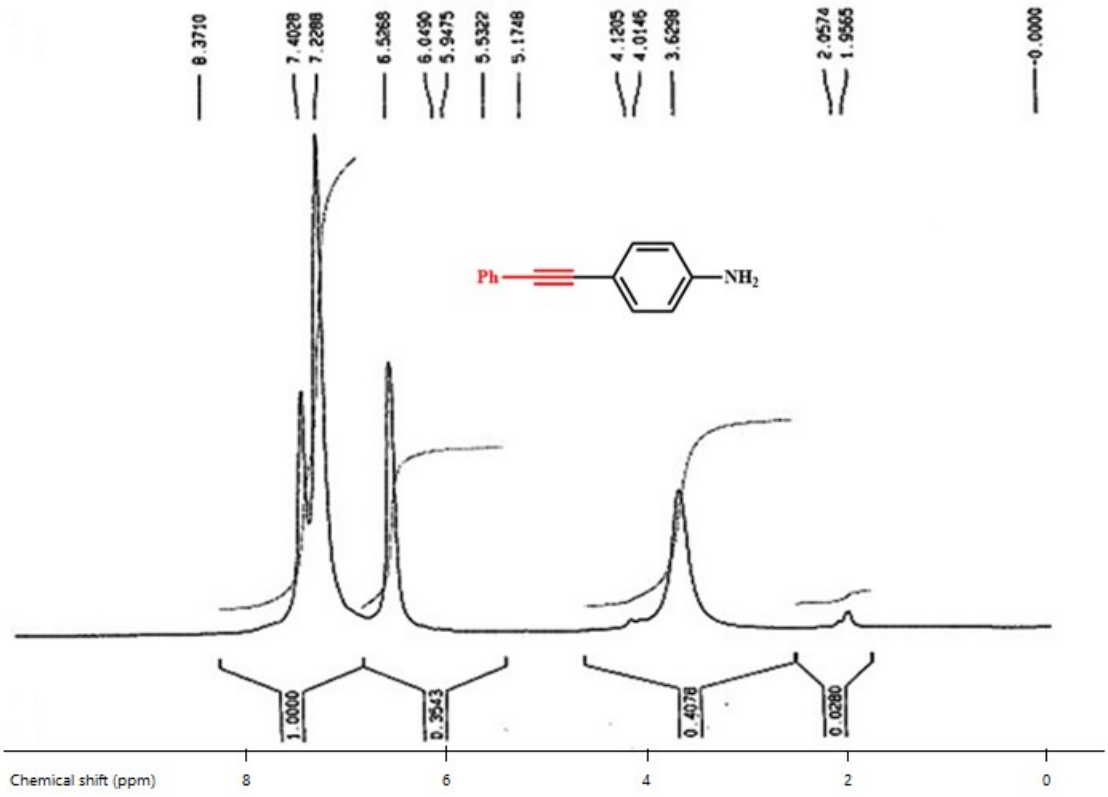


Figure S40. [1]HNMR spectrum of **11e**

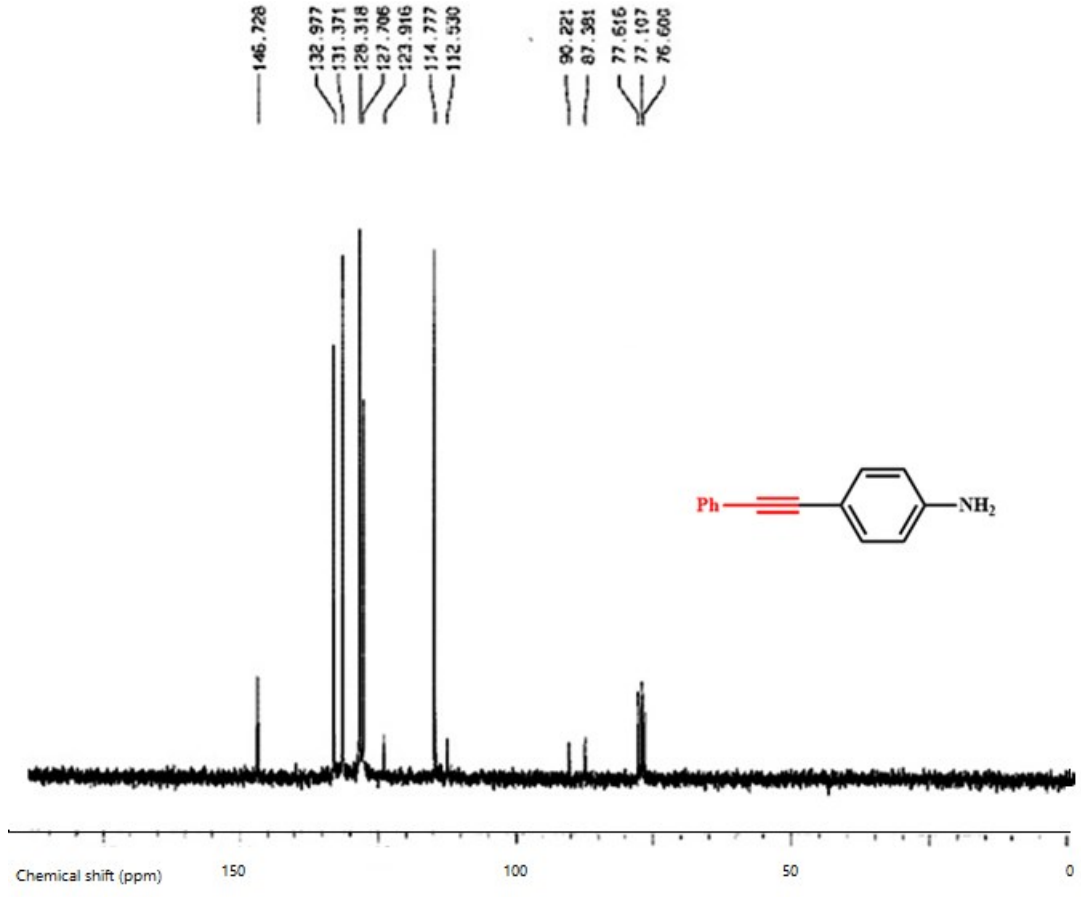


Figure S41. [13]CNMR spectrum of **11e**

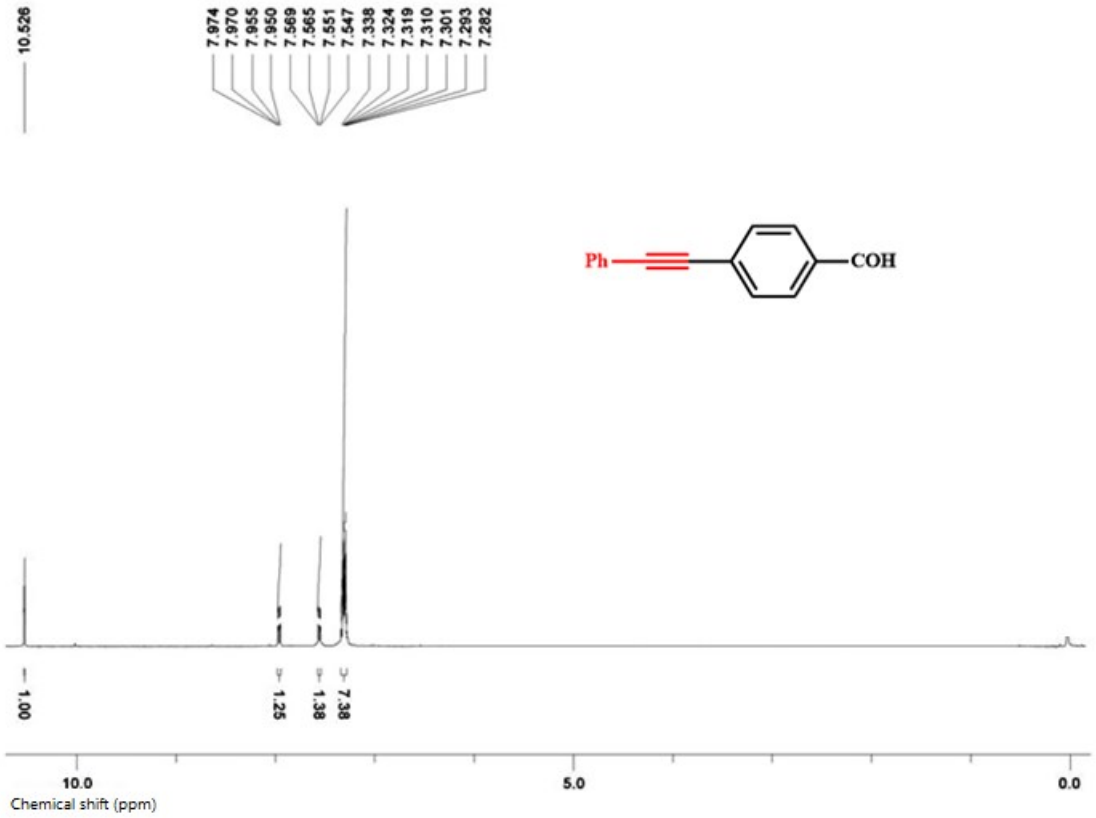


Figure S42. [1]HNMR spectrum of **11f**

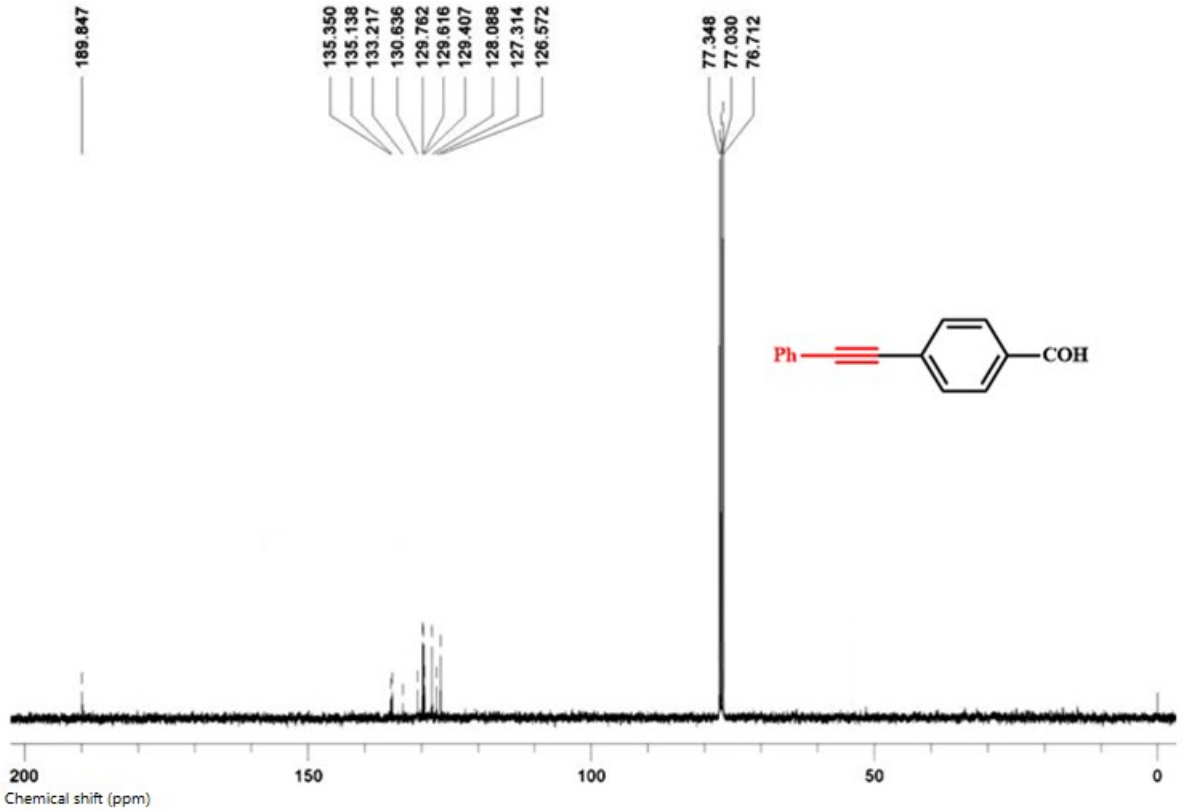


Figure S43. [13]CNMR spectrum of **11f**

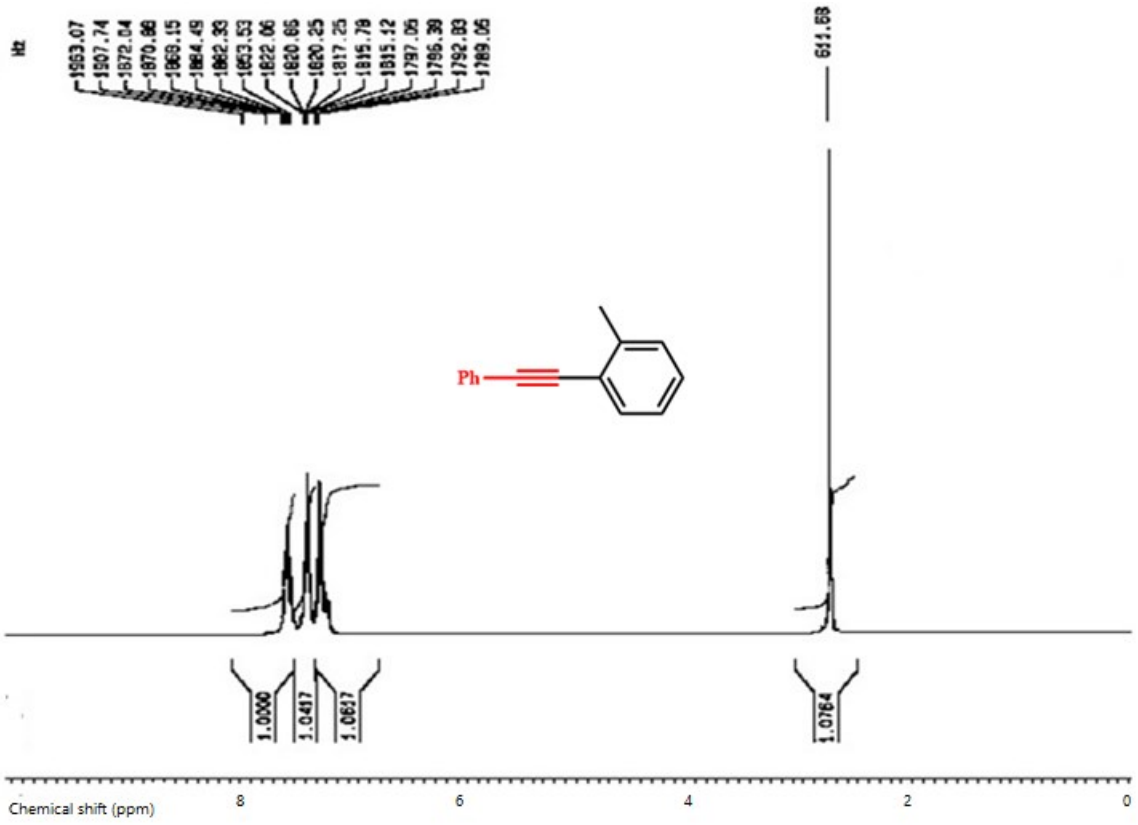


Figure S44. [1]HNMR spectrum of **11g**

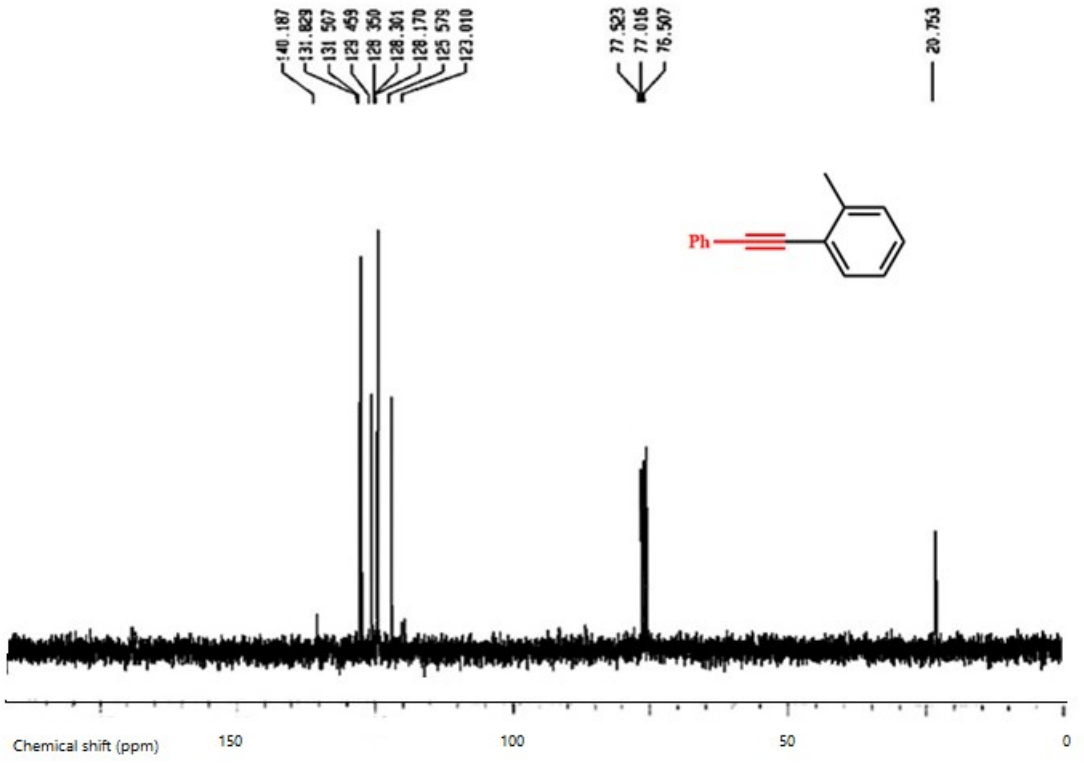


Figure S45. [13]CNMR spectrum of **11g**

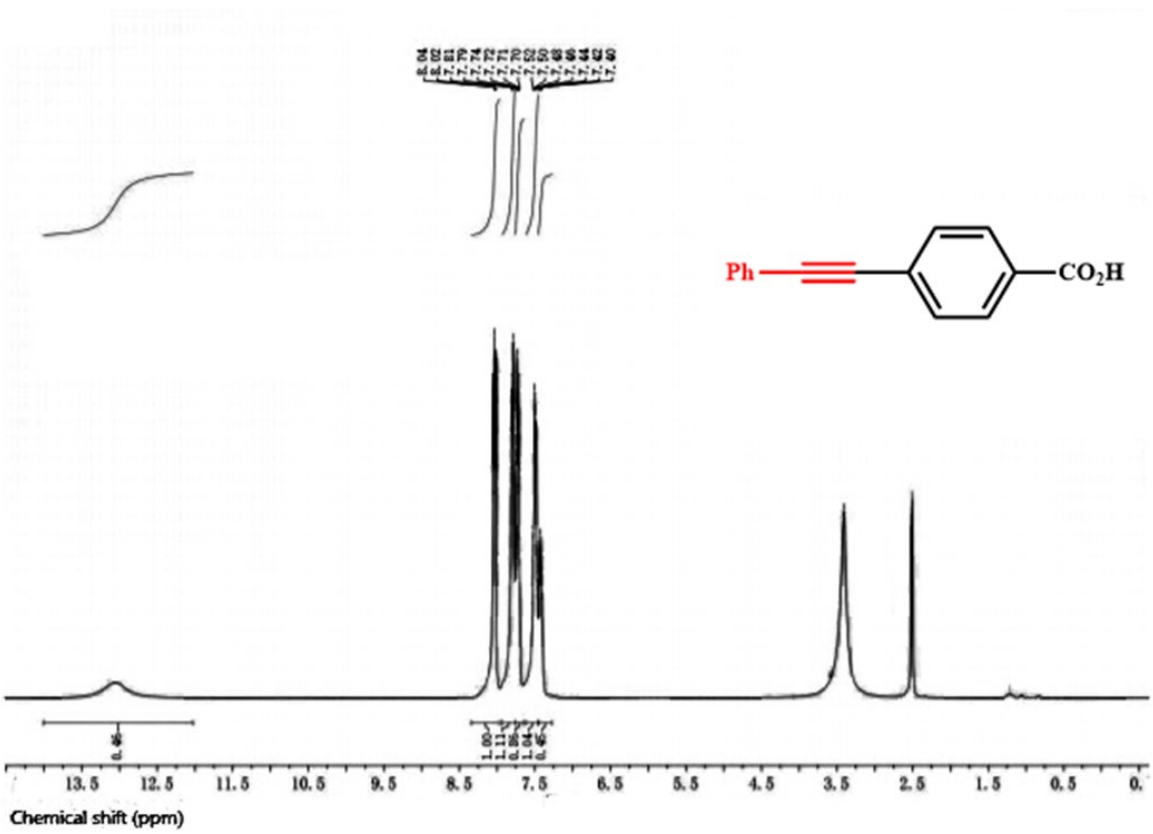


Figure S46. [1]HNMR spectrum of **11h**

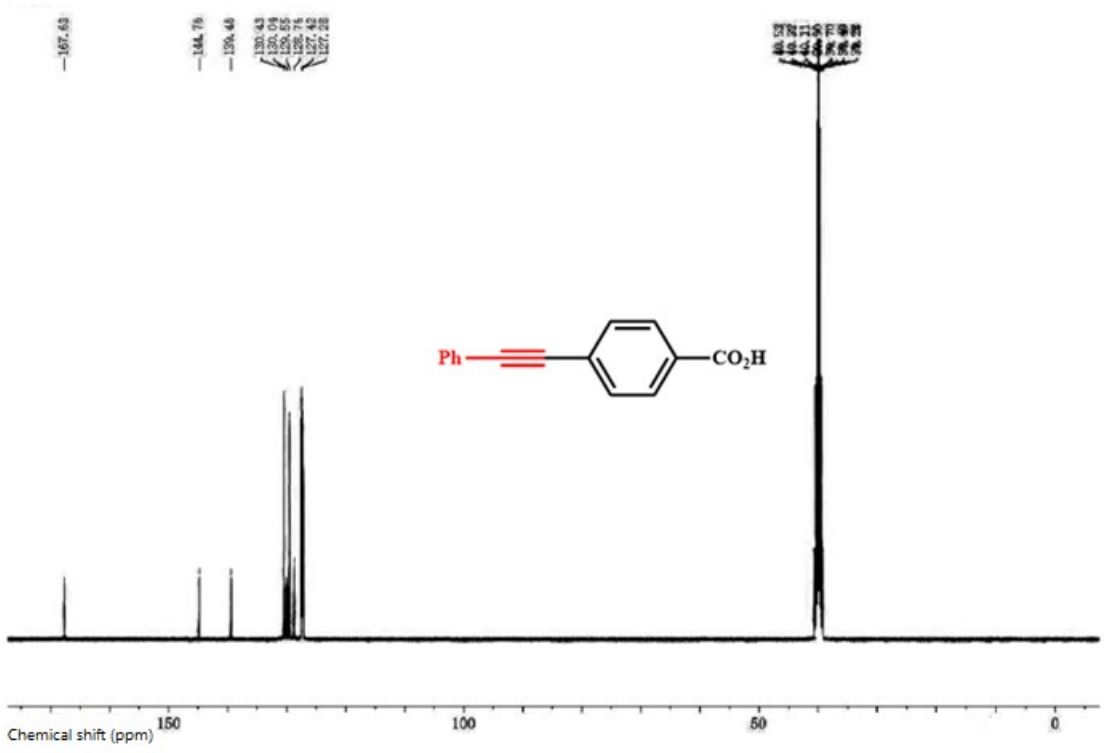


Figure S47. [13]CNMR spectrum of **11h**

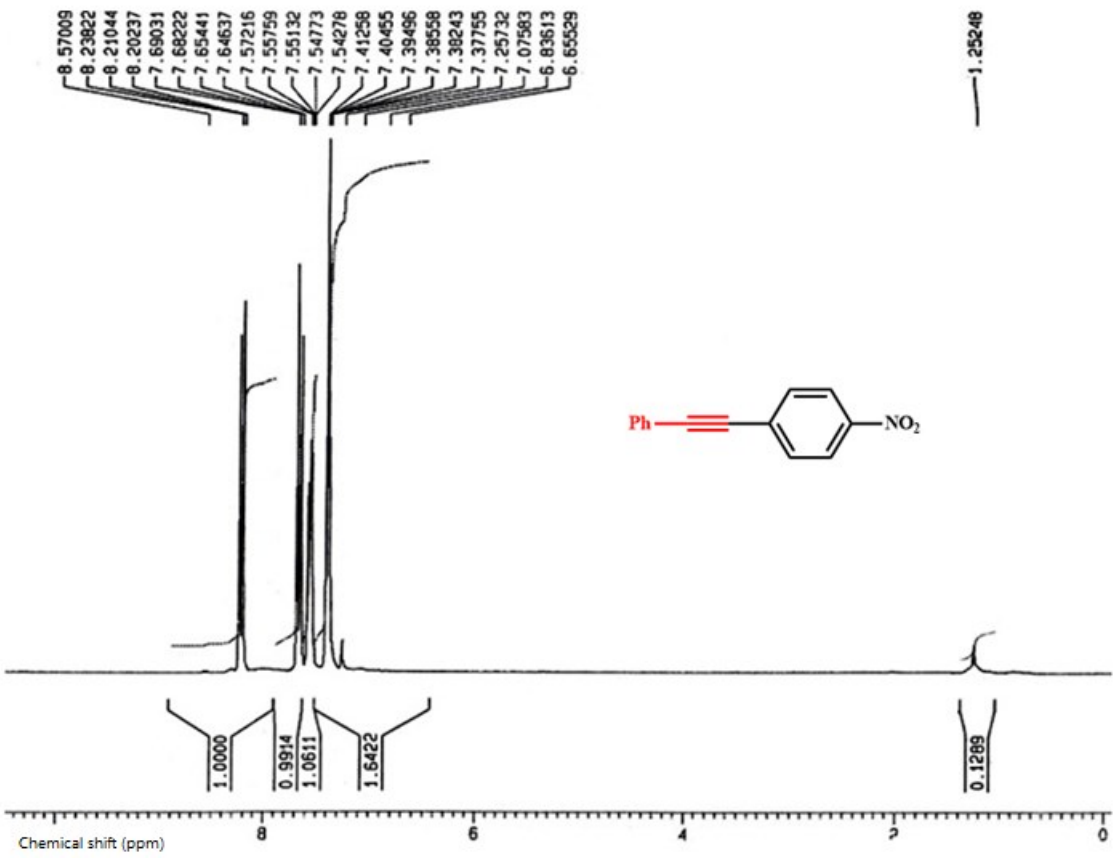


Figure S48. [1]HNMR spectrum of **11i**

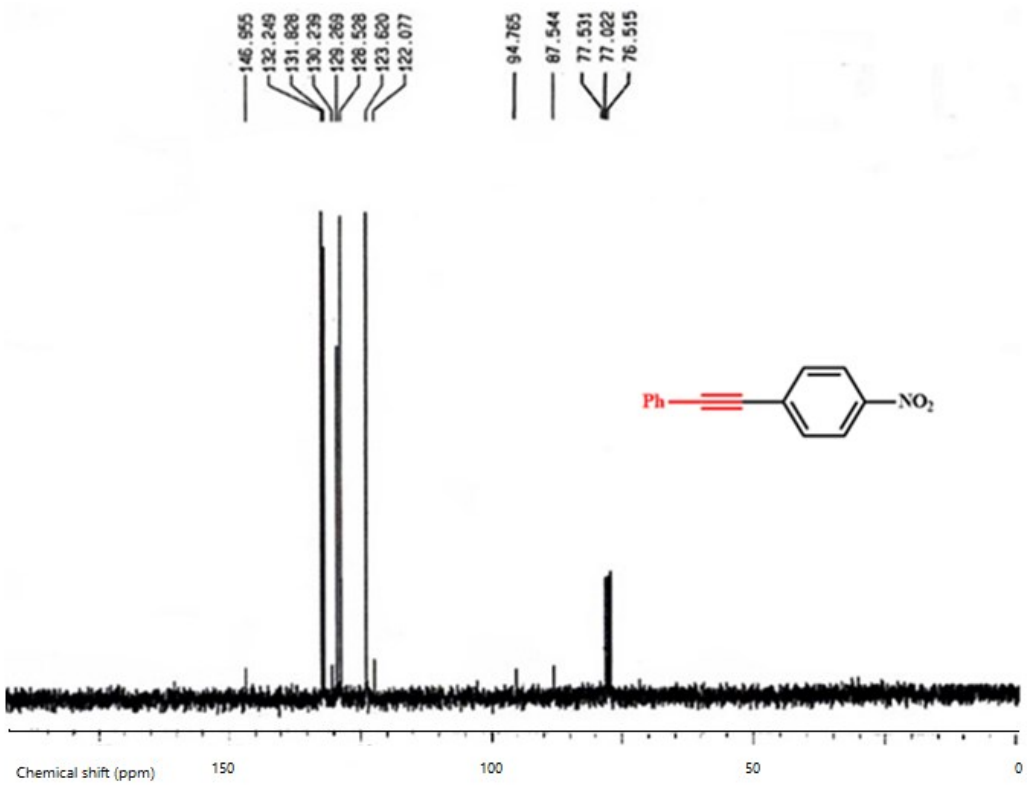


Figure S49. [13]CNMR spectrum of **11i**

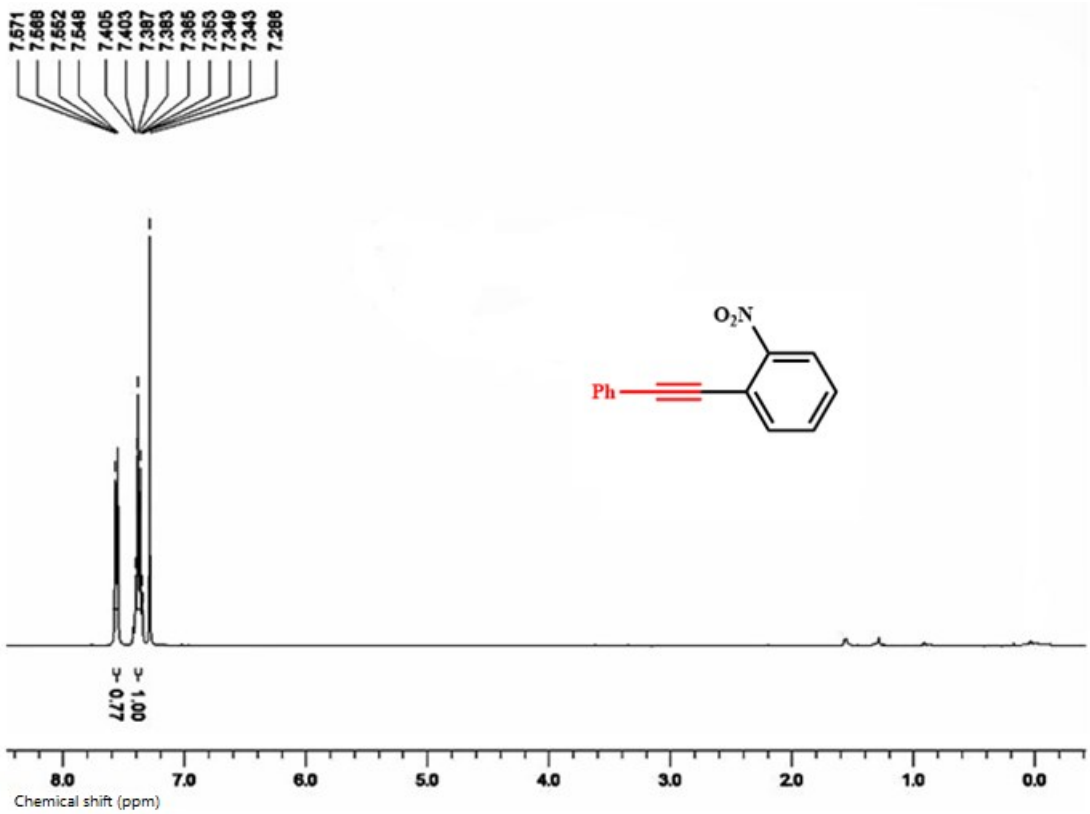


Figure S50. [1]HNMR spectrum of **11j**

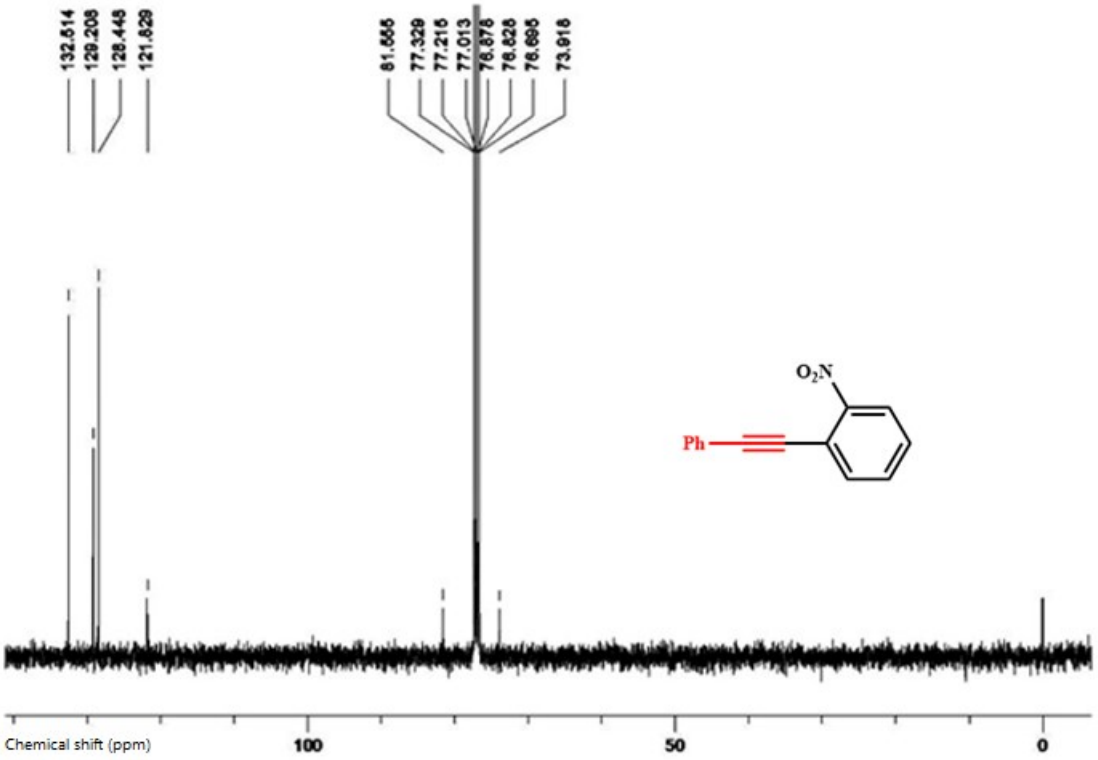


Figure S51. [13]CNMR spectrum of **11j**

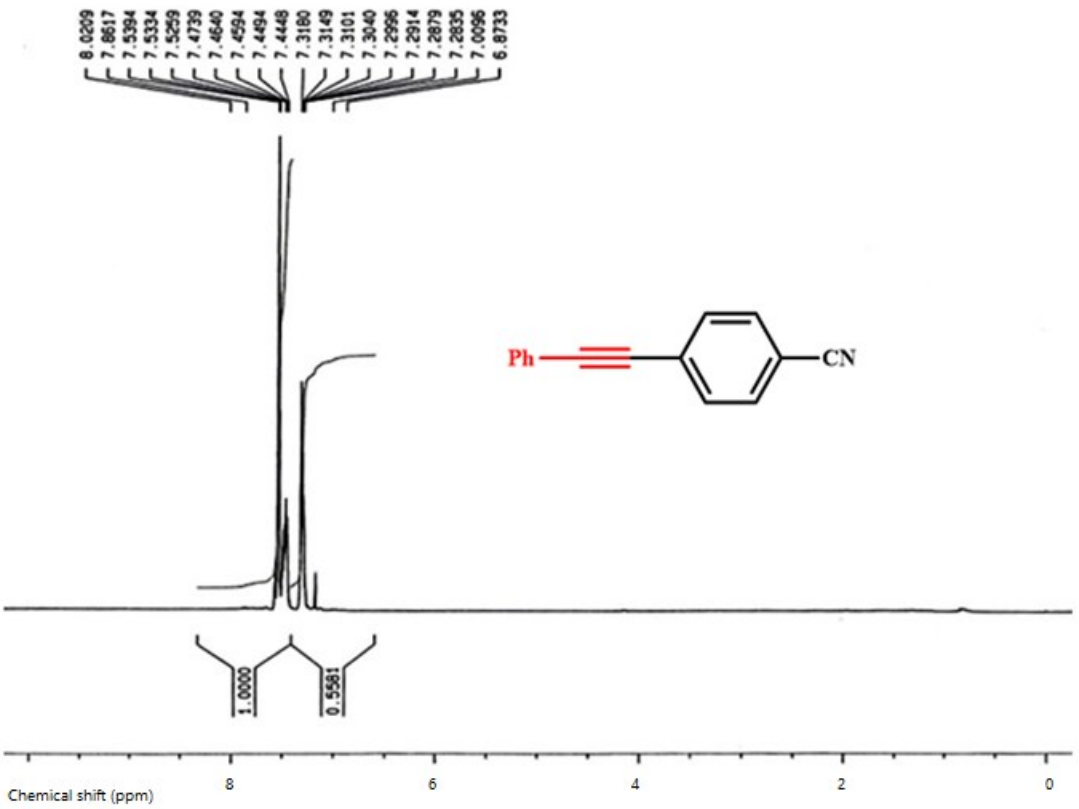


Figure S52. [1]HNMR spectrum of **11k**

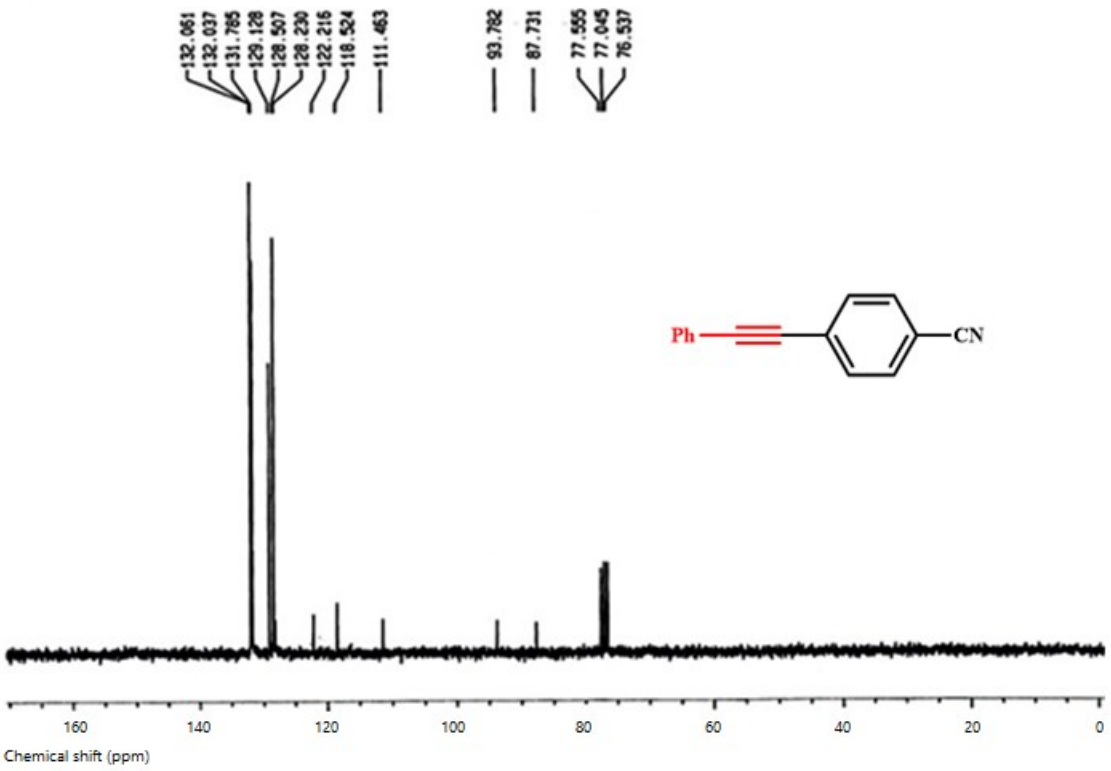


Figure S53. [13]CNMR spectrum of **11k**

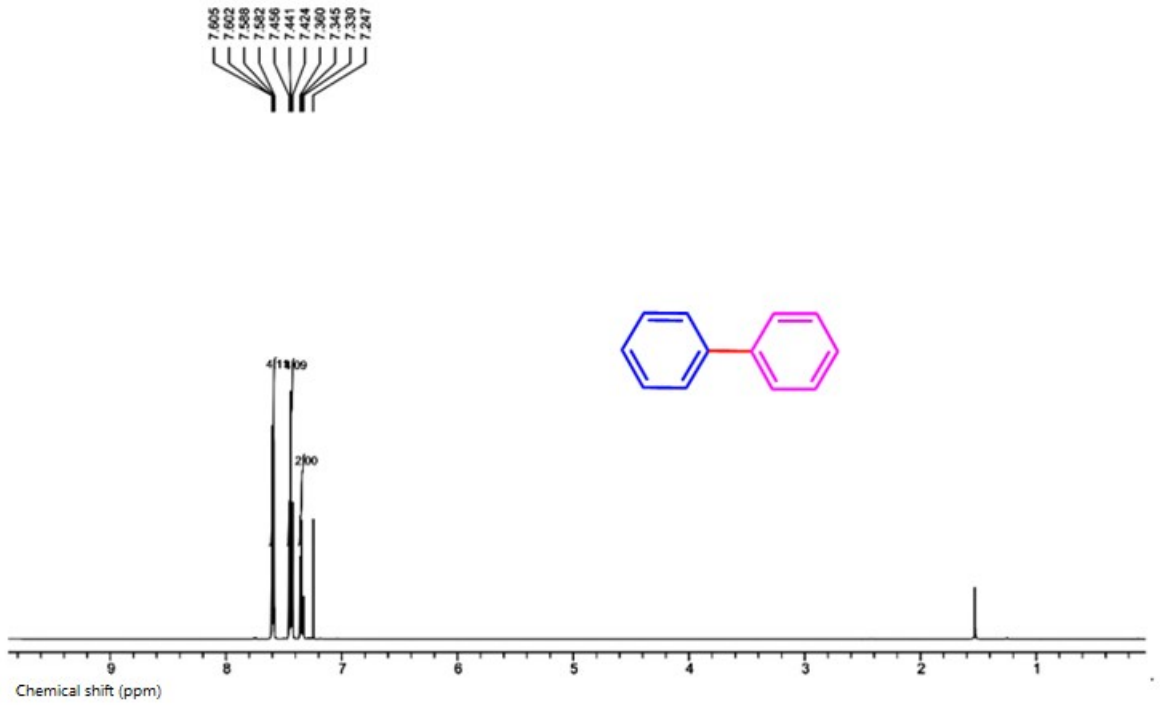


Figure S54. [1]HNMR spectrum of **12a**

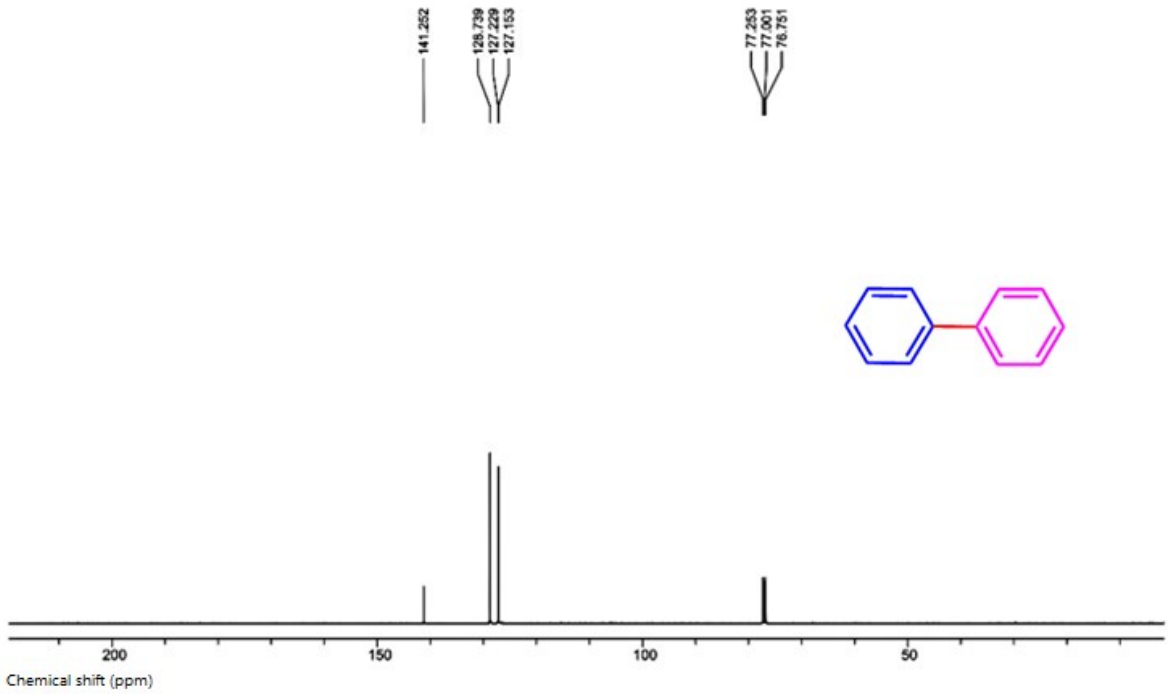


Figure S55. [13]CNMR spectrum of **12a**

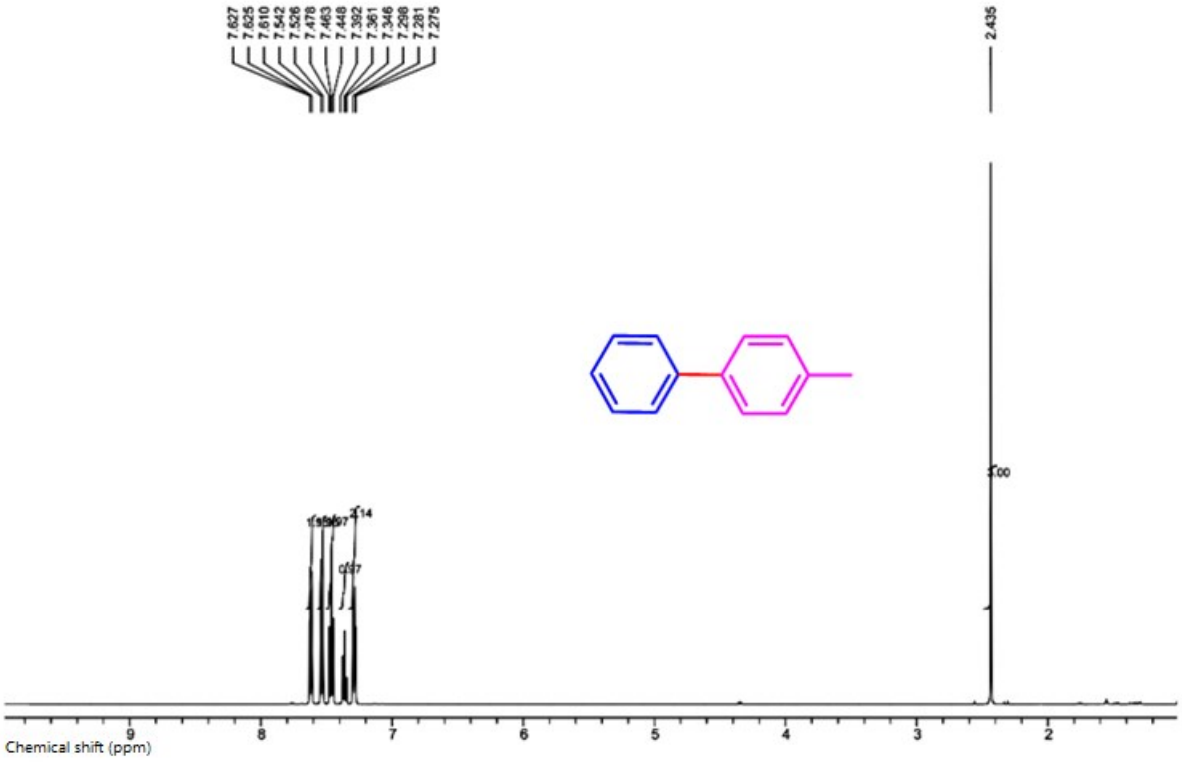


Figure S56. [1]HNMR spectrum of **12b**

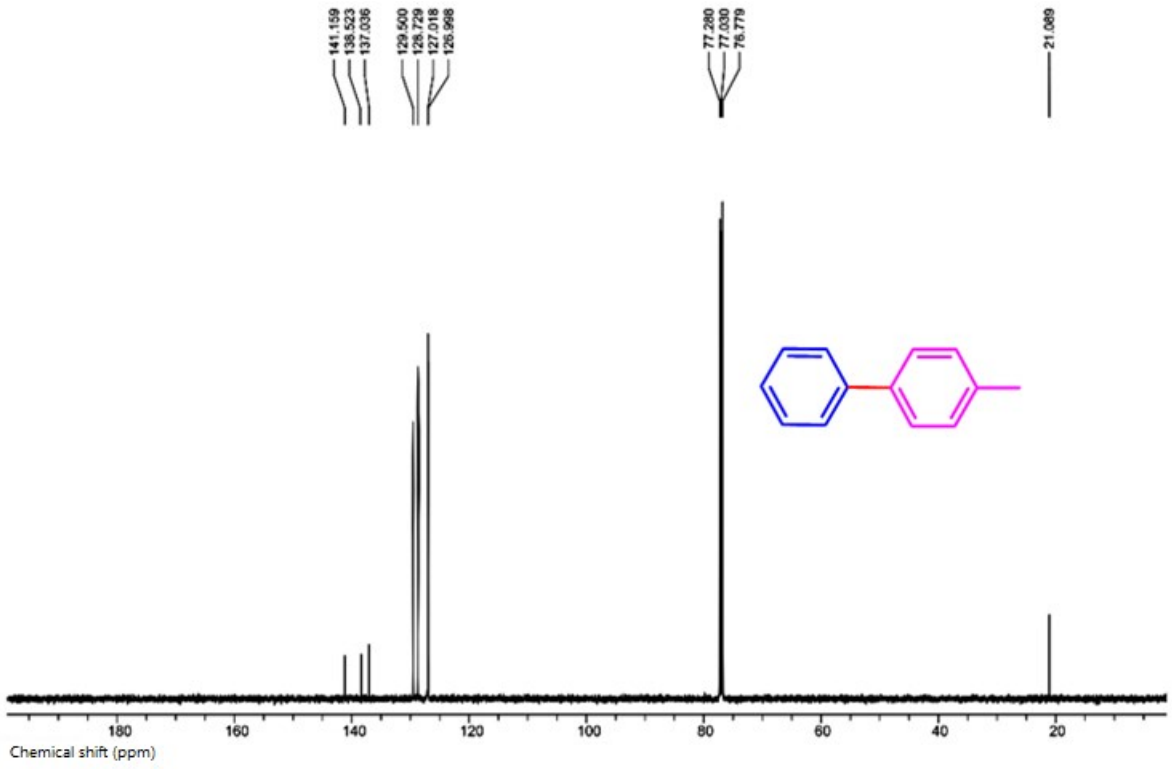


Figure S57. [13]CNMR spectrum of **12b**

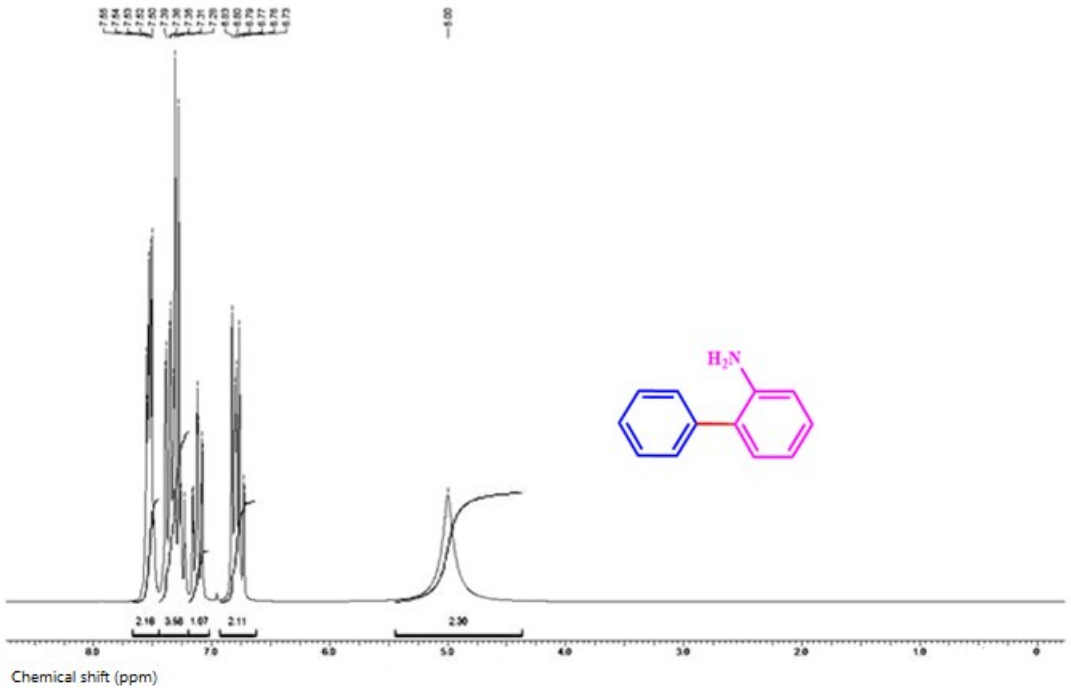


Figure S58. [1]HNMR spectrum of **12c**

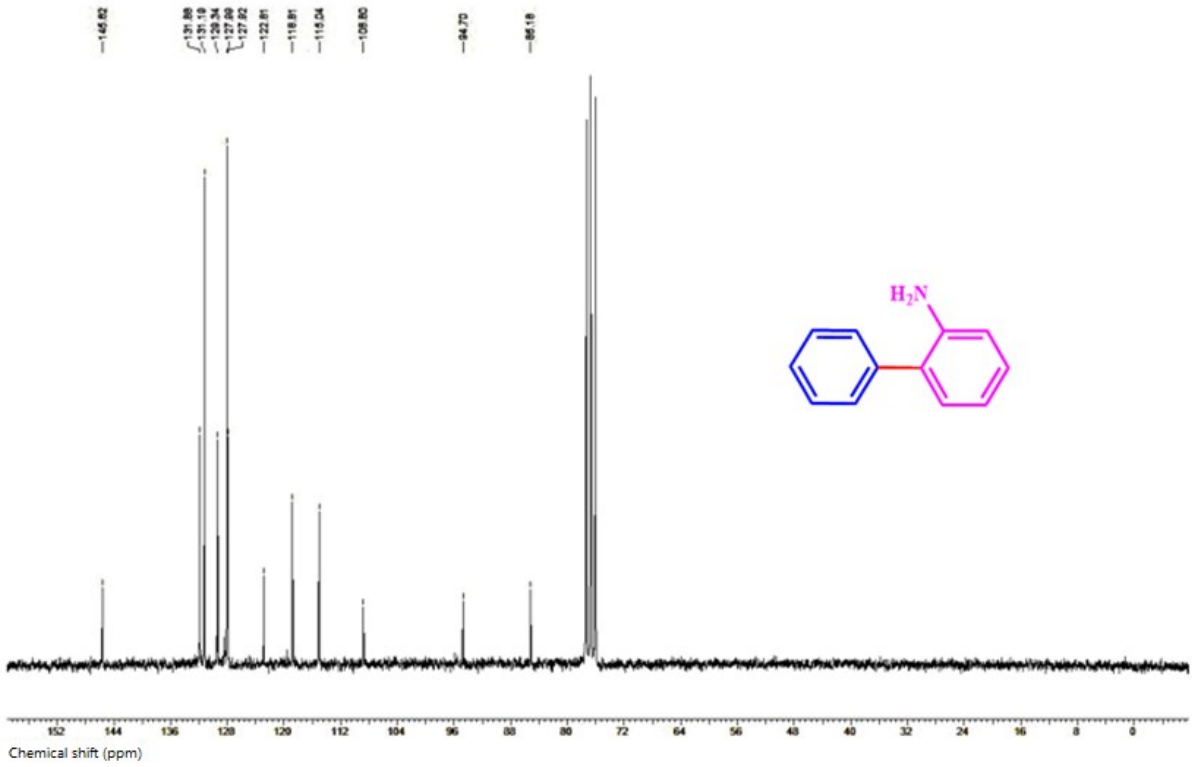


Figure S59. [13]CNMR spectrum of **12c**

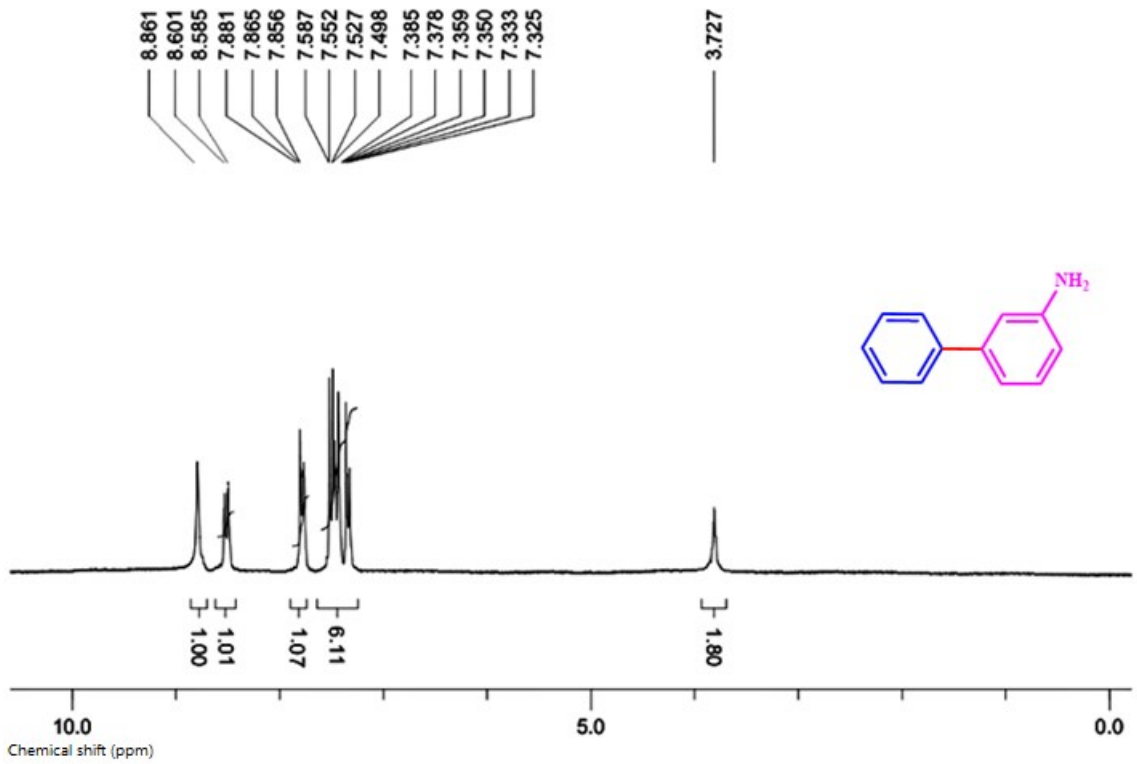


Figure S60. [1]HNMR spectrum of **12d**

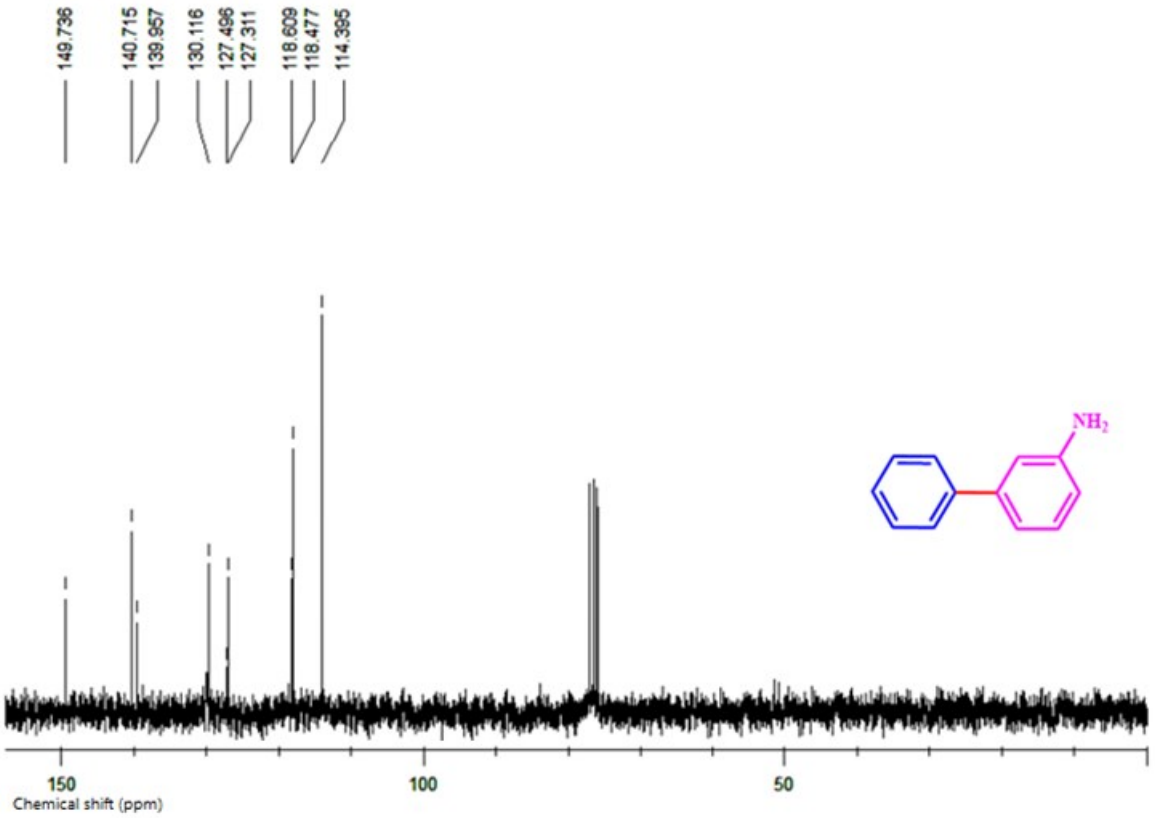


Figure S61. [13]CNMR spectrum of **12d**

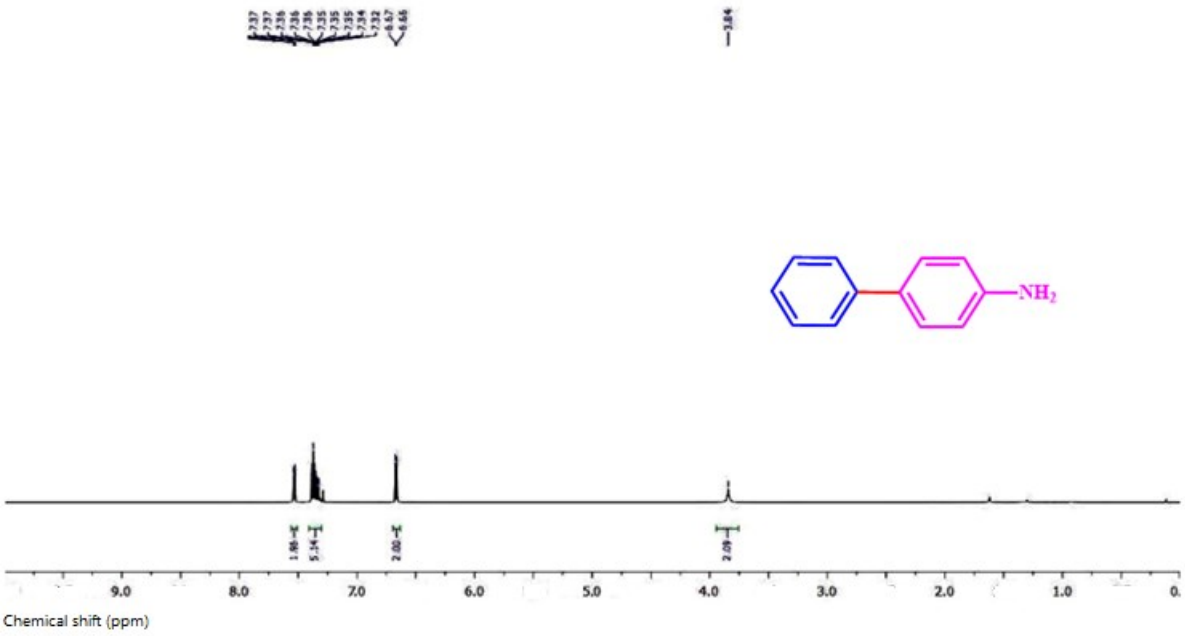


Figure S62. [1]HNMR spectrum of **12e**

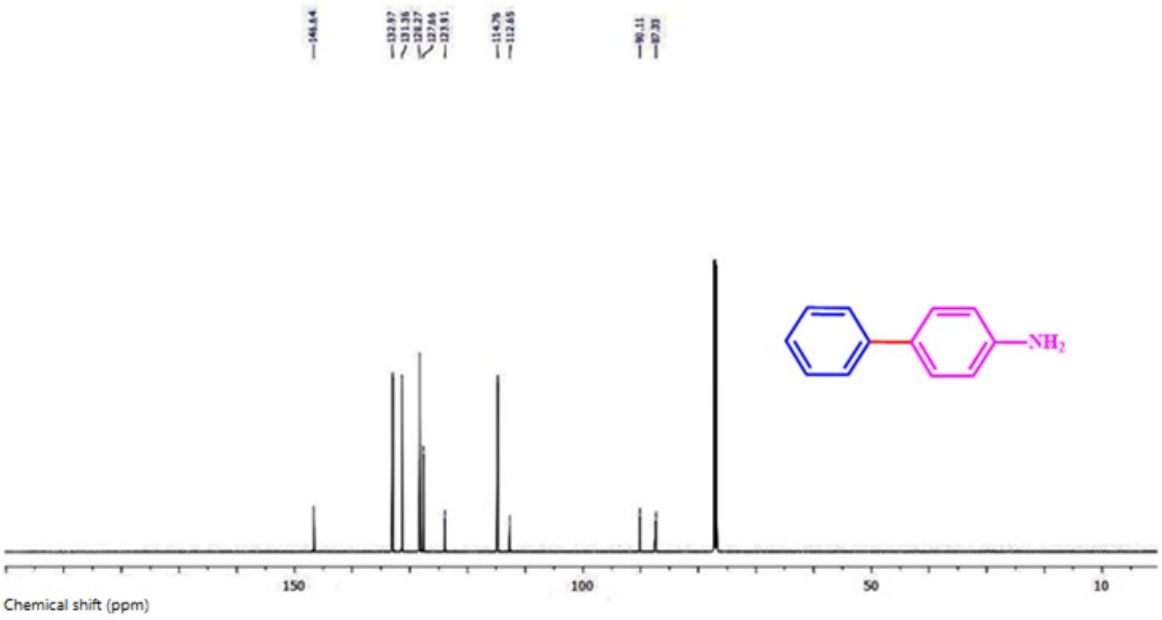


Figure S63. [13]CNMR spectrum of **12e**

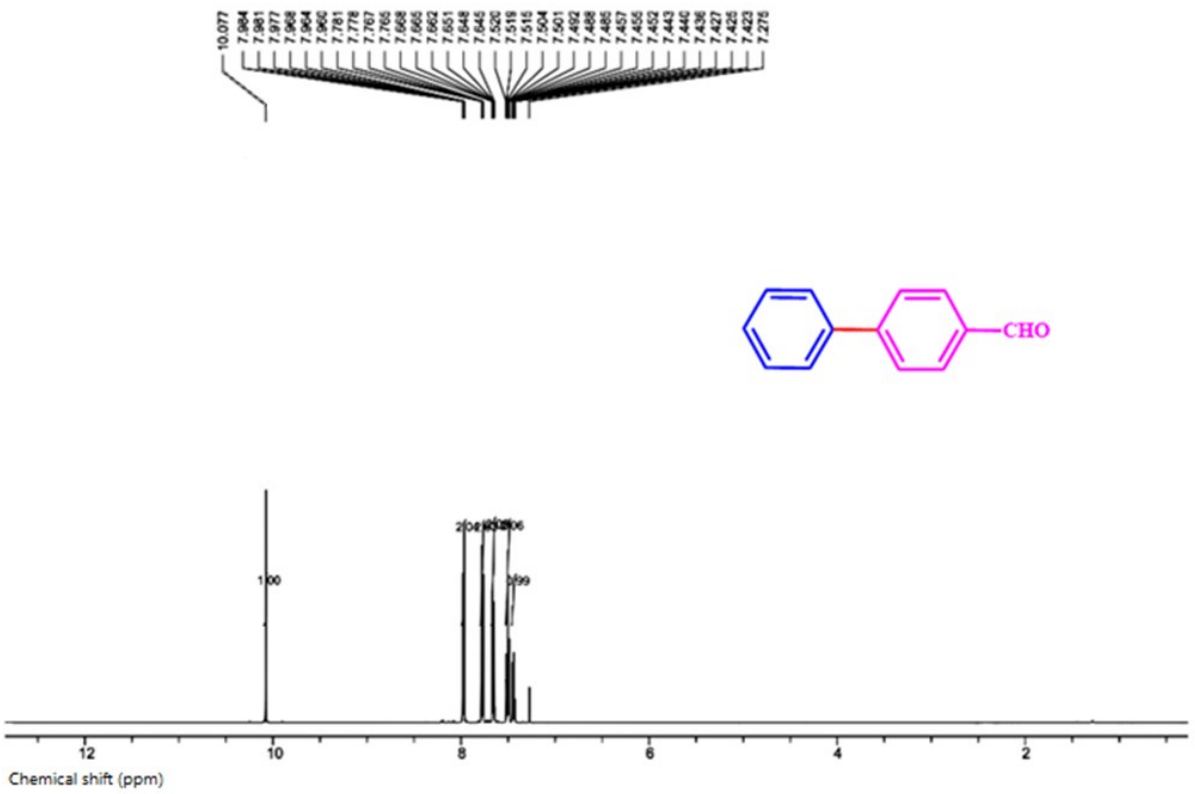


Figure S64. [1]HNMR spectrum of **12f**

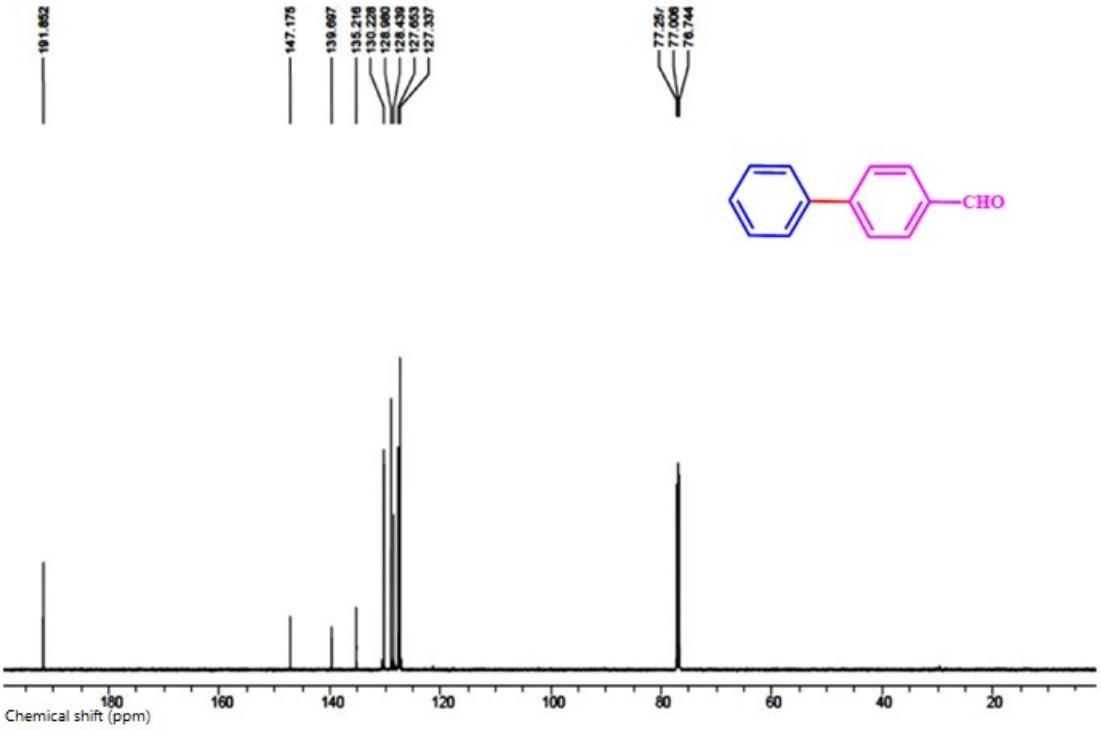


Figure S65. [13]CNMR spectrum of **12f**

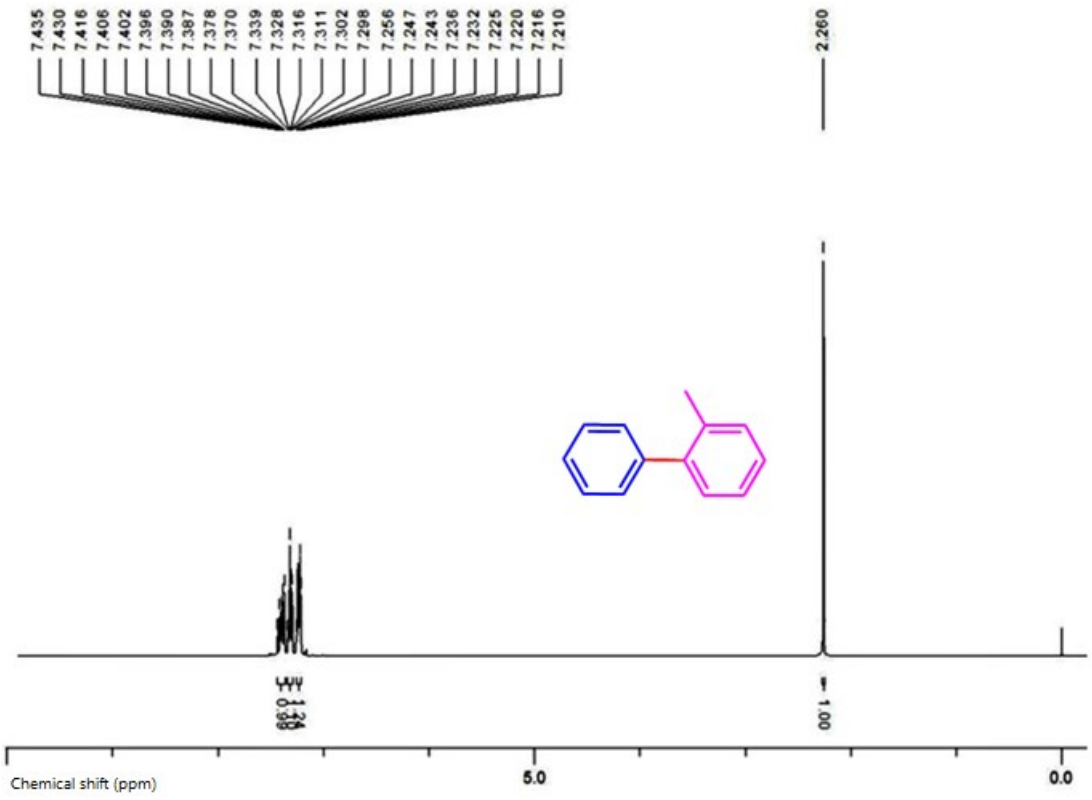


Figure S66. [1]HNMR spectrum of **12g**

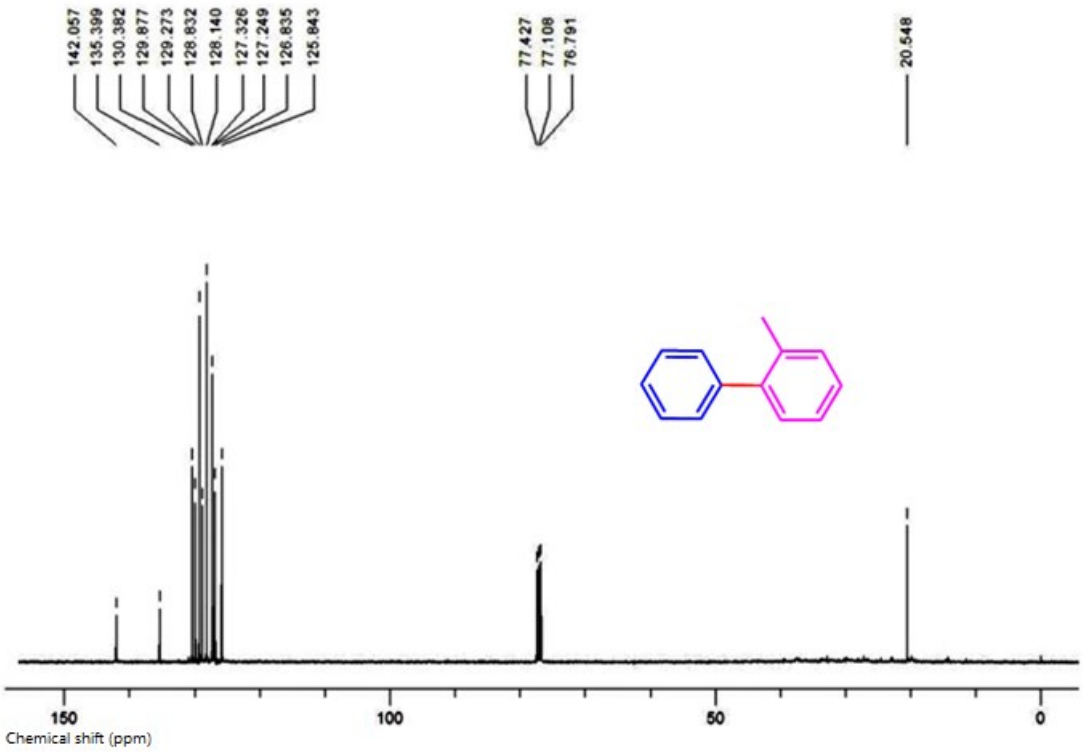


Figure S67. [13]CNMR spectrum of **12g**

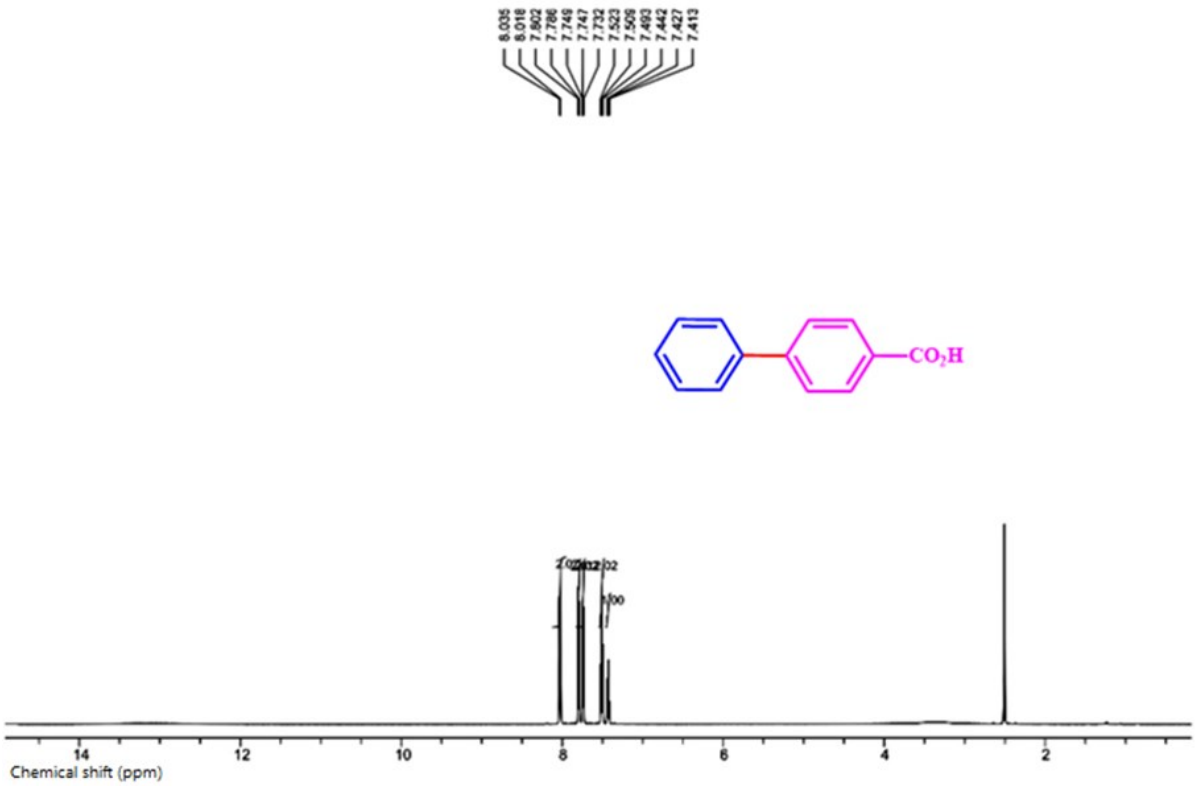


Figure S68. [1]HNMR spectrum of **12h**

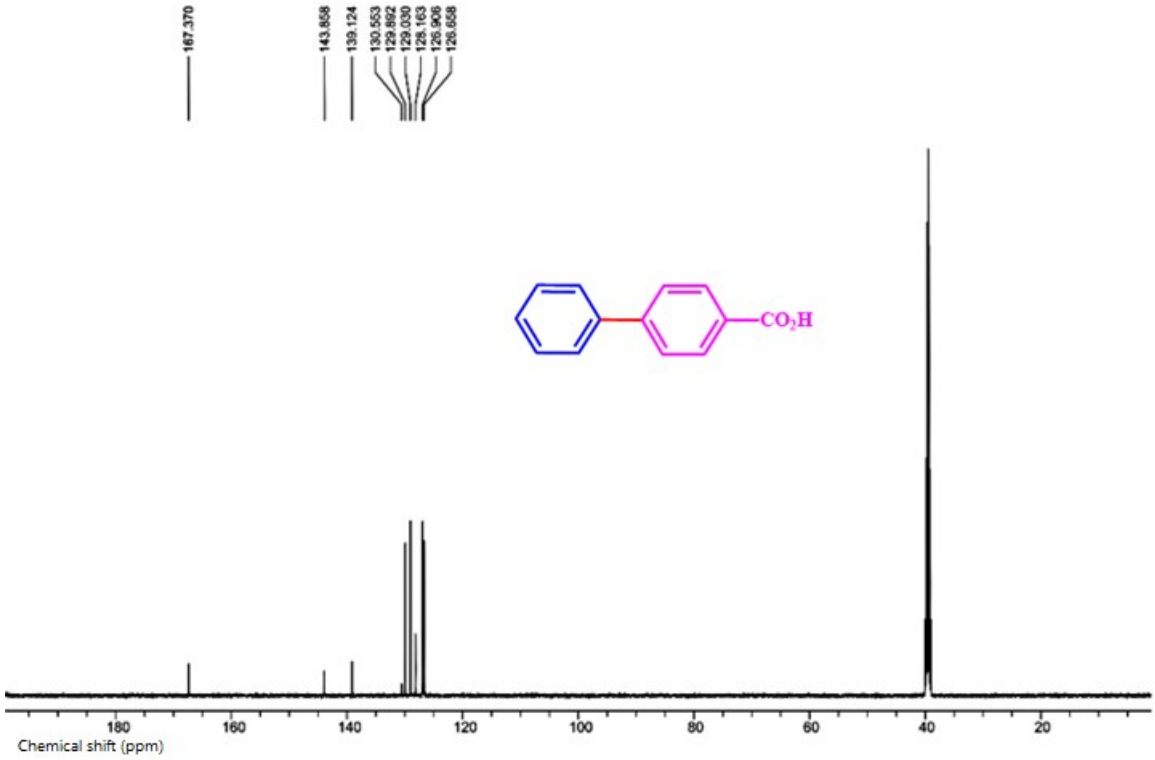


Figure S69. [13]CNMR spectrum of **12h**

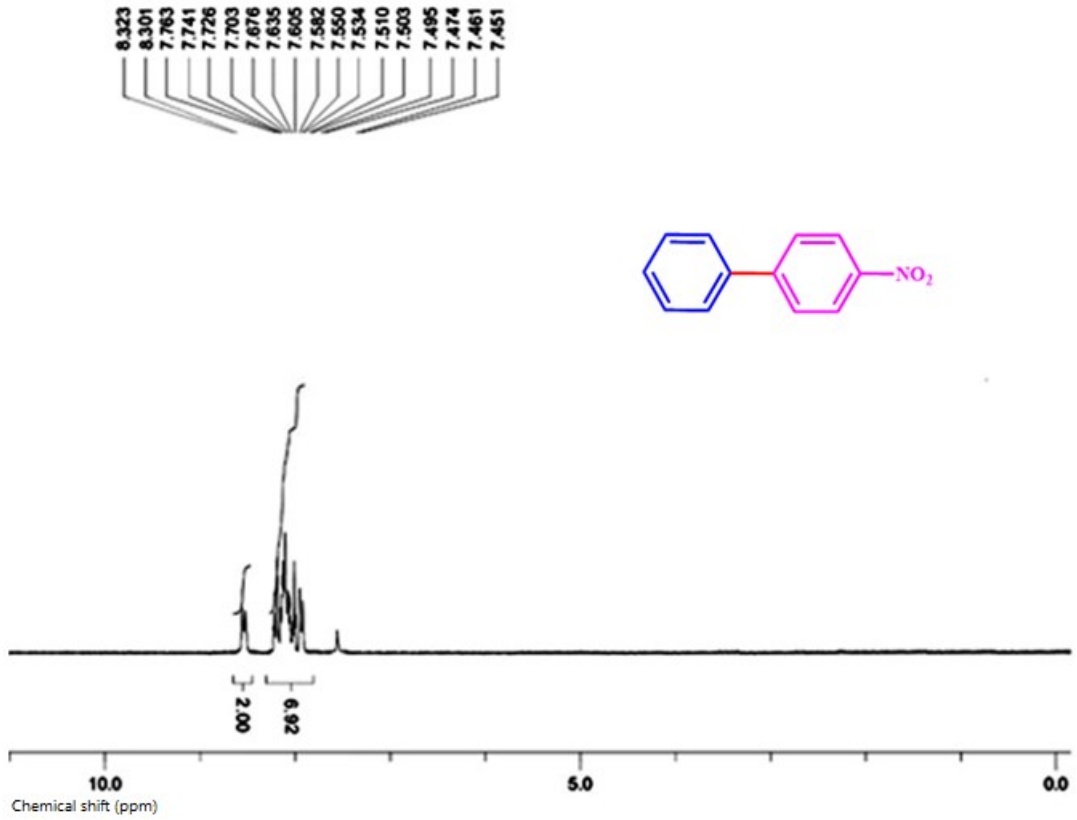


Figure S70. [1]HNMR spectrum of **12i**

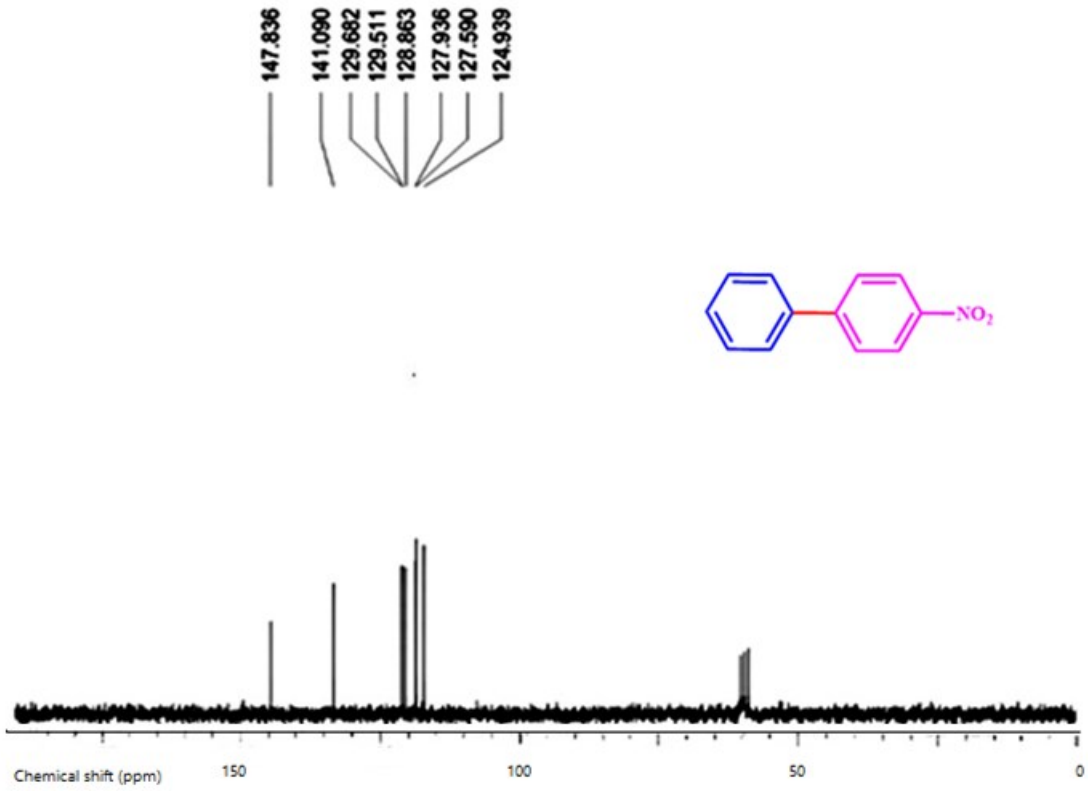


Figure S71. [13]CNMR spectrum of **12i**

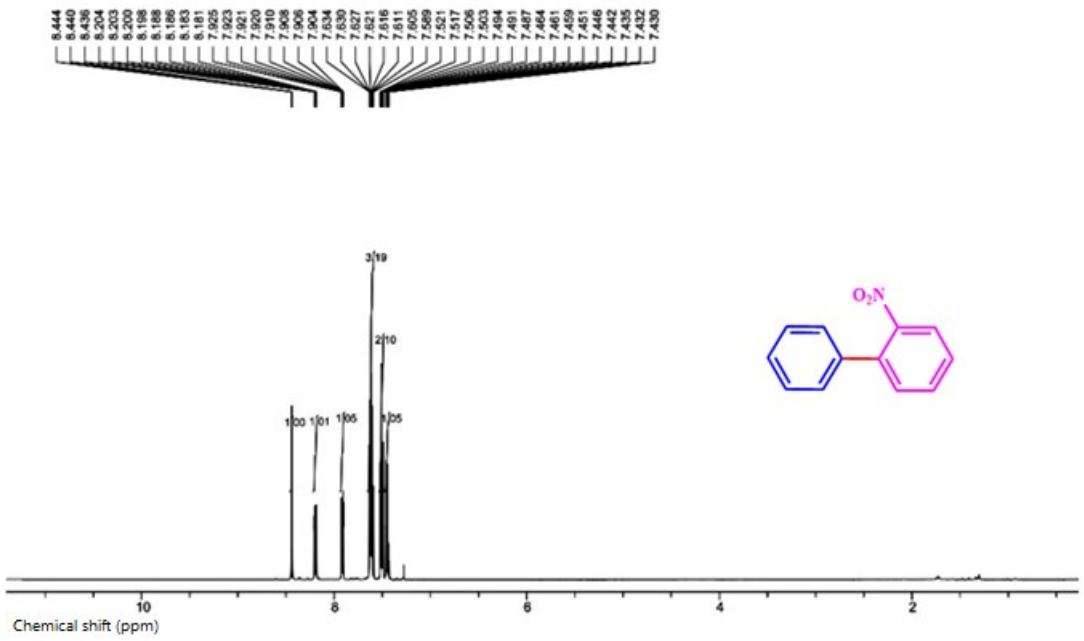


Figure S72. [1]HNMR spectrum of **12j**

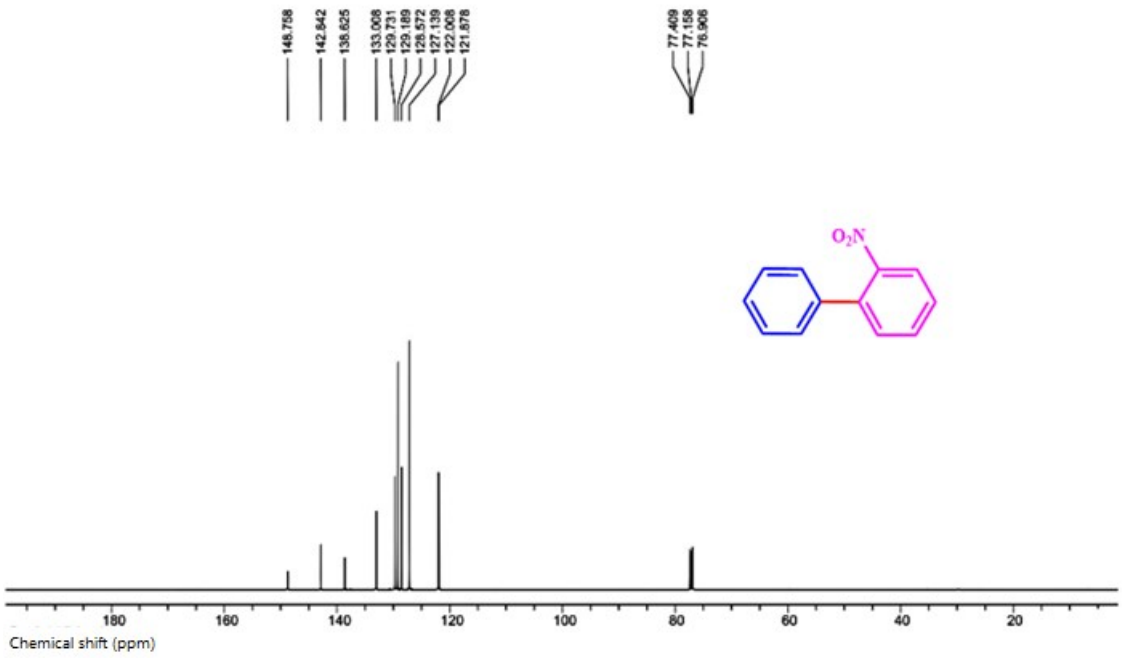


Figure S73. [13]CNMR spectrum of **12j**

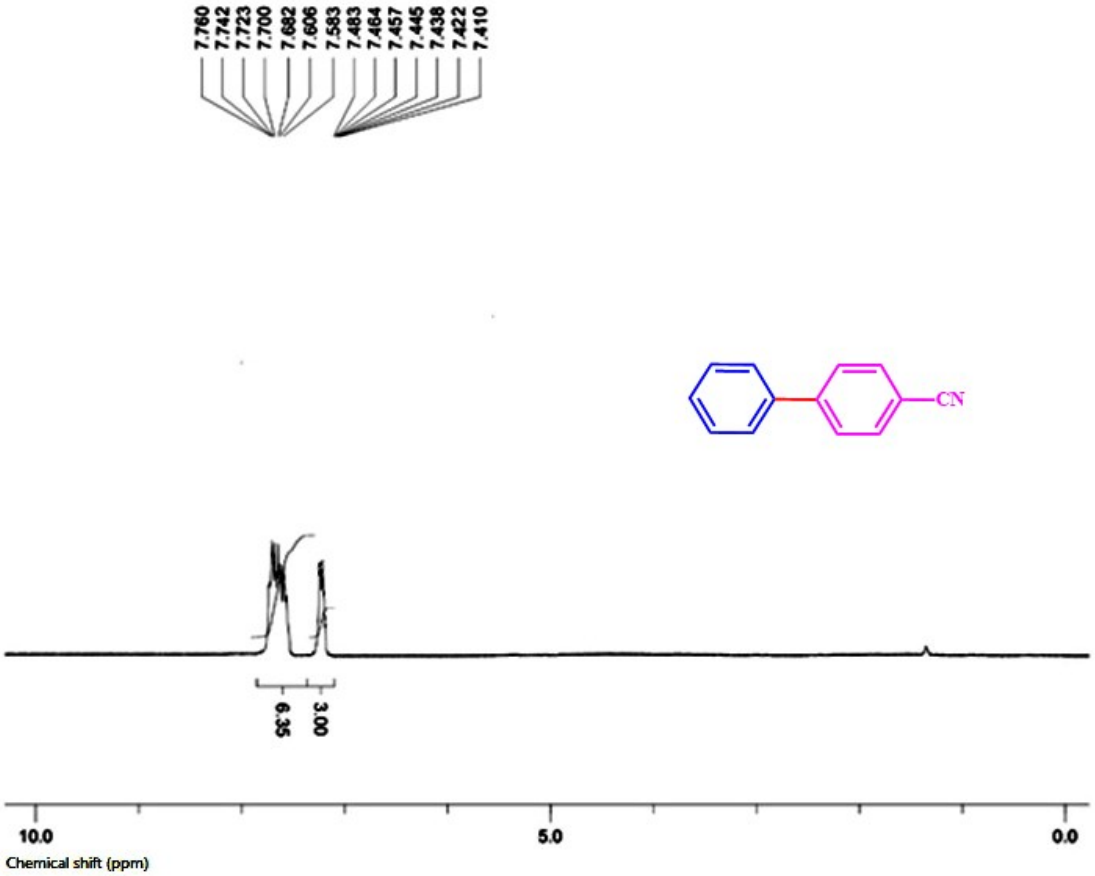


Figure S74. [1]HNMR spectrum of **12k**

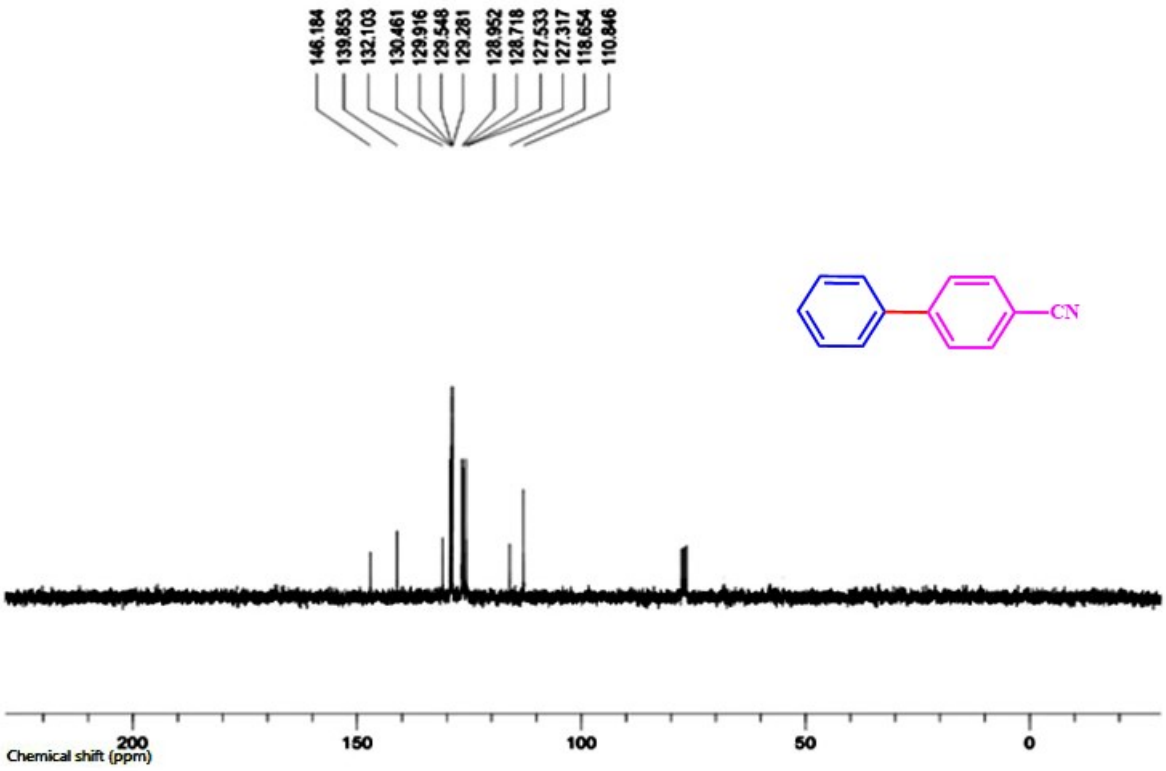


Figure S75. [13]CNMR spectrum of **12k**