Supplementary Information

Bis(NHC)-Pd catalyzed asymmetric one-pot cross-coupling reactions of C-C*C-C, C-C*C-O, C-C*C-N, and C-O*C-N on an aryl di-halide catalyzed by a homogenous basic ionic liquid (TAIm[OH]) under base-free, ligand-free and solvent-free conditions

Yanfang Zhu,[a] Guiyang Xu,[b]* Milad Kazemnejadi*[c]

[a] Xi'an Key Laboratory of Advanced Photo-electronics Materials and Energy Conversion Device, School of Science, Xijing University, Xi'an, 710123.

[b] Xi'an Modern Chemistry Research Institute, Xi'an 710065, P.R. China.

[c] Department of Chemistry, College of Science, Shiraz University, Shiraz 7194684795, Iran.

* Corresponding authors: xuguiyang90@163.com (Guiyang Xu), miladkazemnejad@yahoo.com (Milad Kazemnejadi)

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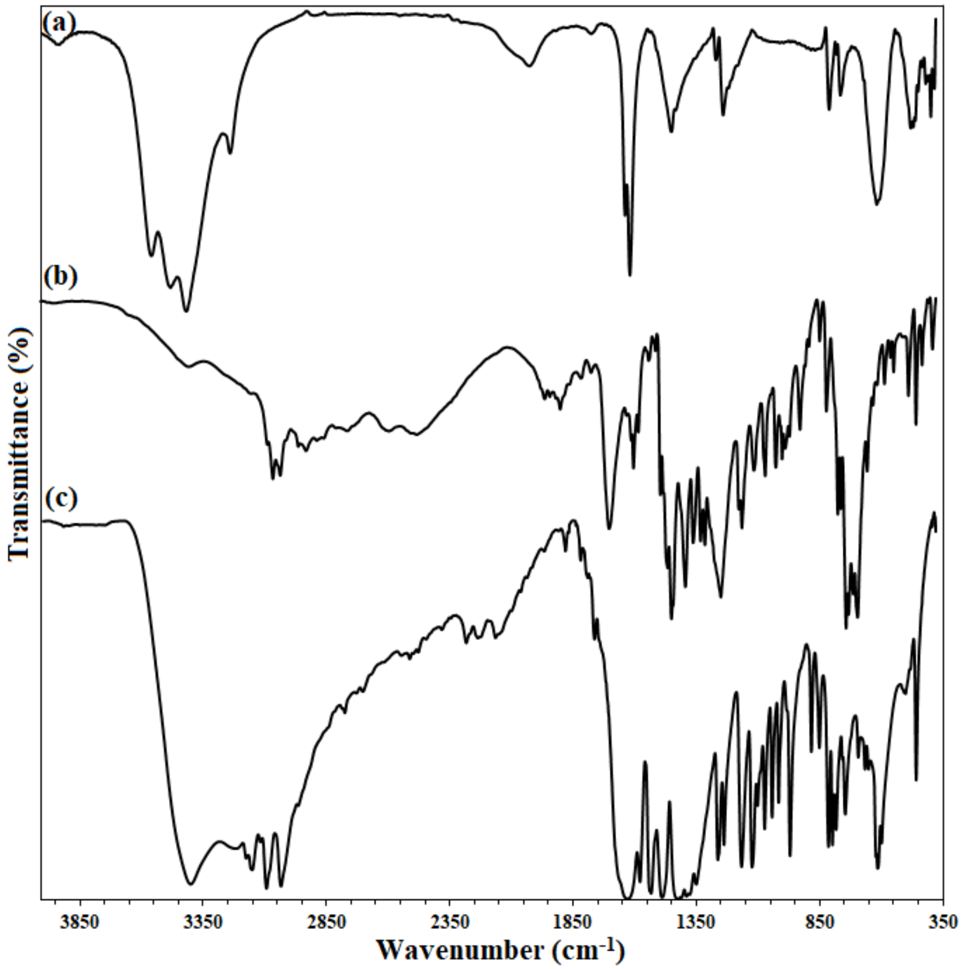


Fig. S1 FTIR spectra of (a) cyanuric iodide **1**, (b) Im[I]TA **2**, and (c) Im[OH]TA **3**

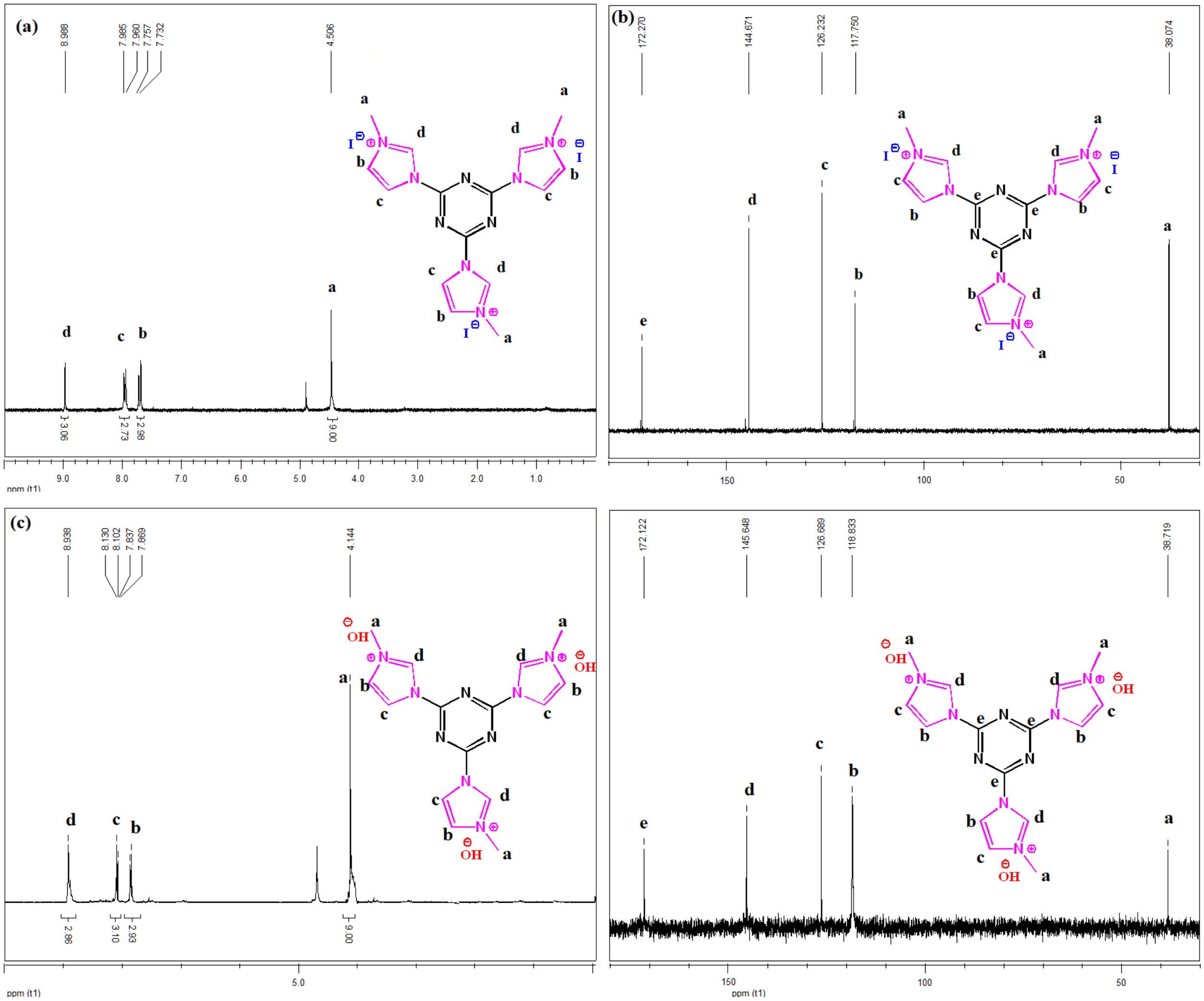


Fig. S2 ^{1}H-NMR (250 MHz, D_2O) spectra of (a) Im[I]TA **2**, and (c) Im[OH]TA **3**. ^{13}C-NMR (62.9 MHz, D_2O) spectra of (b) Im[I]TA **2**, and (d) Im[OH]TA **3**.

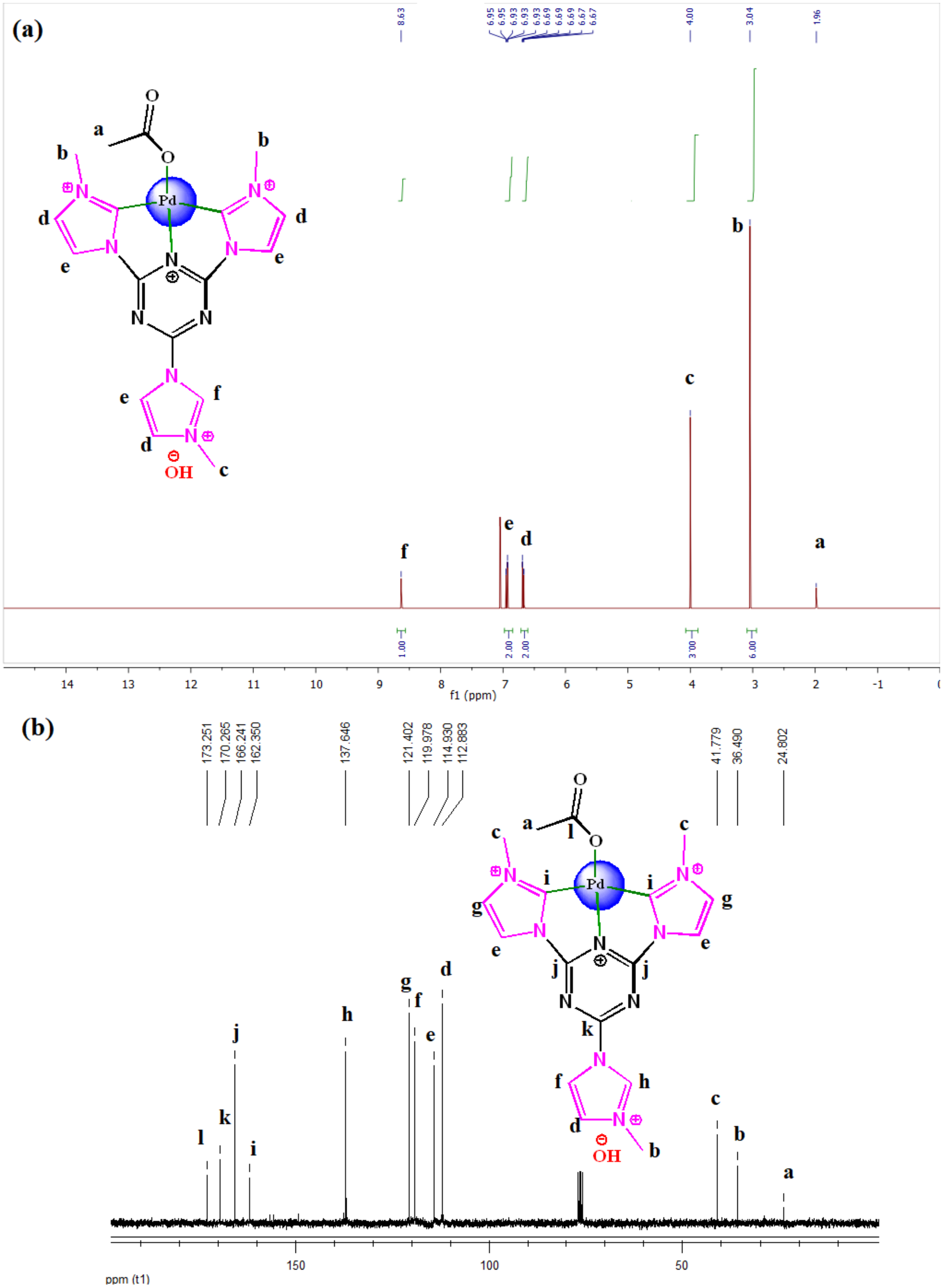


Fig. S3 (a) [1]H-NMR (400 MHz, $CDCl_3$) and [13]C-NMR (100 MHz, $CDCl_3$) spectra of TAIm[OH]-Pd (**4**)

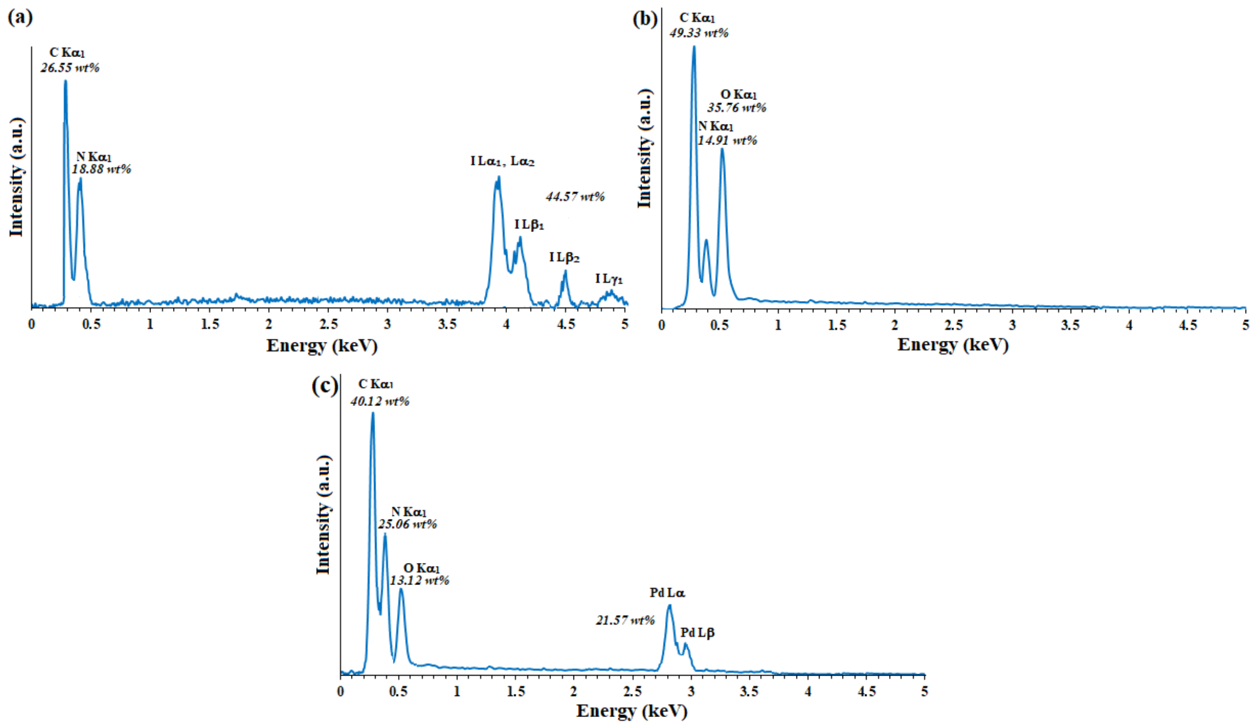


Fig. S4 EDX spectra of (a) TAIm[I] **2**, and (b) TAIm[OH] **3**, and TAIm[OH]-Pd (**4**)

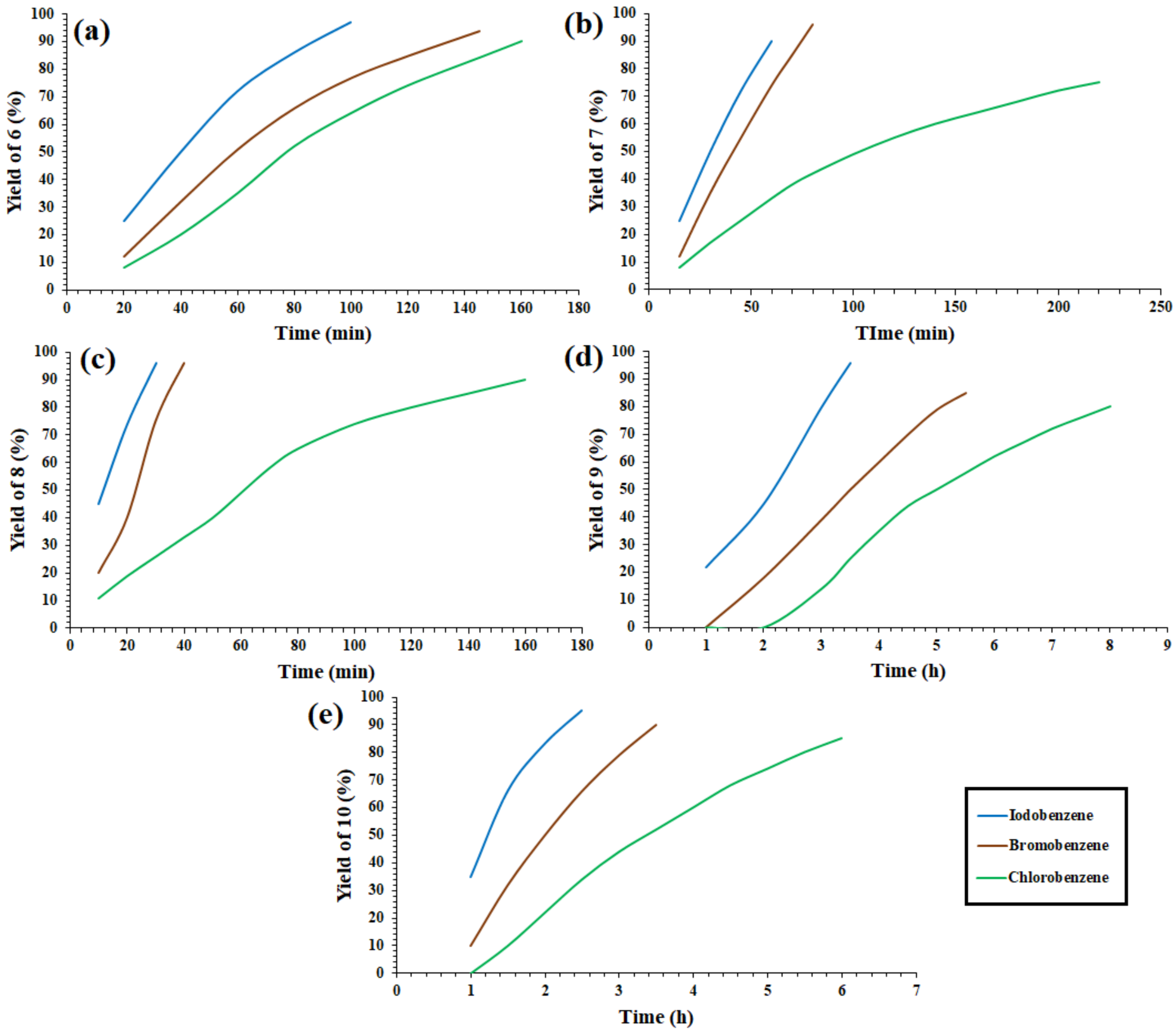


Fig. S5 Kinetics of the (a) Sonogashira, (b) Heck, (c) Suzuki, (d) C-N cross-coupling, and (e) C-O of phenyl acetylene, styrene, phenylboronic acid, imidazole and phenol, respectively with aryl halides catalyzed by TAIm[OH]-Pd. *The reactions were performed under optimized conditions according to the described procedure in Experimental section.*

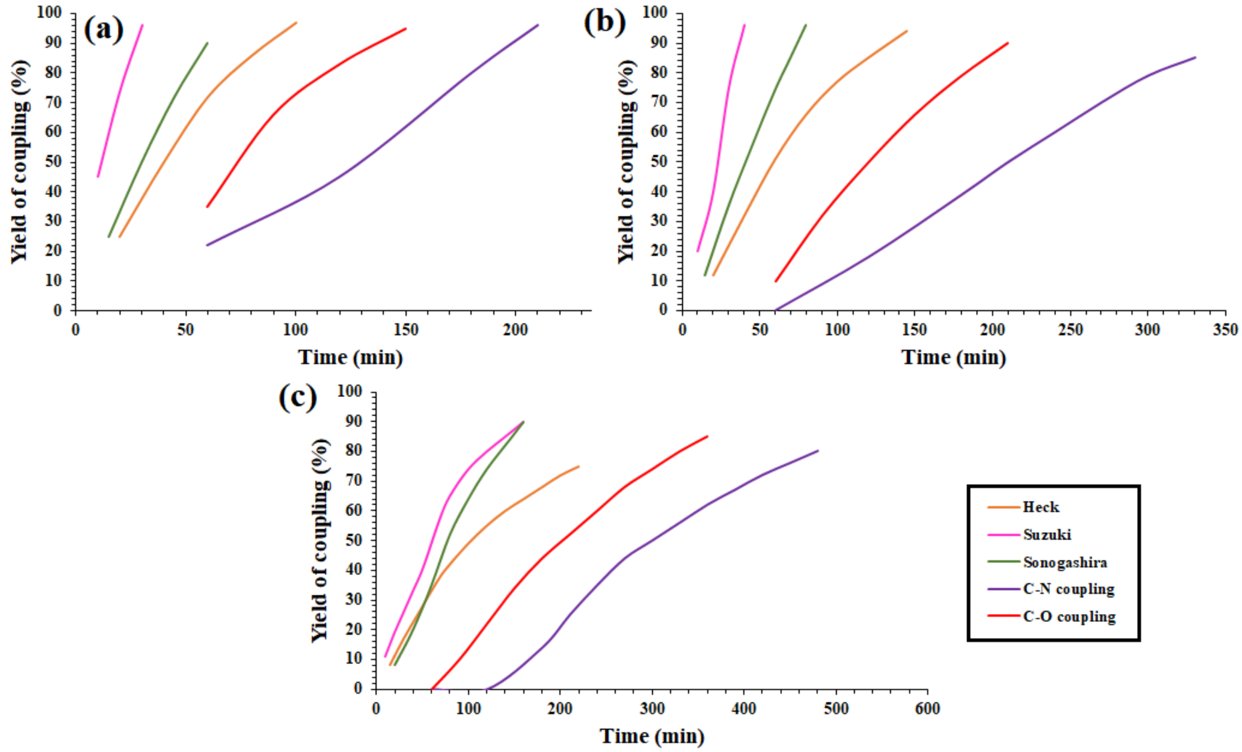


Fig. S6 Kinetics of (a) iodobenzene, (b) bromobenzene, and (c) chlorobenzene for the Heck, Suzuki, Sonogashira, C-N, and C-C cross-coupling reactions catalyzed by TAIm[OH]-Pd. *The reactions were performed under optimized conditions according to the described procedure in Experimental section.*

Optimization of reaction parameters

To find optimum conditions for the C-C cross-coupling reactions catalyzed by TAIm[OH]-Pd, the reaction parameters of temperature and catalyst amount was studied. For this goal, the Heck coupling reaction of iodobenzene with styrene was chosen as a model reaction for study of the reaction parameters. It worth noted that didn't use any external base in all experiments and the reactions were performed with the intrinsic high basicity of TAIm[OH]-Pd.

Effect of temperature was evaluated in the first step (Fig. S6-a). As shown in Fig. S6 there is not any product at temperatures below 40 °C; and 120 °C was the premium temperature providing 90% isolated yield (Fig. S6-a). Raising temperature didn't effect on reaction efficiency. Next, the $Pd(OAc)_2$ amount was studied over the model reaction (Fig. S6-b). The results demonstrated that 1.0 mol% was the premium amount of $Pd(OAc)_2$. The relationship between catalyst amount mol% and reaction isolated yield was shown in Fig. S6-b.

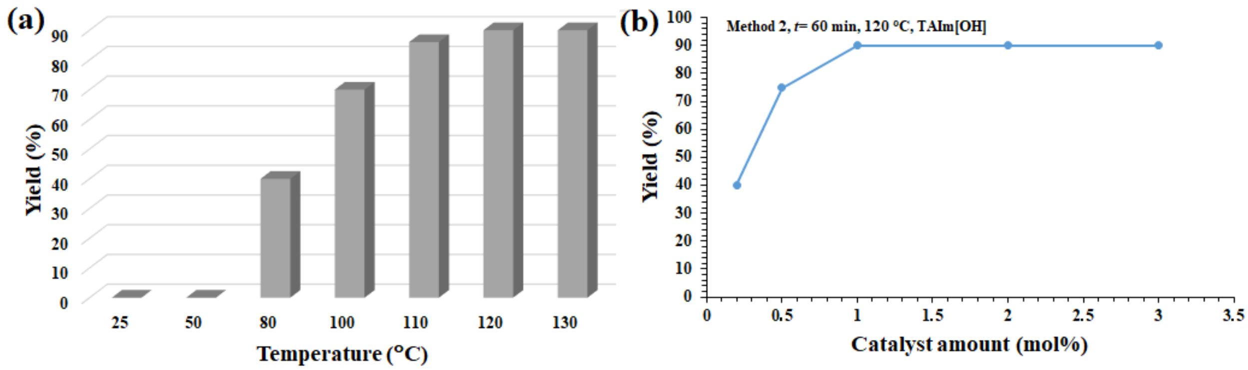


Fig. S7 Effect of (a) temperature (1.0 mol% $Pd(OAc)_2$) and (b) $Pd(OAc)_2$ amount (at 120 °C) over the Heck cross-coupling reaction of iodobenzene (1.0 mmol) with styrene (1.3 mmol) catalyzed by TAIm[OH]-Pd for 60 min.

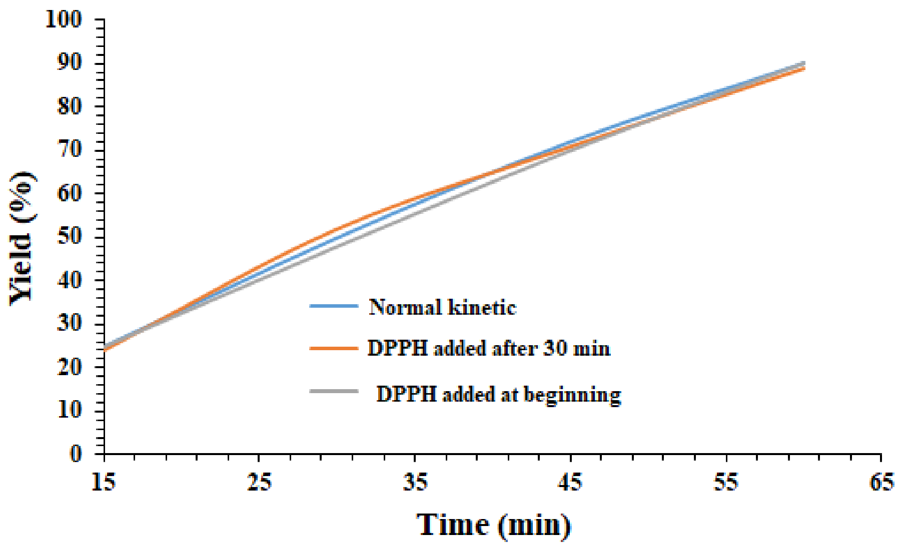
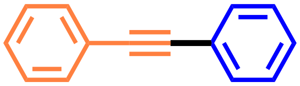


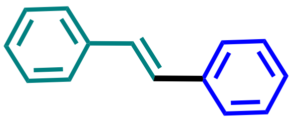
Fig. S8 Influence of DPPH in the beginning and after 30 min on the Heck reaction of styrene with iodobenzene

Characterization data for the coupling products:



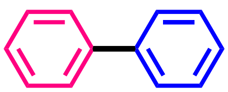
1,2-Diphenylethyne (Table 2, product 6)

White solid. M.P. 63 °C (Lit. [1], 65 °C). ^{1}H NMR (250 MHz, $CDCl_3$); *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, 127.2, 128.6, 128.8, 132.4. Elemental Analysis: Anal. Calcd. (%) for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found (%): C, 94.44; H, 5.56. EI-MS (*m/z*): 178 (M^+).



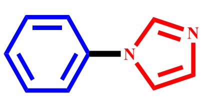
1,2-Diphenylethene (Table 2, product 7)

White solid. M.P. 122-125 °C (Lit. [1], 124-125 °C). ^{1}H-NMR (250 MHz, $CDCl_3$): *δ*(ppm)= 7.13 (d, 2H), 7.31 (m, 6H), 7.52 (m, 4H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): *δ* (ppm)= 127.0, 128.1, 128.5, 137.4. Elemental Analysis: Anal. Calcd. (%) for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found (%): C, 93.44; H, 6.83. EI-MS (*m/z*): 180 (M^+).



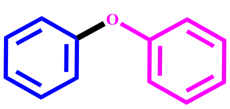
1,1'-Biphenyl (Table 2, product 8)

White solid. M.P. 68-70 °C (Lit. [1], 66-68 °C). ^{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)= 126.3, 127.4, 129.3, 142.5. Elemental Analysis: Anal. Calcd. (%) for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found (%): C, 93.44; H, 6.56. EI-MS (*m/z*): 154 (M^+).



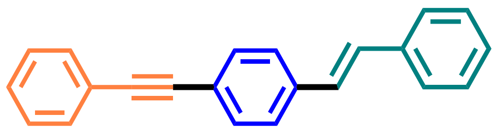
1-Phenyl-1*H*-imidazole (Table 2, product 9)

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. EI-MS (*m/z*): 144 (M^+).



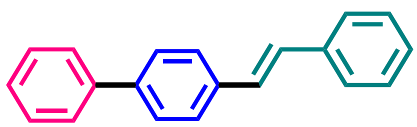
Oxydibenzene (Table 2, product 10)

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.33-7.37 (m, 4H), 7.09-7.14 (t, J = 7.2 Hz, 2H), 7.01-7.04 (t, J = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 118.9, 1210.9, 128.9, 157.2. EI-MS (m/z): 170 (M^+).



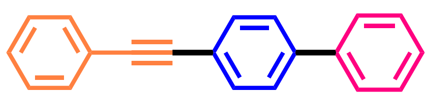
1-(Phenylethynyl)-4-styrylbenzene (Table 3, product 11)

White solid. M.P. 222-226 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.04 (s, 2H), 7.39-7.56 (m, 10H), 7.70 (d, J=7.5 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm)= 89.1, 121.8, 127.1, 127.6, 128.0, 128.1, 128.6, 128.7, 131.9, 132.4. Elemental Analysis: Anal. Calcd. (%) for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found (%): C, 94.28; H, 6.72. EI-MS (m/z): 280 (M^+).



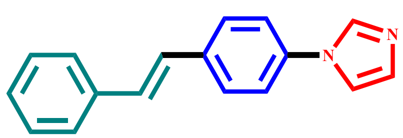
4-Styryl-1,1'-biphenyl (Table 4, product 12)

White solid. M.P. 240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.19 (s, 2H), 7.23-7.38 (m, 2H), 7.43-7.60 (m, 8H), 7.70-7.72 (dd, J=8.2, 1.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 127.0, 127.3, 127.5, 128.0, 128.5, 128.8, 129.5, 136.3, 136.8, 140.0, 140.5. Elemental Analysis: Anal. Calcd. (%) for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found (%): C, 93.66; H, 6.34. EI-MS (m/z): 256 (M^+).



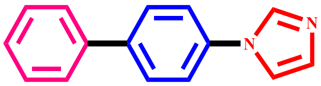
4-(Phenylethynyl)-1,1'-biphenyl (Table 5, product 13)

Pale yellow solid. M.P. 95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.31-7.49 (m, 6H), 7.57-7.62 (m, 4H), 7.66-7.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=90.2, 121.3, 127.3, 127.6, 128.0, 128.2, 128.7, 129.1, 132.3, 132.8, 140.4, 140.9. Elemental Analysis: Anal. Calcd. (%) for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found (%): C, 94.55; H, 5.45. EI-MS (m/z): 254 (M^+).



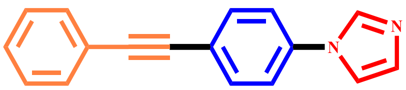
1-(4-Styrylphenyl)-1*H*-imidazole (Table 6, product 14)

Pale yellow solid. M.P. 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.08 (s, 1H), 7.11 (s, 1H), 7.21-7.29 (m, 3H), 7.34-7.38 (m, 6H), 7.67 (dd, *J*=7.9, 1.9 Hz, 1H), 7.78 (t, *J*=8.6 Hz, 1H), 7.79 (t, *J*=8.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 118.2, 127.1, 127.3, 127.9, 128.3, 127.9, 128.3, 128.5, 129.0, 15.3, 136.0, 136.9, 137.7. Elemental Analysis: Anal. Calcd. (%) for $C_{17}H_{14}N_2$: C, 82.90; H, 5.55, N, 11.37. Found (%): C, 82.80; H, 5.63, N, 11.39. EI-MS (*m/z*): 246 (M^+).



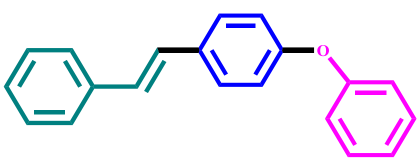
1-([1,1'-Biphenyl]-4-yl)-1*H*-imidazole (Table 6, product 15)

White solid. M.P. 88-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.27-7.33 (m, 2H), 7.48-7.52 (m, 2H), 7.57-7.69 (m, 6H), 7.81 (d, *J*=8.5 Hz, 1H), 7.82 (d, *J*=8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 114.9, 118.3, 127.5, 128.0, 128.7, 129.3, 130.0, 135.1, 135.9, 140.4, 140.9. Elemental Analysis: Anal. Calcd. (%) for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49, N, 12.72. Found (%): C, 81.77; H, 5.46, N, 12.67. EI-MS (*m/z*): 220 (M^+).



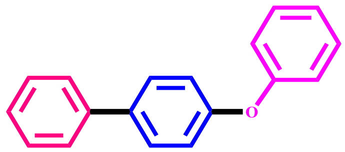
1-(4-(Phenylethynyl)phenyl)-1*H*-imidazole (Table 6, product 16)

White solid. M.P. 82-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.27-7.39 (m, 4H), 7.46-7.50 (m, 2H), 7.36-7.65 (m, 2H), 7.68-7.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 89.2, 118.2, 121.3, 122.3, 127.2, 128.2, 128.5, 129.7, 132.4, 135.6, 136.5. Elemental Analysis: Anal. Calcd. (%) for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95, N, 11.47. Found (%): C, 82.64; H, 5.42, N, 11.94. EI-MS (*m/z*): 244 (M^+).



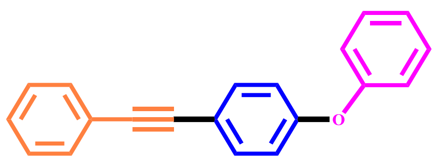
1-Phenoxy-4-styrylbenzene (Table 7, product 17)

Pale yellow solid. M.P. 212-214 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 6.98-7.01 (m, 6H), 7.12-7.23 (m, 4H), 7.36-7.40 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 118.7, 121.7, 124.5, 127.3, 127.9, 128.4, 128.7, 130.0, 136.8, 155.9, 156.9. Elemental Analysis: Anal. Calcd. (%) for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found (%): C, 88.28; H, 5.84. EI-MS (*m/z*): 272 (M^+).



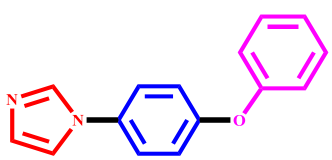
4-Phenoxy-1,1'-biphenyl (Table 7, product 18)

White solid, M.P. 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 6.97 (d, J=8.0 Hz, 1H), 7.00 (d, J=8.0 Hz, 1H), 7.13-7.22 (m, 3H), 7.36-7.49 (m, 5H), 7.58-7.63 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm)= 118.1, 119.7, 121.6, 127.4, 127.8, 128.4, 128.7, 129.3, 134.4, 141.0, 155.7, 157.5. EI-MS (m/z): 246 (M^+). Elemental Analysis: Anal. Calcd. (%) for $C_{18}H_{14}O$: C, 87.70; H, 5.93. Found (%): C, 87.44; H, 6.07. EI-MS (m/z): 272 (M^+).



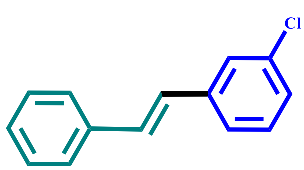
1-Phenoxy-4-(phenylethynyl)benzene (Table 7, product 19)

White solid, M.P. 186-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 6.97-7.00 (m, 4H), 7.13-7.20 (m, 2H), 7.26 (d, J=8.8 Hz, 1H), 7.27 (d, J=8.8 Hz, 1H), 7.60-7.62 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 89.4, 115.2, 117.7, 119.4, 121.8, 127.5, 128.3, 128.8, 131.7, 132.2, 156.7, 157.3. Elemental Analysis: Anal. Calcd. (%) for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found (%): C, 88.94; H, 6.08. EI-MS (m/z): 270 (M^+).



1-(4-Phenoxyphenyl)-1*H*-imidazole (Table 7, product 20)

Yellow solid, M.P. 94-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 6.92 (d, J=8.1 Hz, 2H), 6.94 (d, J=8.1 Hz, 2H), 7.05-7.13 (m, 4H), 7.17-7.19 (m, 4H), 7.36-7.40 (m, 4H), 7.62-7.67 (m, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm)= 118.1, 118.6, 119.0, 121.5, 126.4, 128.1, 130.0, 130.4, 135.4, 156.5, 157.9. Elemental Analysis: Anal. Calcd. (%) for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86; O, 6.77. Found (%): C, 76.29; H, 5.10, N, 11.84, O, 6.77. EI-MS (m/z): 236 (M^+).



1-Chloro-4-styrylbenzene (Scheme 4, product 21)

White solid. mp: 127-129 °C [2]; ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.11-7.01 (m, 2H), 7.28 (dd, J = 15.3, 8.0 Hz, 2H), 7.38-7.32 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 2H),7.50 (d, *J* = 7.5 Hz, 2H). 13C NMR (62.5 MHz, CDCl3): δ (ppm)= 127.6, 128.5, 128.6, 128.8, 129.3, 133.1, 135.1, 137.0. Elemental Analysis: Anal. Calcd. (%) for $C_{14}H_{11}Cl$: C, 78.32; H, 5.16; Cl, 16.51. Found (%): C, 78.28; H, 5.18, Cl, 16.53. EI-MS (*m/z*): 154 (M^+). EI-MS (*m/z*): 214 (M^+).

References

[1] Cheng, S., Wei, W., Zhang, X., Yu, H., Huang, M., & Kazemnejadi, M. (2020). *Green Chem.*, 2020, **22**, 2069-2076.

[2] J.Q. Zhang, J. Cao, W. Li, S.M. Li, Y.K. Li, J.T. Wang and L. Tang, *New J. Chem.*, 2017, *41*, 437-441.

Copy of ^{1}H-NMR and ^{13}C-NMR spectra of the coupling products

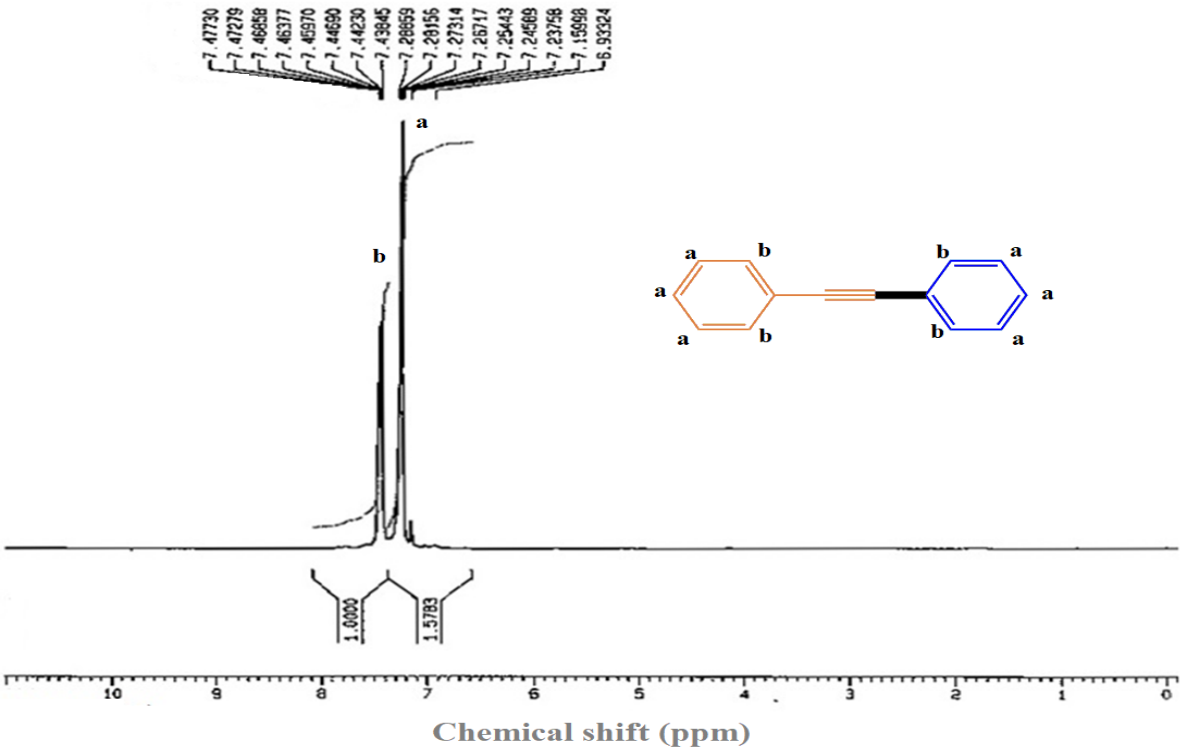


Fig. S9 ^{1}H-NMR (250 MHz) spectrum of **6**

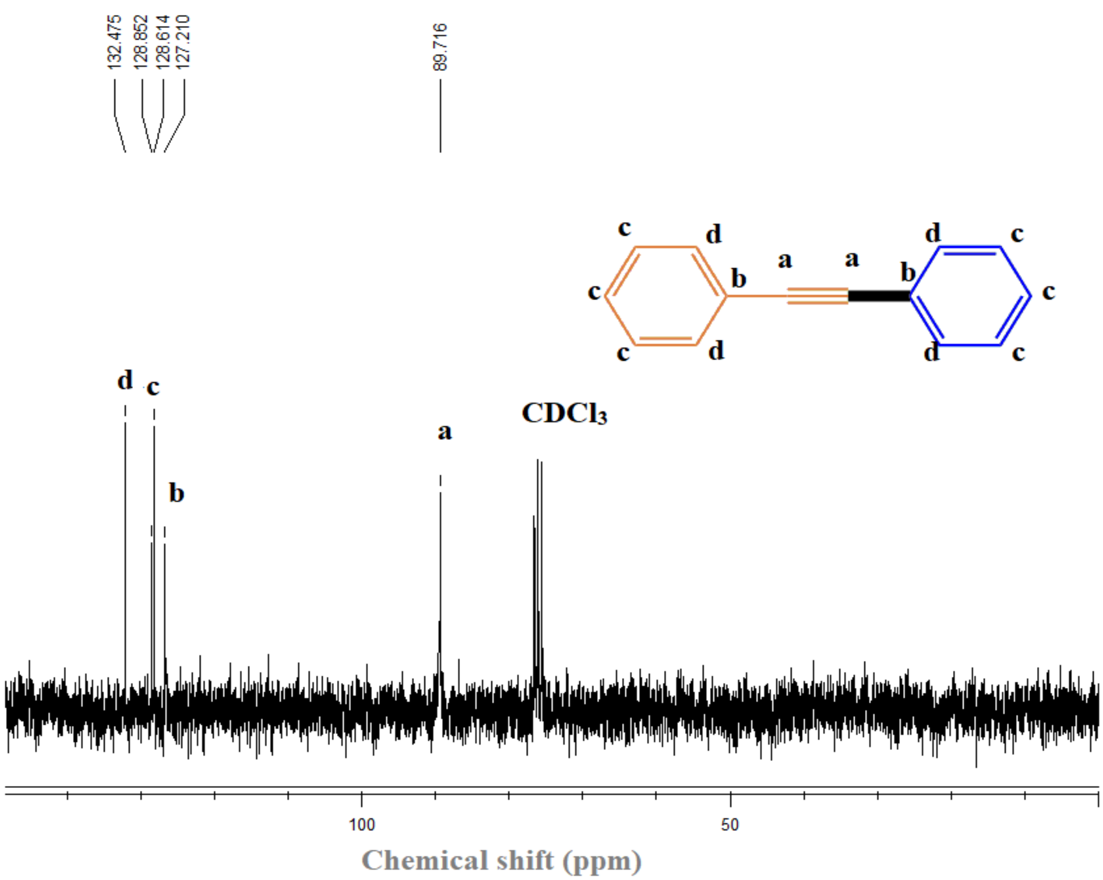


Fig. S10 ^{13}C-NMR (62.9 MHz) spectrum of **6**

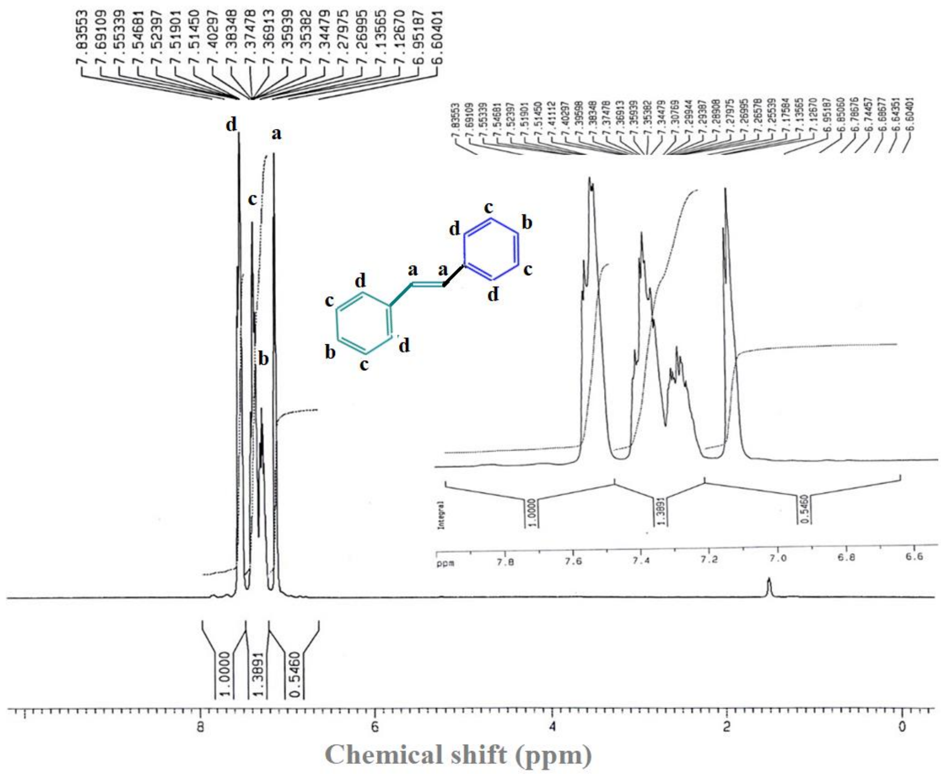


Fig. S11 ^{1}H-NMR (250 MHz) spectrum of **7**

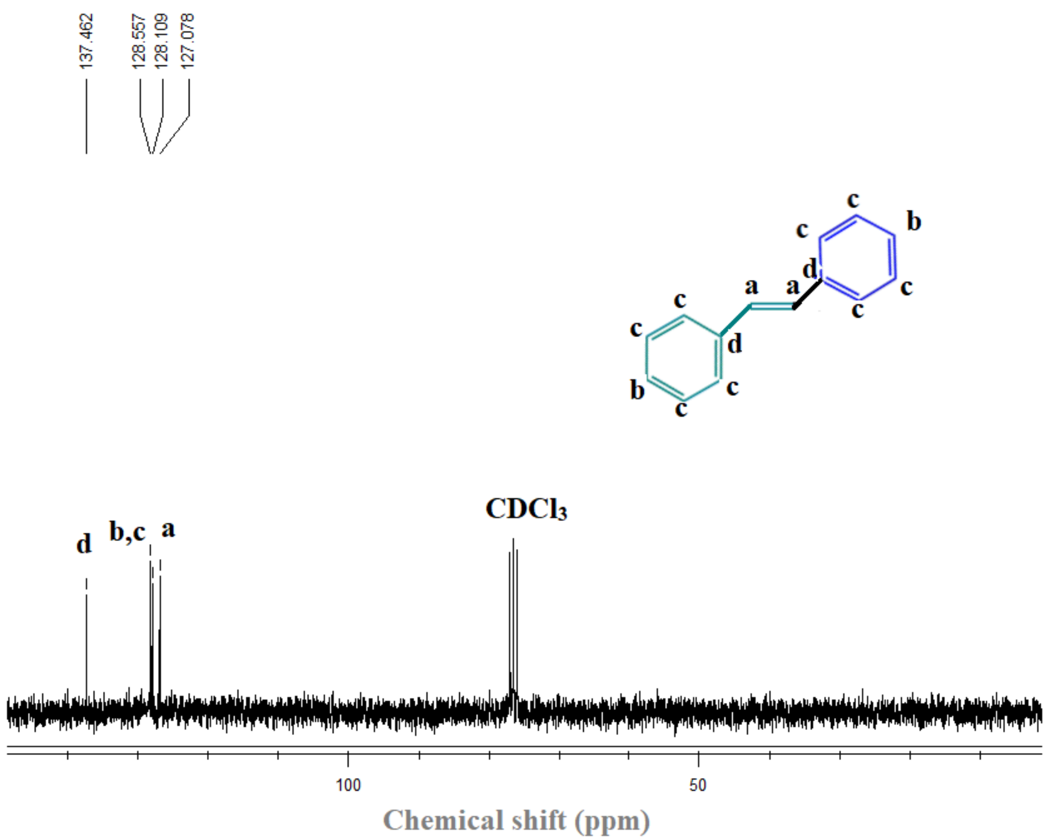


Fig. S12 ^{13}C-NMR (62.9 MHz) spectrum of **7**

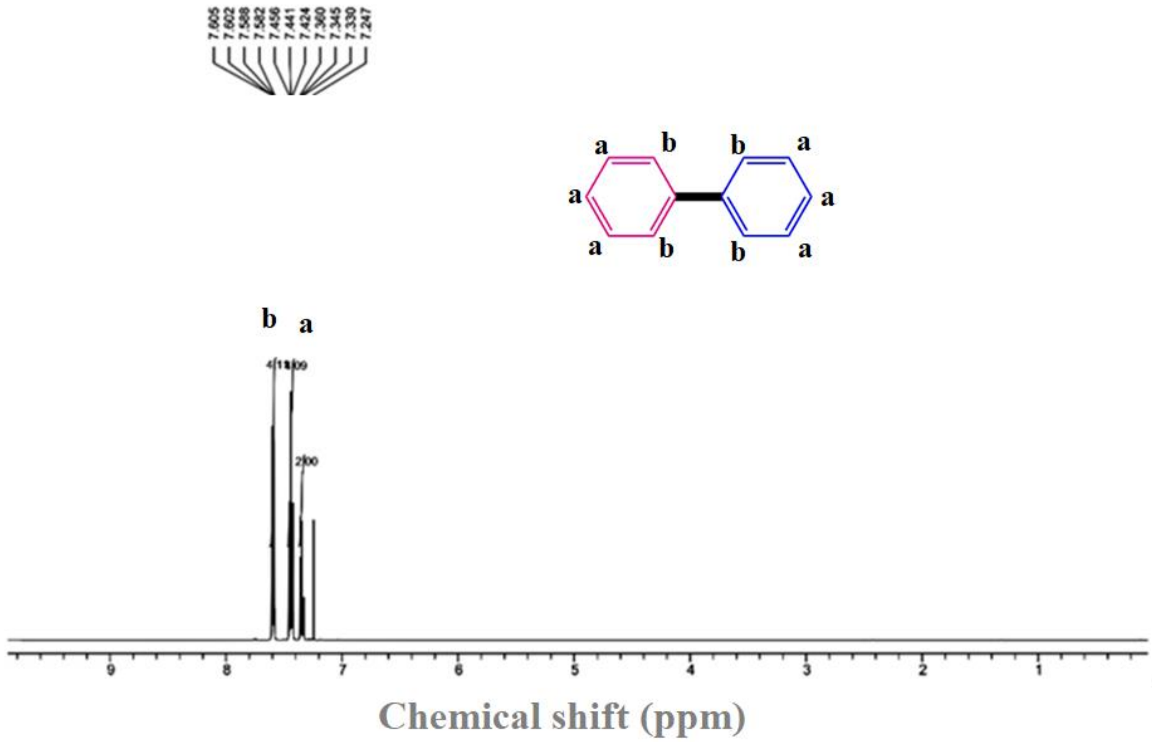


Fig. S13 ^{1}H-NMR (250 MHz) spectrum of **8**

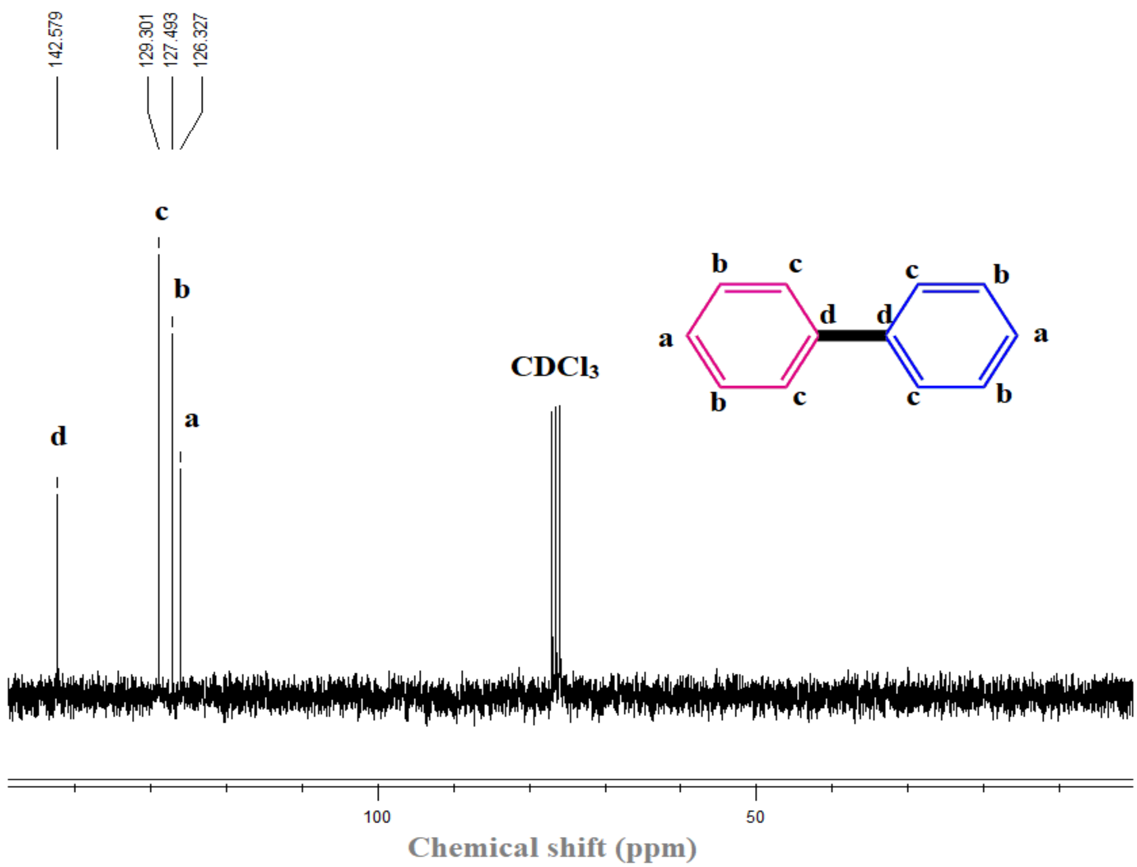


Fig. S14 ^{13}C-NMR (62.9 MHz) spectrum of **8**

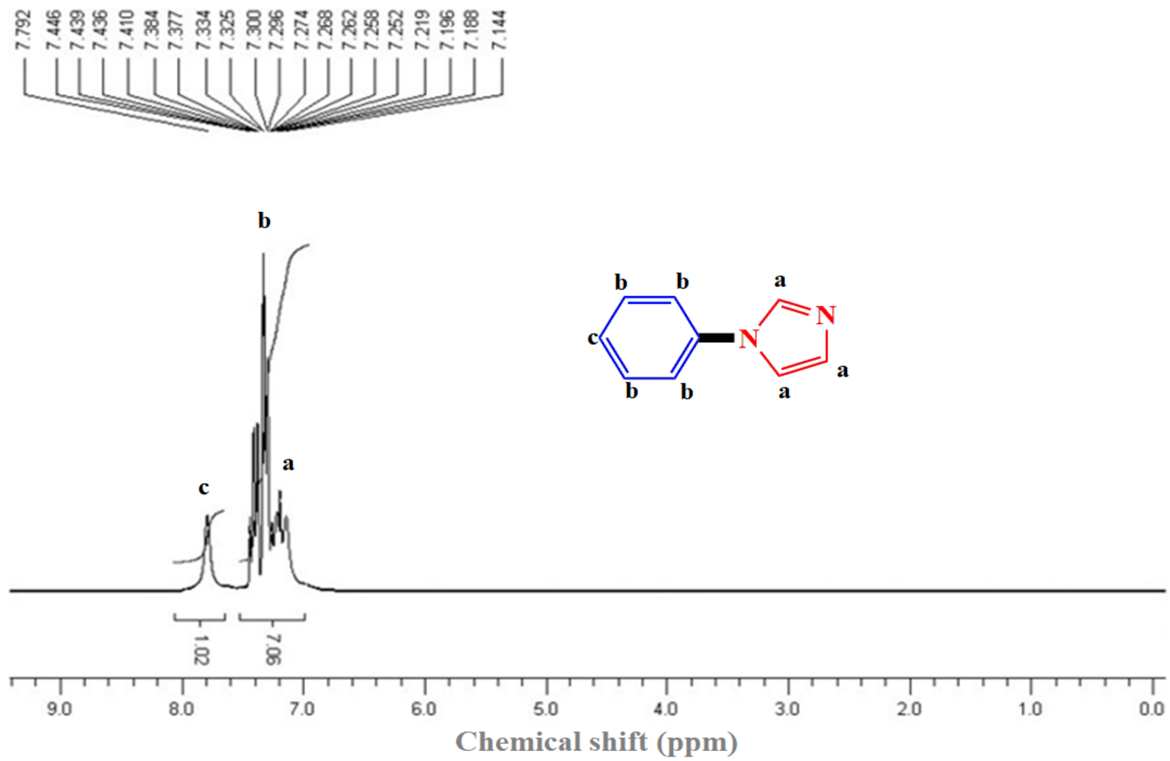


Fig. S15 ^{1}H-NMR (250 MHz) spectrum of **9**

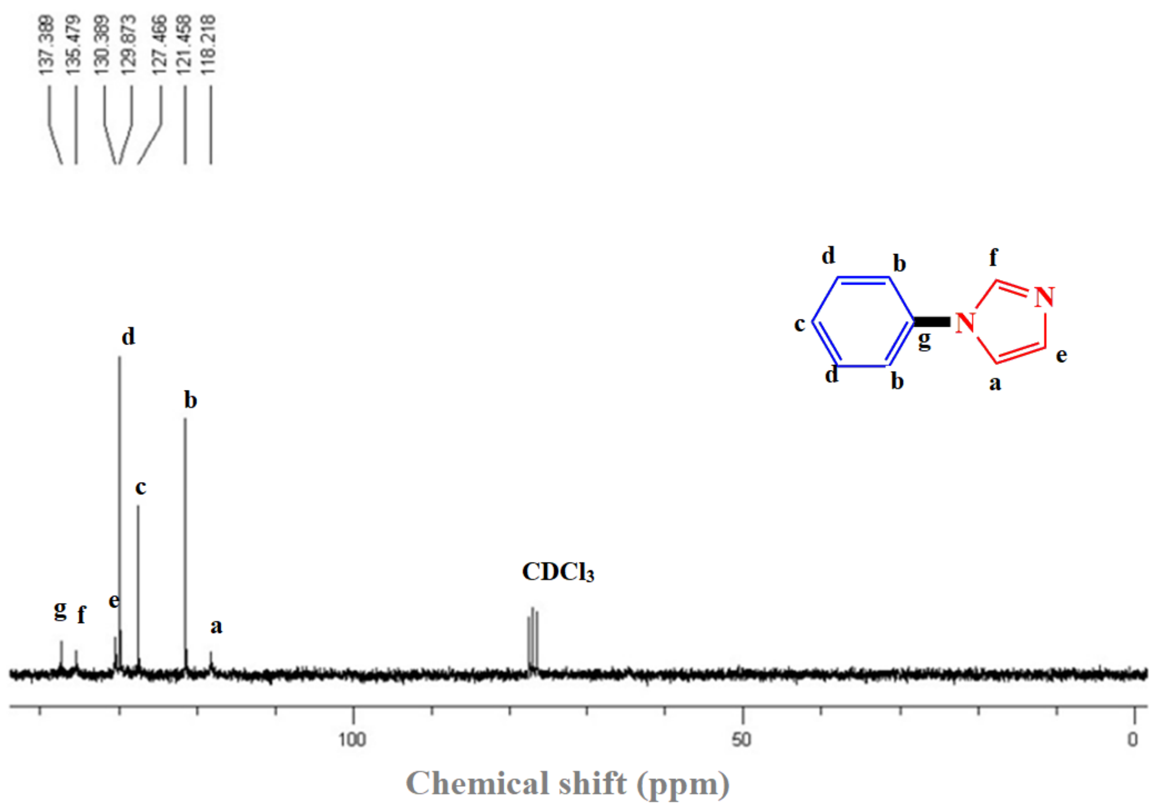


Fig. S16 ^{13}C-NMR (62.9 MHz) spectrum of **9**

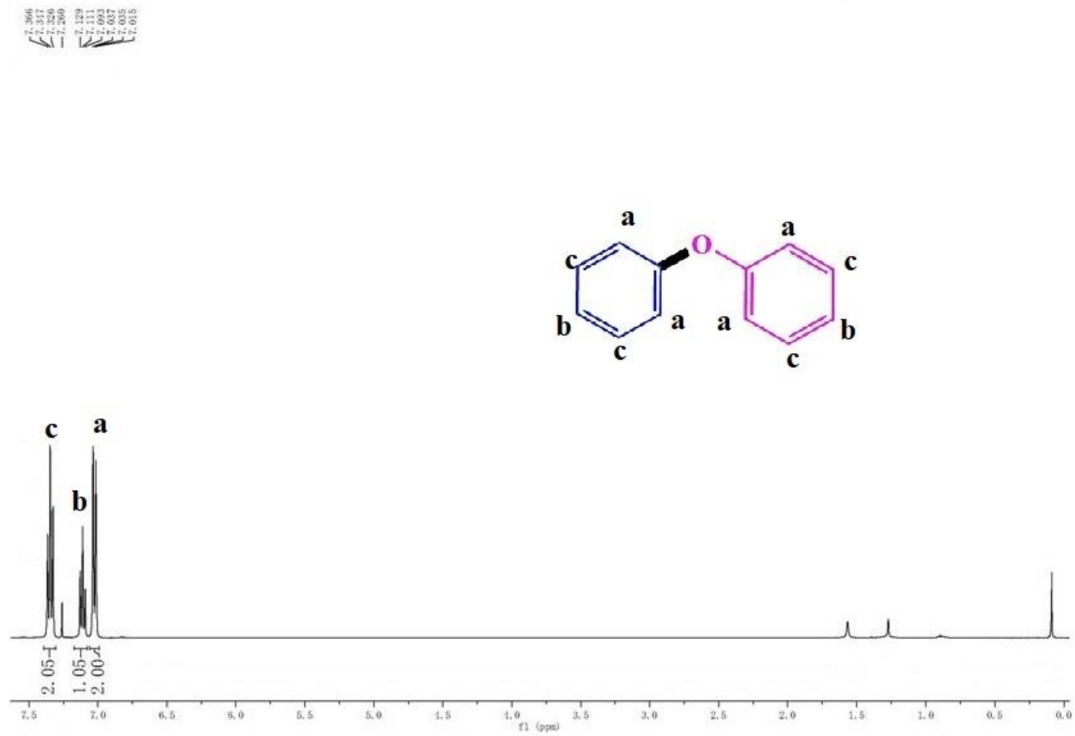


Fig. S17 ^{1}H-NMR (250 MHz) spectrum of **10**

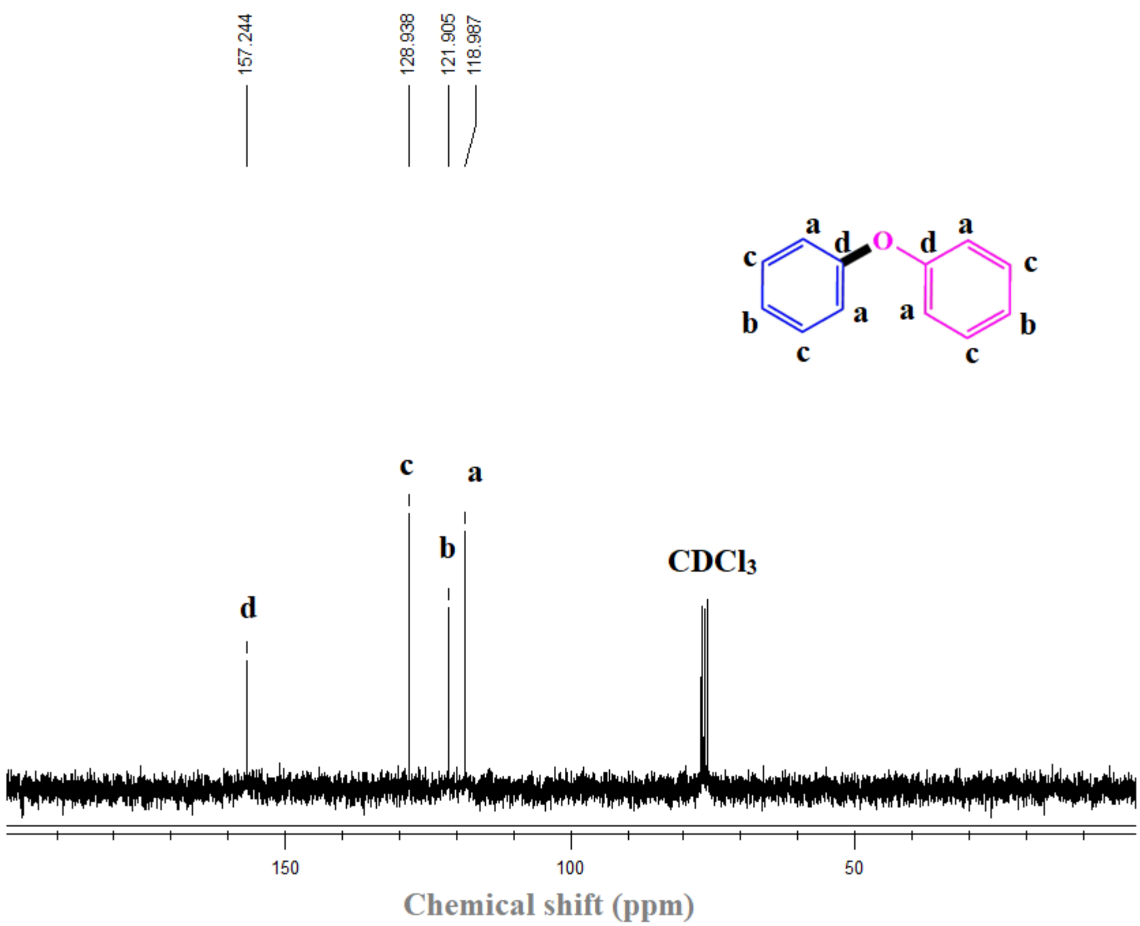


Fig. S18 ^{13}C-NMR (62.9 MHz) spectrum of **10**

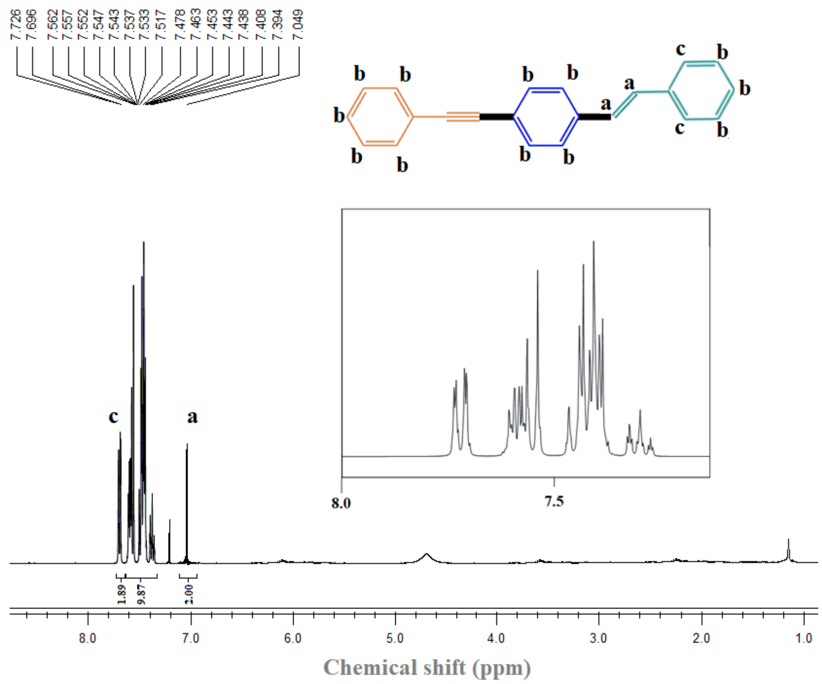


Fig. S19 ^{1}H-NMR (250 MHz) spectrum of **11**

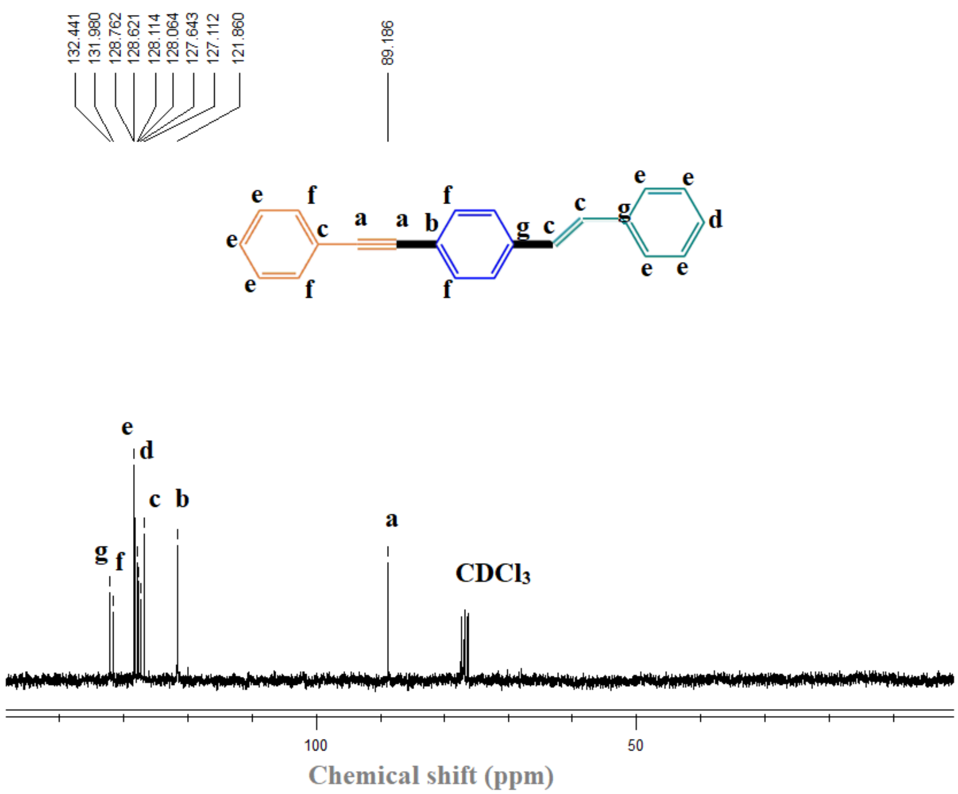


Fig. S20 ^{13}C-NMR (62.9 MHz) spectrum of **11**

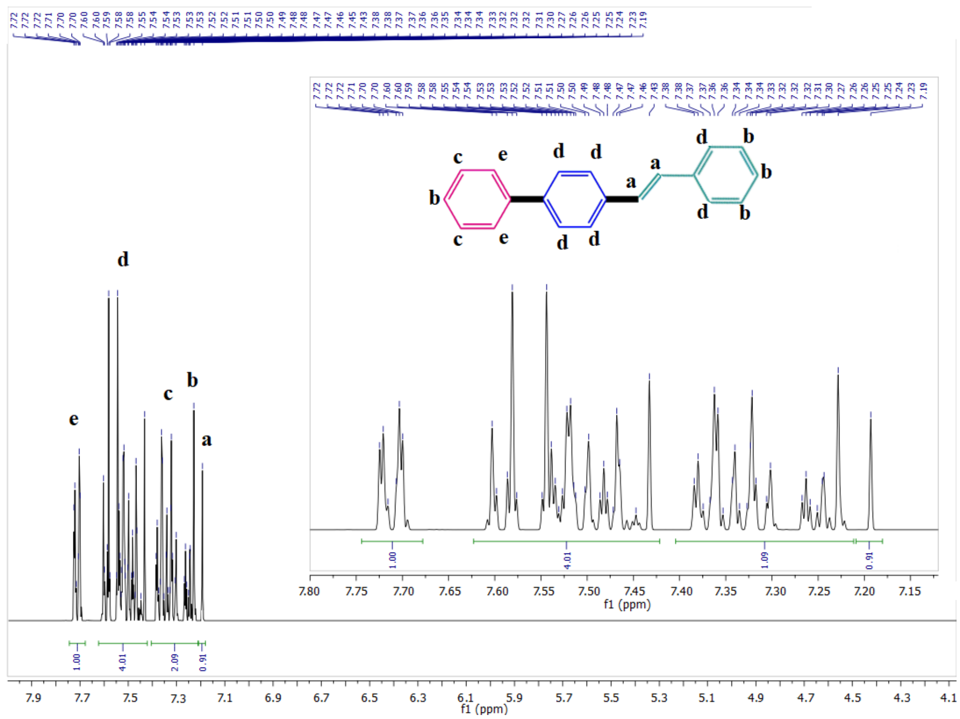


Fig. S21 ^{1}H-NMR (250 MHz) spectrum of **12**

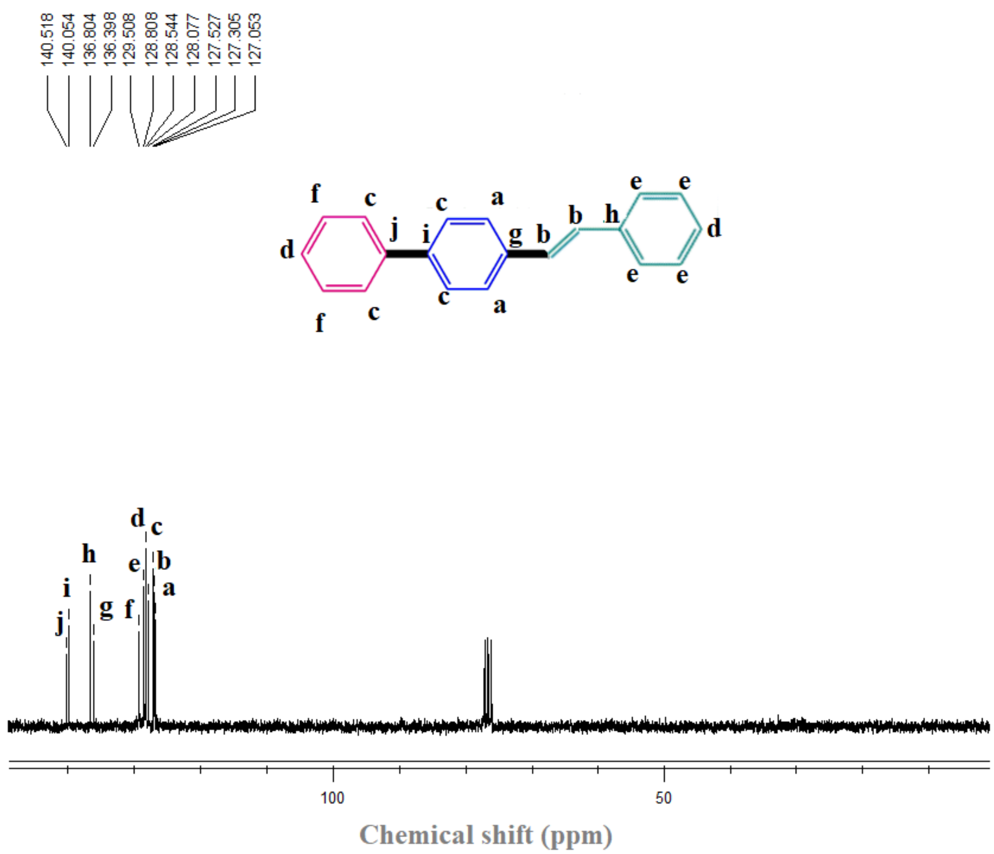


Fig. S22 ^{13}C-NMR (62.9 MHz) spectrum of **12**

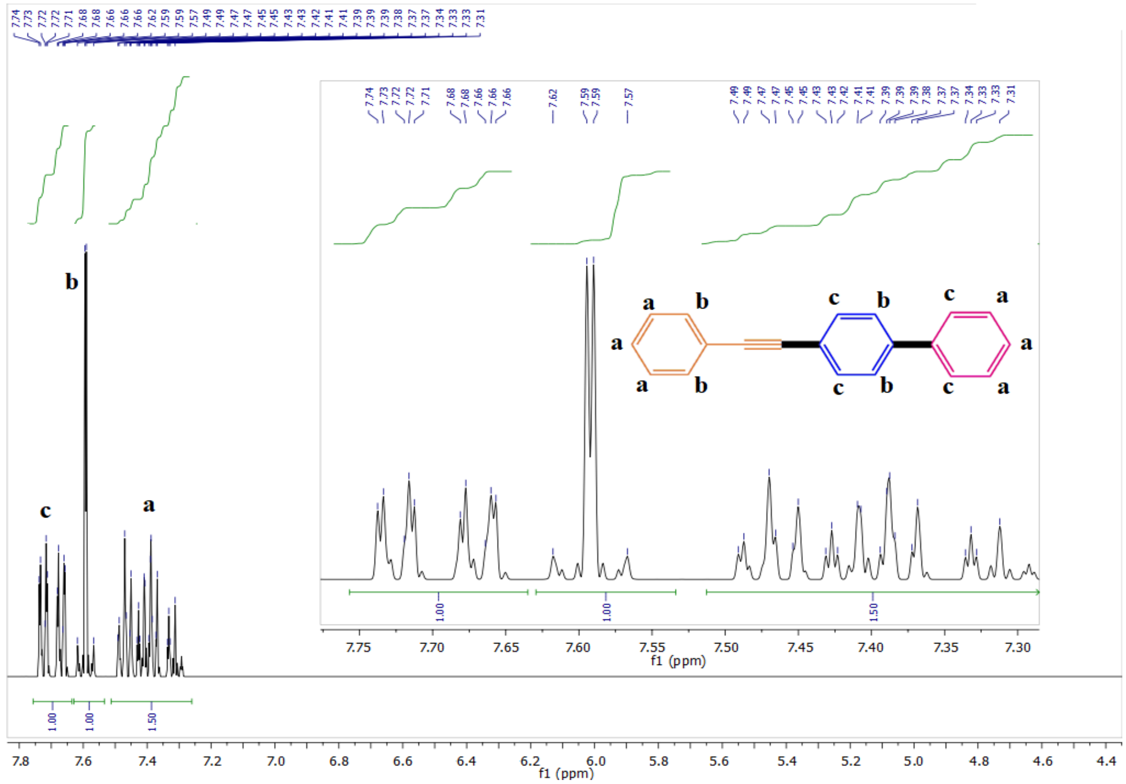


Fig. S23 [1]H-NMR (250 MHz) spectrum of **13**

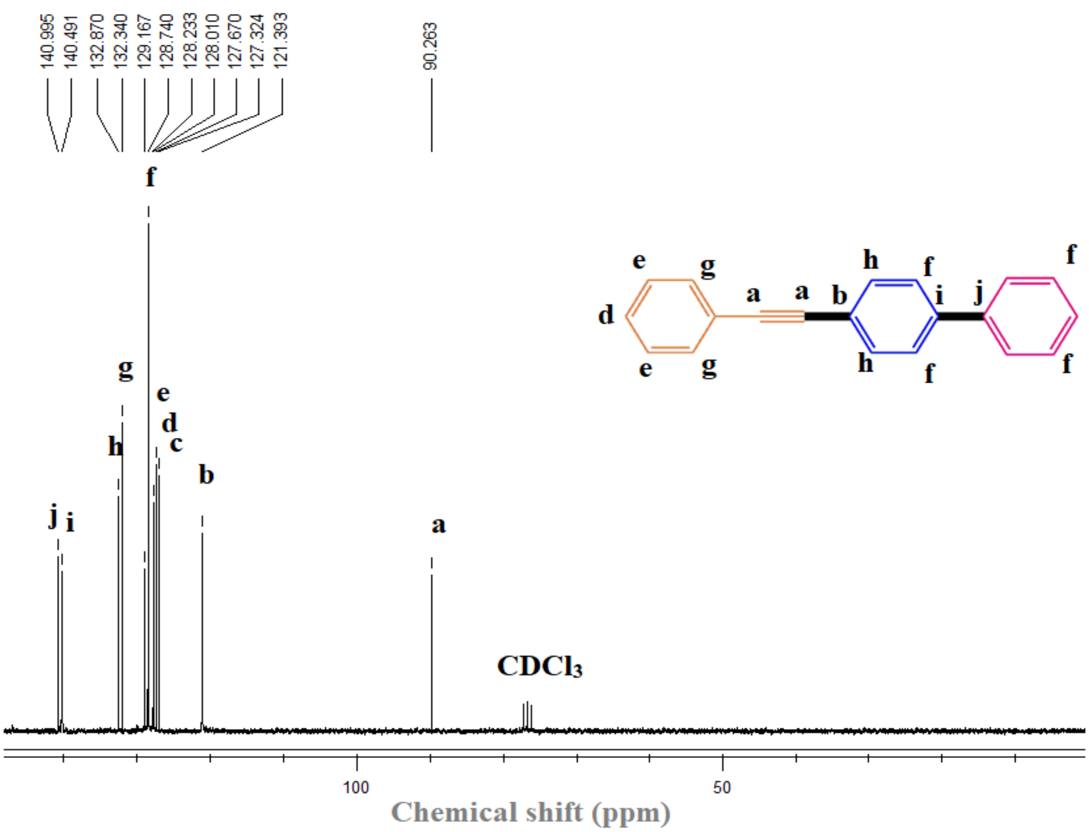


Fig. S24 [13]C-NMR (62.9 MHz) spectrum of **13**

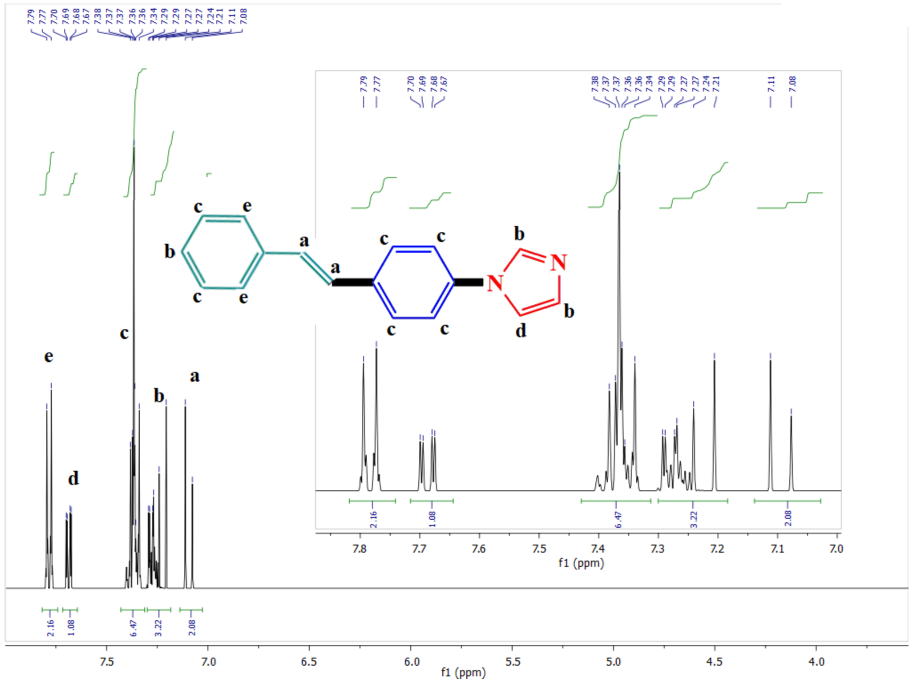


Fig. S25 [1]H-NMR (250 MHz) spectrum of **14**

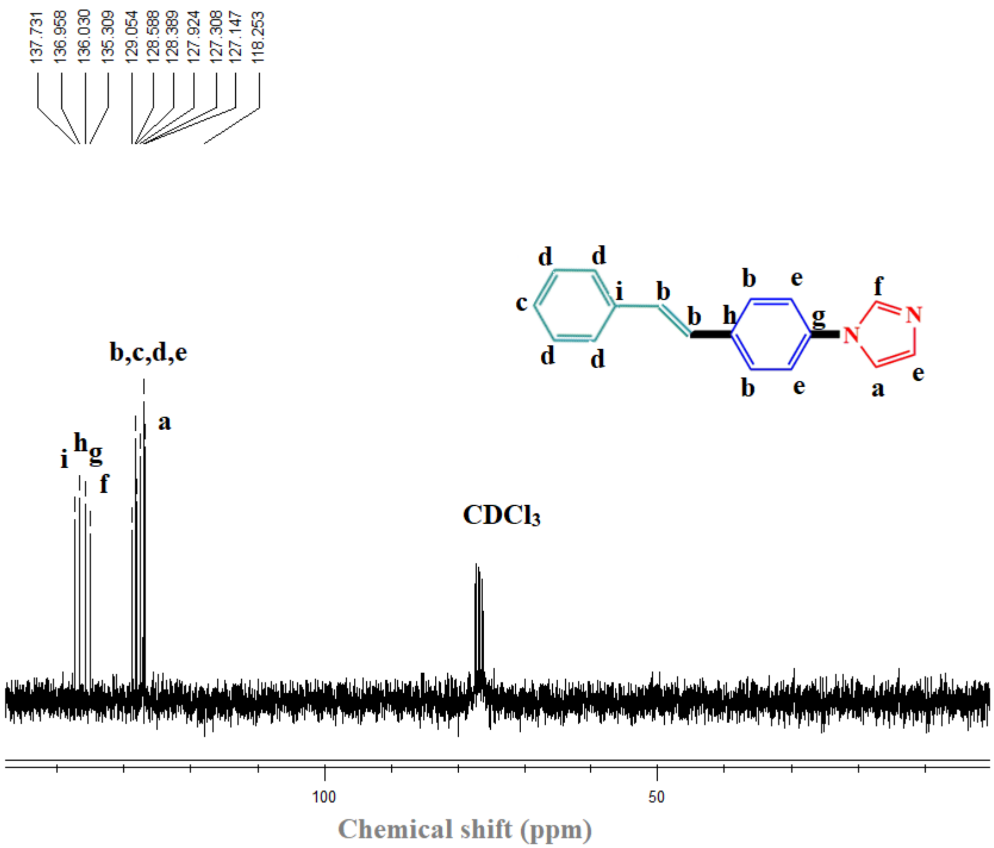


Fig. S26 [13]C-NMR (62.9 MHz) spectrum of **14**

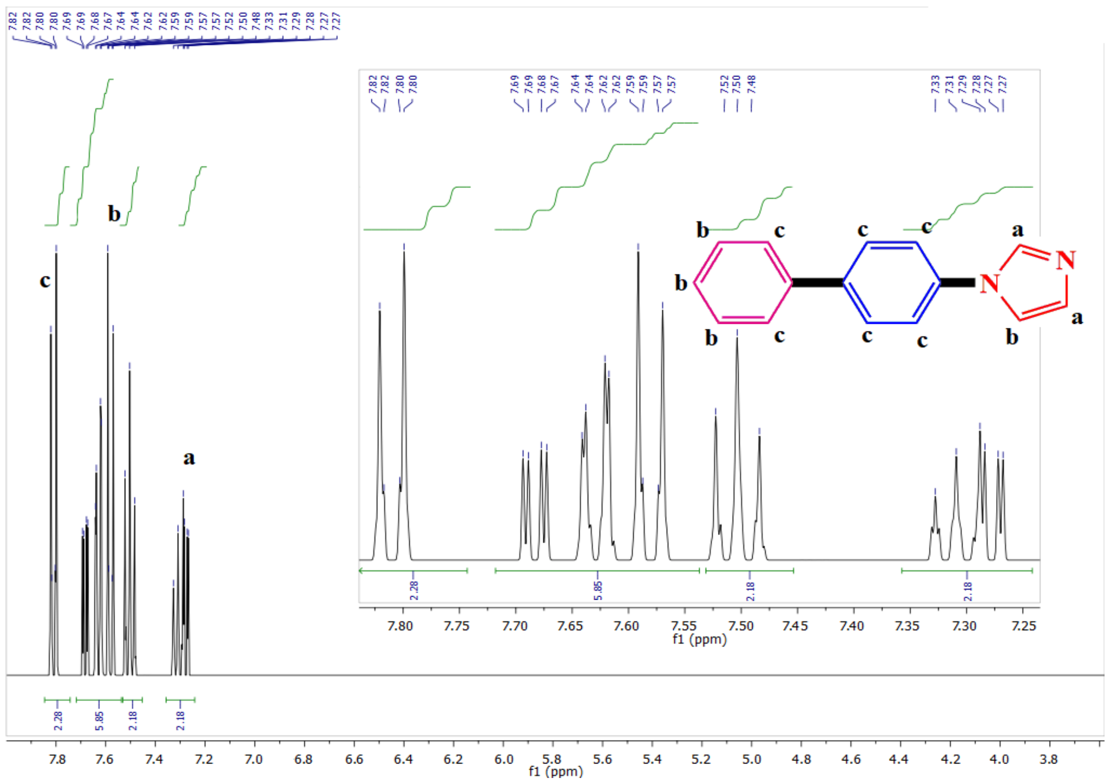


Fig. S27 ^{1}H-NMR (250 MHz) spectrum of **15**

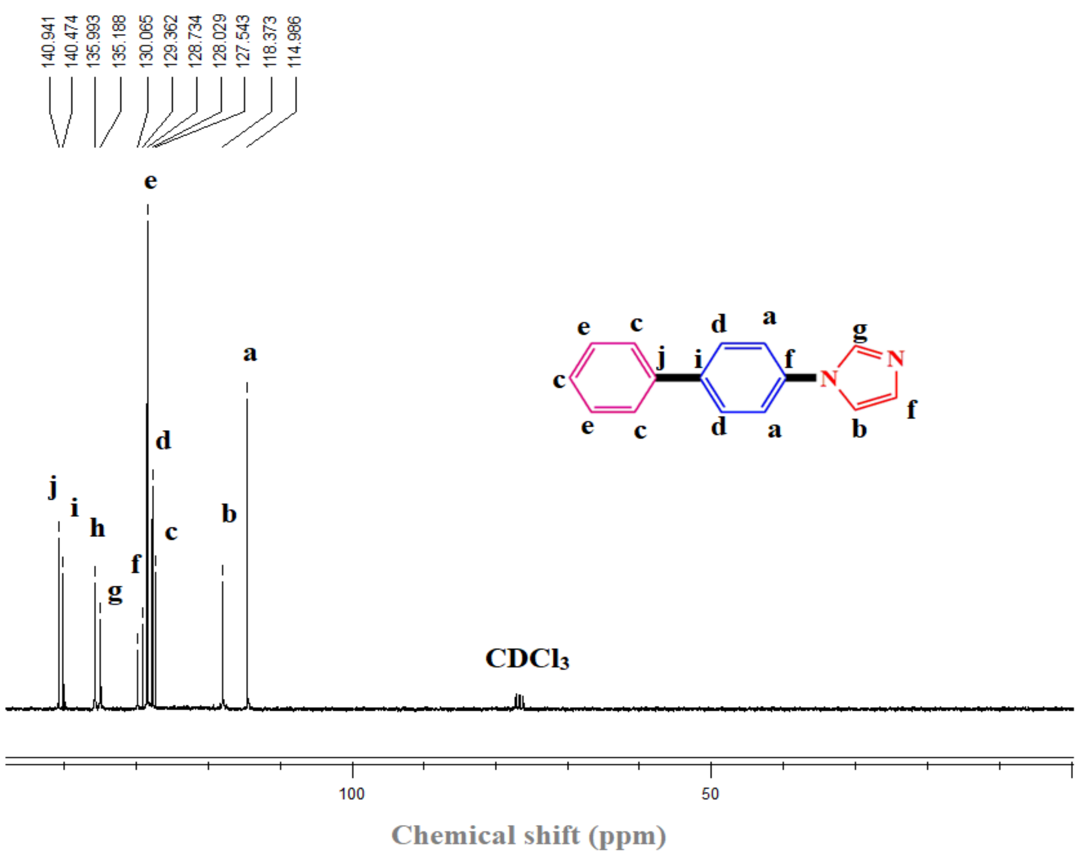


Fig. S28 ^{13}C-NMR (62.9 MHz) spectrum of **15**

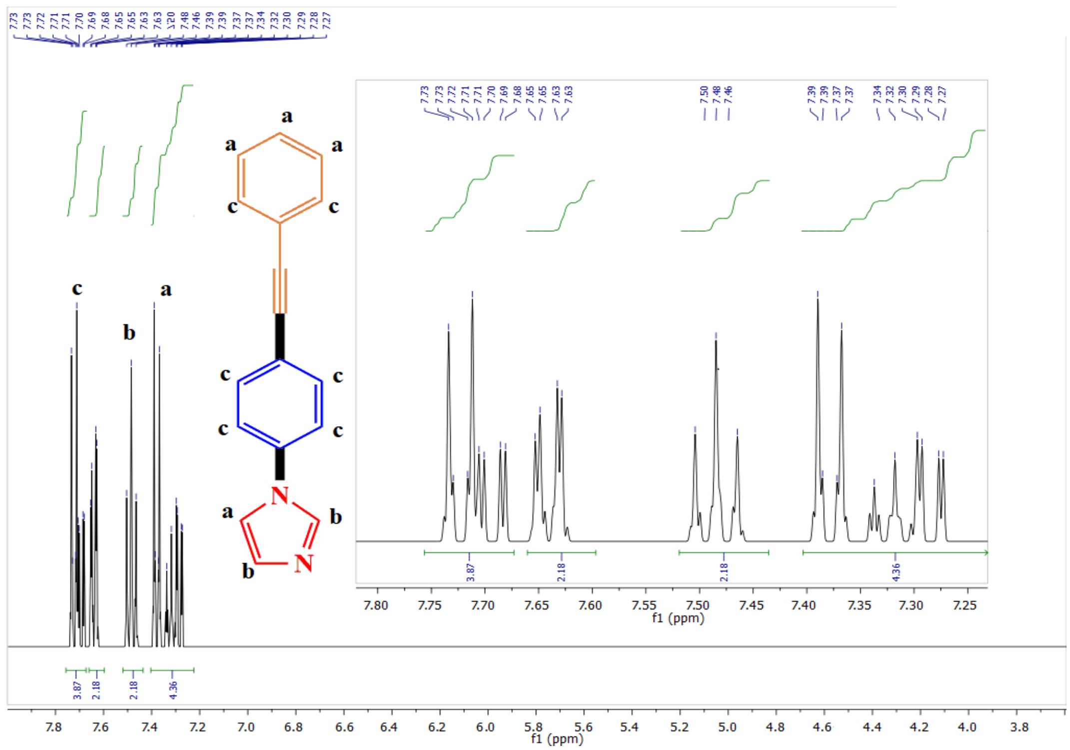


Fig. S29 [1]H-NMR (250 MHz) spectrum of **16**

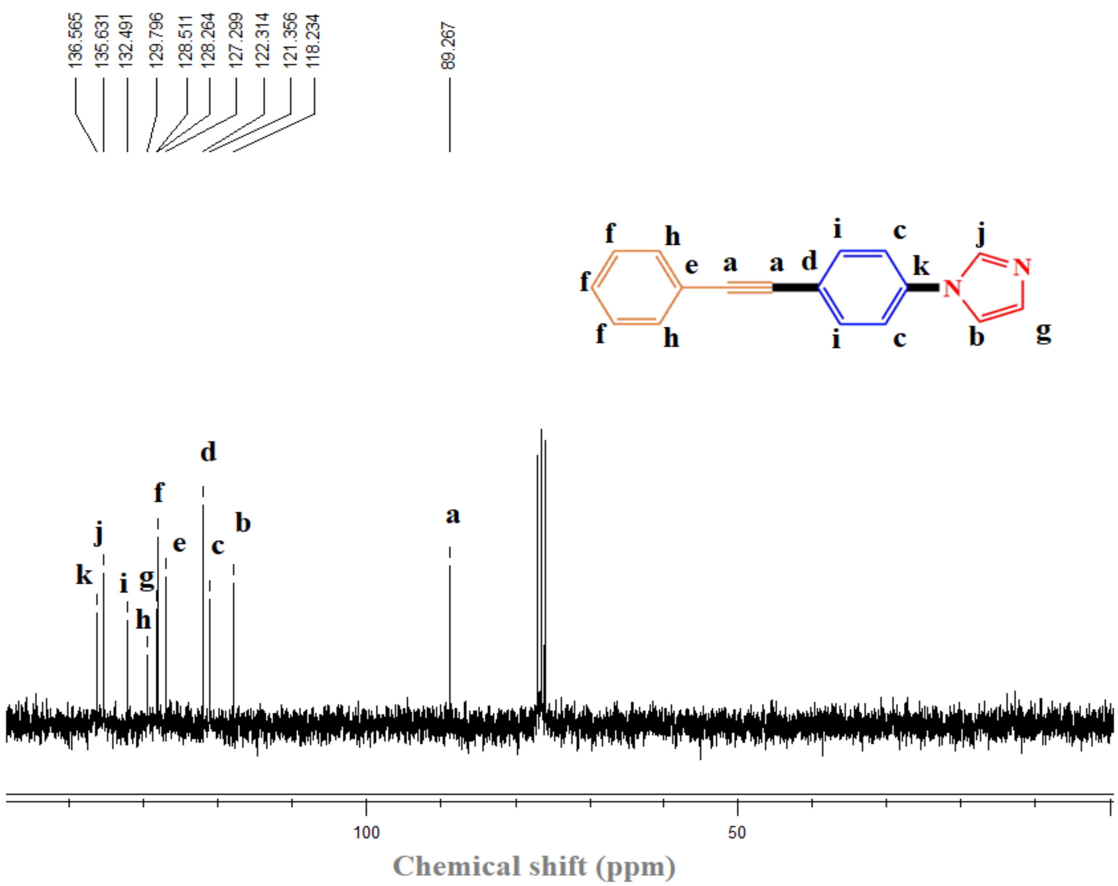


Fig. S30 [13]C-NMR (62.9 MHz) spectrum of **16**

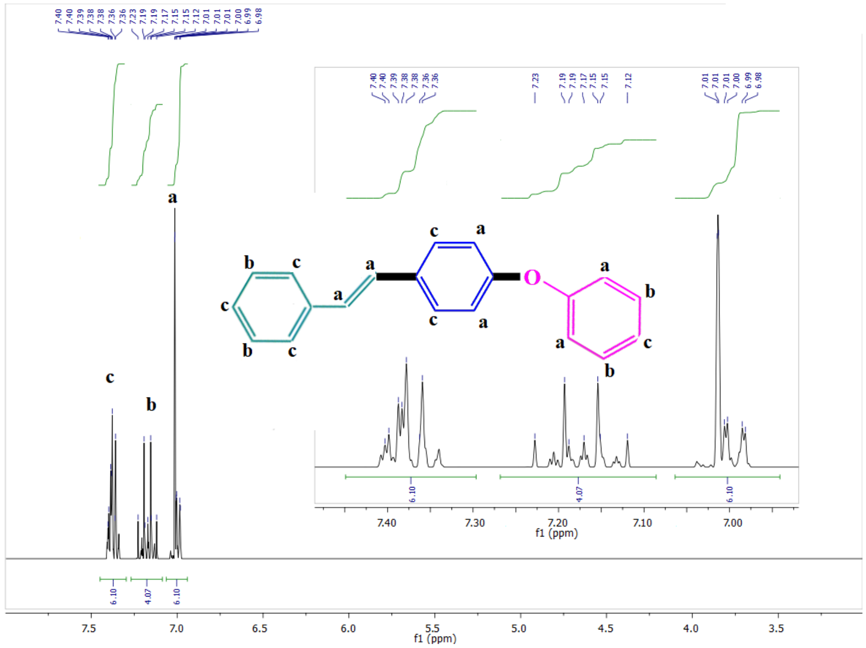


Fig. S31 ^{1}H-NMR (250 MHz) spectrum of **17**

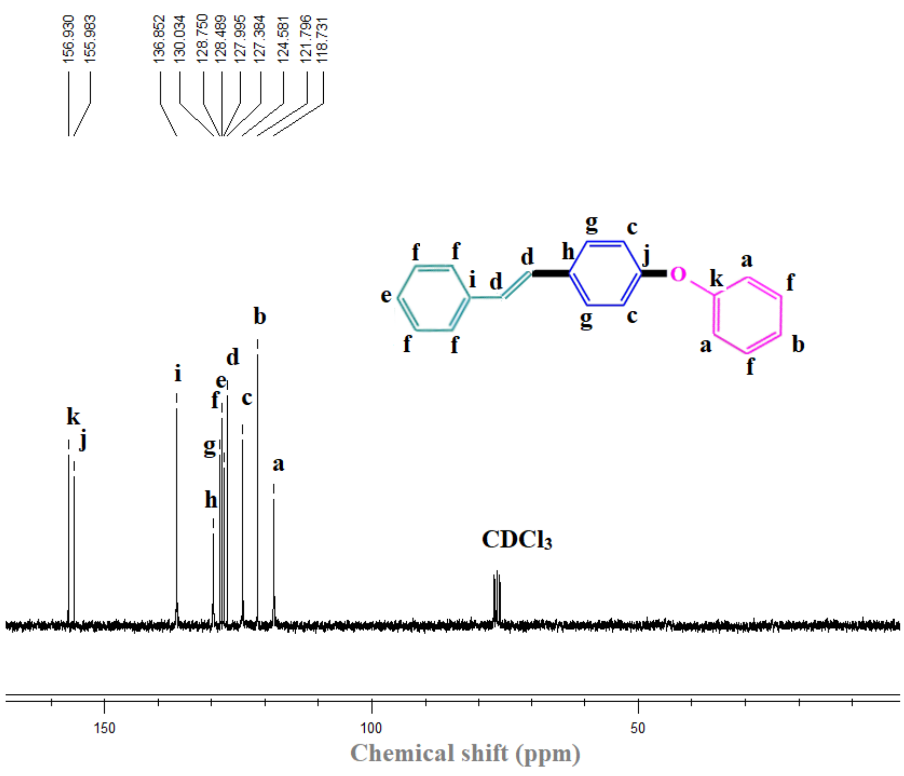


Fig. S32 ^{13}C-NMR (62.9 MHz) spectrum of **17**

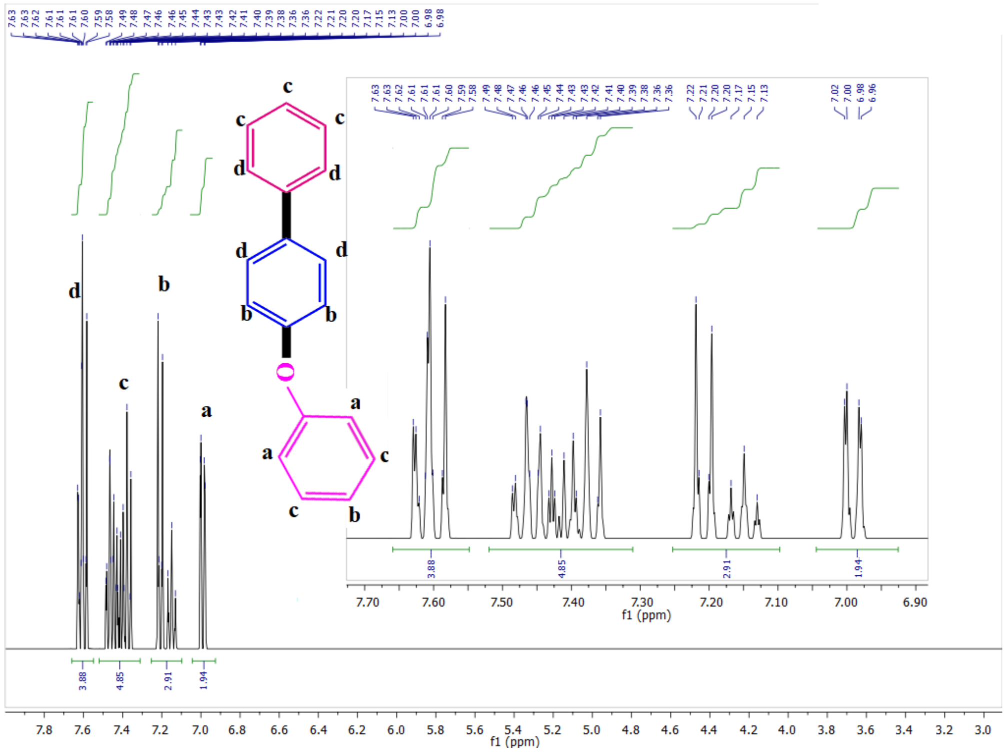


Fig. S33 ^{1}H-NMR (250 MHz) spectrum of **18**

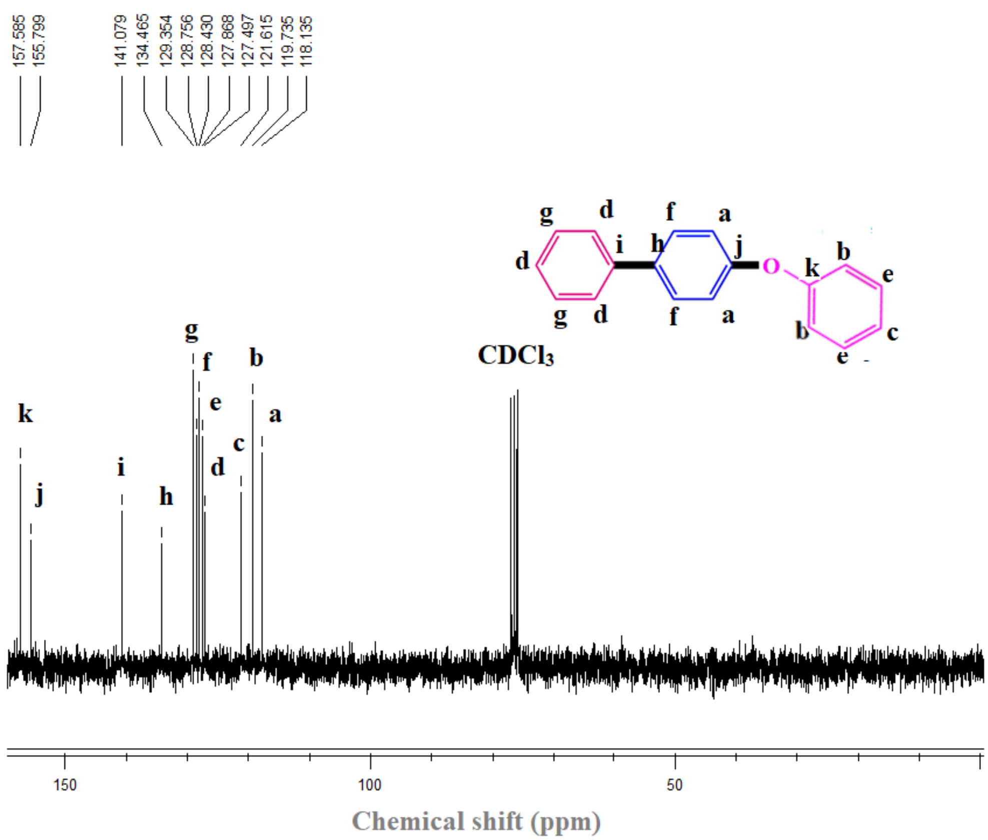


Fig. S34 ^{13}C-NMR (62.9 MHz) spectrum of **18**

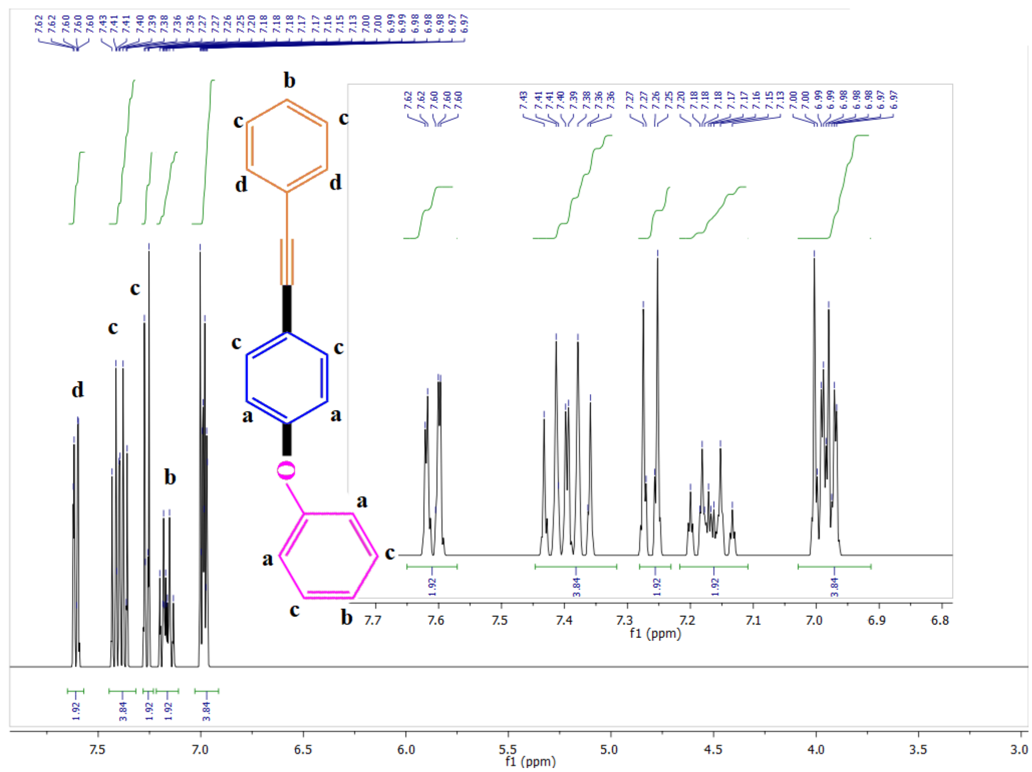


Fig. S35 ^{1}H-NMR (250 MHz) spectrum of **19**

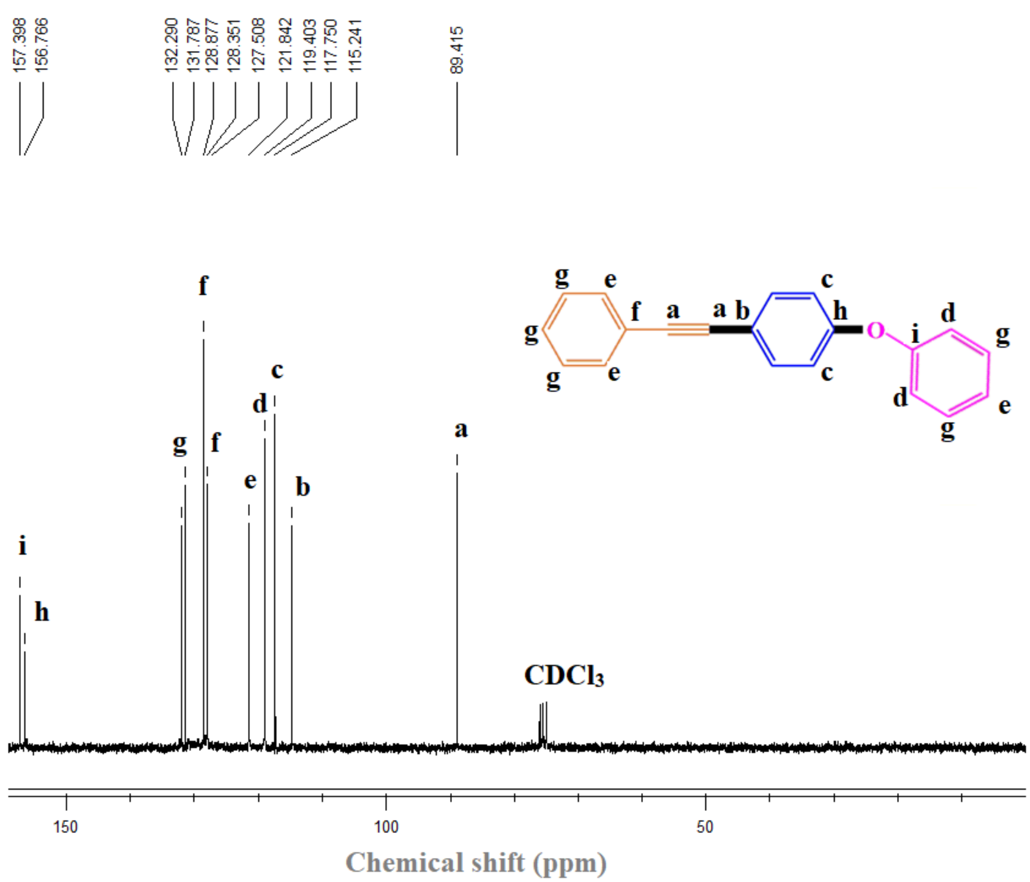


Fig. S36 ^{13}C-NMR (62.9 MHz) spectrum of **19**

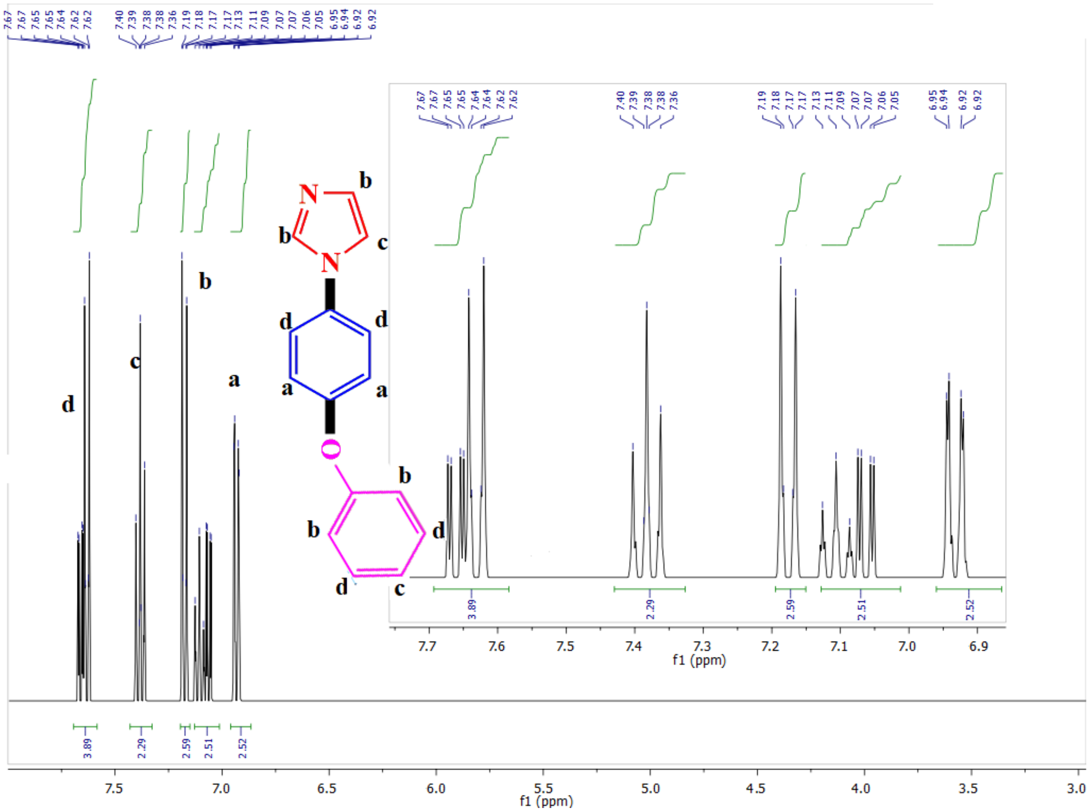


Fig. S37 [1]H-NMR (250 MHz) spectrum of **20**

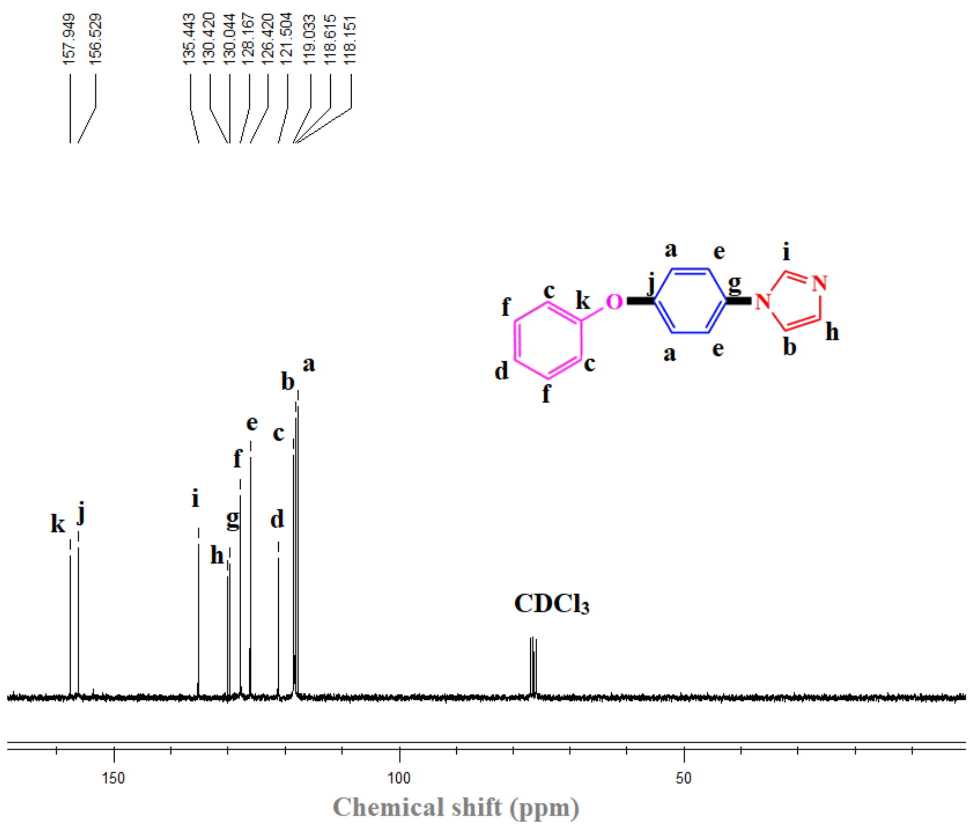


Fig. S38 [13]C-NMR (62.9 MHz) spectrum of **20**

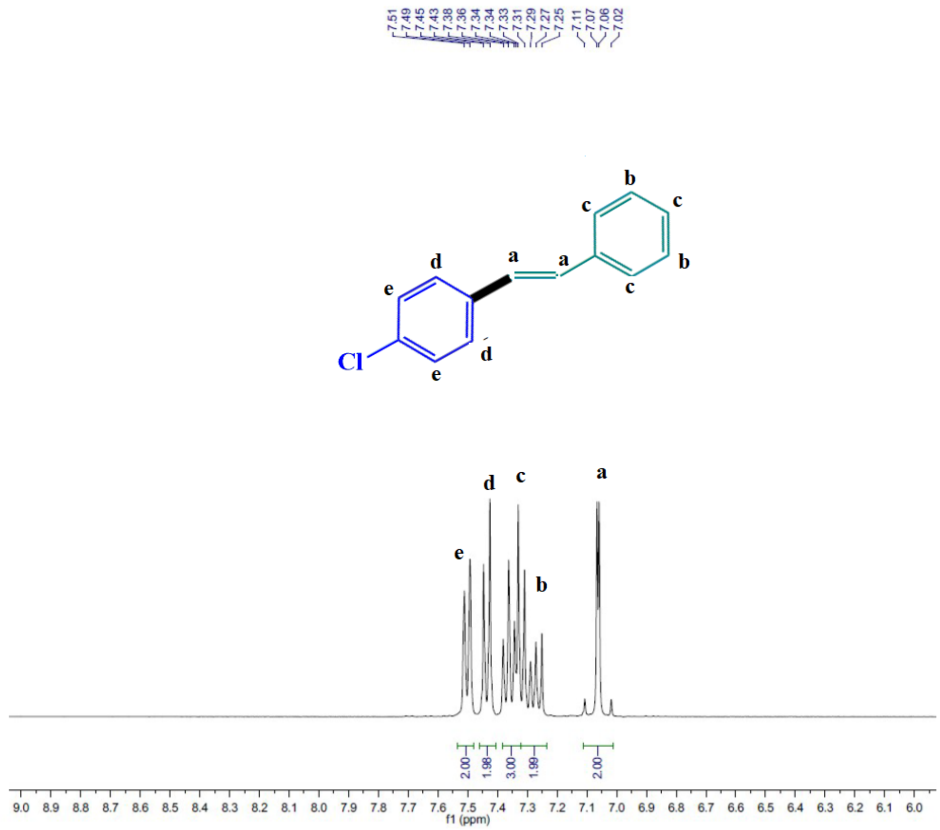


Fig. S39 ^{1}H-NMR (250 MHz) spectrum of **21**

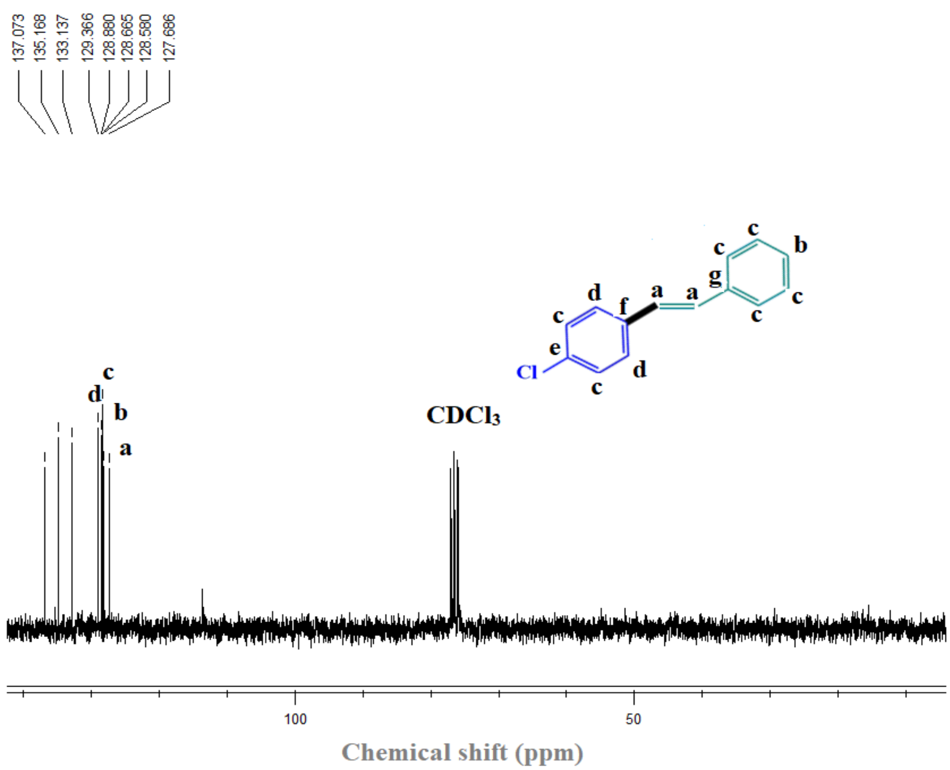


Fig. S40 ^{13}C-NMR (62.9 MHz) spectrum of **21**