Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Pd/Cu bimetallic nanoparticles embedded in macroporous ion-exchange resins: An excellent heterogeneous catalyst for the Sonogashira reaction

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Supporting Information

1. Powder XRD

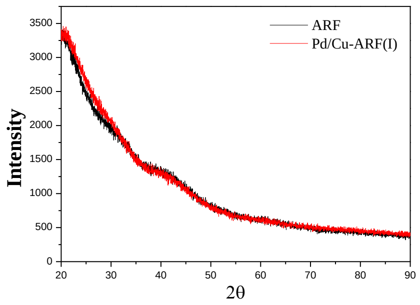
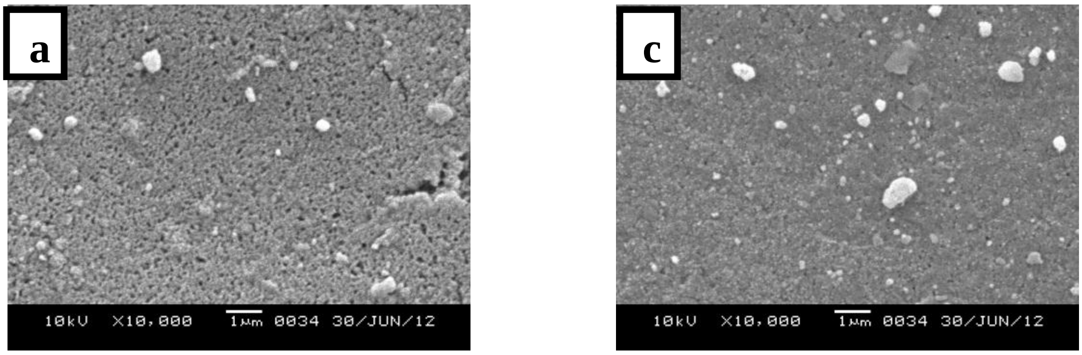


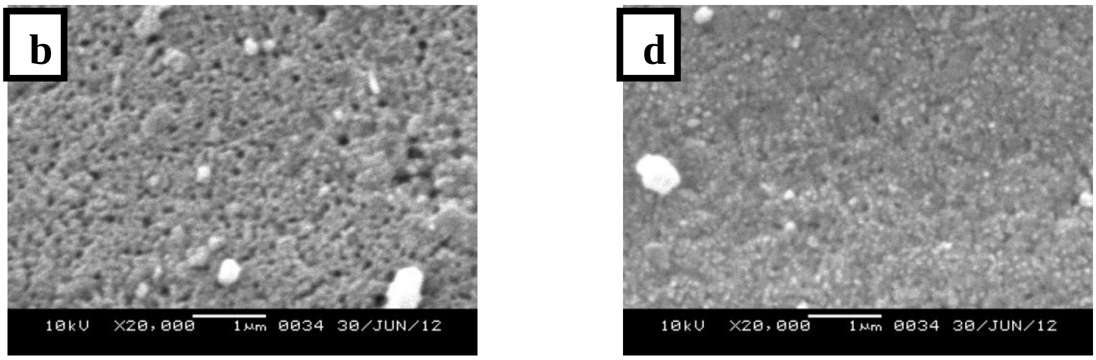
Fig. S1 XRD of amberlite resin formate (**ARF**) and the corresponding Pd-Cu incorporated resin (**Pd/Cu-ARF(I)**).

2. SEM images



ARF

Pd/Cu-ARF(I)



ARF

Pd/Cu-ARF(I)

Fig. S2 Scanning electron micrographs of **ARF** (**a, b**), **Pd/Cu-ARF(I)** (**c, d**) at different magnifications.

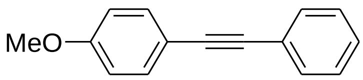
3. Comparative chart highlighting improved catalytic performance

Sl. No.	Previous ARF-Pd Cat.	Present Pd-Cu/ARF Cat.	Other related mono- or bimetallic Cats.
1.	Successful only with aryl iodides.	Works also with aryl bromides bearing electron-withdrawing groups.	
2.	No studies with heteroaryl bromides	Works with heteroaryl bromides.	
3.		Our catalyst does not require any phosphine ligands	Sonogashira cross-coupling using Pd/Cu- based catalysts requires phosphine ligands References are: (a) D. D. Dolliver, B. T. Bhattarai, A. Pandey, M. L. Lanier, A. S. Bordelon, S. Adhikari, J. A. Dinser, P. F. Flowers, V. S. Wills, C. L. Schneider, K. H. Shaughnessy, J. N. Moore, S. M. Raders, T. S. Snowden, A. S. McKim, F. R. Fronczek, *J. Org. Chem.*, 2013, **78**, 3676; (b) V. O. Iaroshenko, S. Ali, T. M. Babar, M. S. A. Abbasi, V. Y. Sosnovskikh, A. Villinger, A. Tolmachev and P. Langer, *Tetrahedron*, 2013, **69**. 3167; (c) D. Gelman and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2003, **42**, 5993; (d) L. Yin and J. Liebscher, *Chem. Rev.*, 2007, **107**, 133.)
4.		Our catalyst is effective for electron-deficient aryl bromide without the presence of any ionic liquids.	Pd NPs are used in Sonogashira coupling ligand-free conditions, aryl iodides and electron-deficient aryl bromides are successful, but only in the presence of ionic liquid Ref.: A. R. Gholap, K. Venkatesan, R. Pasricha, T. Daniel, R. J. Lahoti, and K. V. Srinivasan, *J. Org. Chem.*, 2005, **70**, 4869.
5.		Our catalyst is recyclable with no apparent leaching, experimentally verified. To the best of our knowledge, there is no such heterogeneous	One reference (Z. Novak, A. Szabo, J. Repasi, A. Kotschy, *J. Org. Chem.* 2003, **68**, 3327), where the authors have used heterogeneous Pd/C (5%) along with CuI (10 mol%) and PPh_3 ligand for the Sonogashira reaction. However, recycling was tested by adding CuI in

		Pd/Cu bimetallic catalyst that is reported to be recyclable in Sonogashira coupling.	every run. In another reference (B.-N. Lin, S.-H. Huang, W.-Y. Wu, C.-H. Mou, F.-Y. Tsai, *Molecules*, 2013, **15**, 9157), authors have employed heterogeneous nano-sized MCM-41-Pd catalyst along with CuI in the Sonogashira reaction. Again, recycling ability was tested by using additional co-catalyst in every run. Our catalyst does not require additional copper salt for reuse in the Sonogashira reaction.
6.		The reluctance of deactivated aryl bromide to undergo Sonogashira coupling in the presence of our catalyst could be exploited.	To the best of our knowledge, no such example of chemoselectivity has been reported in the literature using heterogeneous Pd/Cu catalysts.
7.		The present catalytic structure has been examined in more details by SEM, XRD and TEM showing fairly homogeneous distribution of NPs throughout the matrix with the mean diameter of the particle ~4.9 nm.	

4. Spectral data

Table 1, entry 1

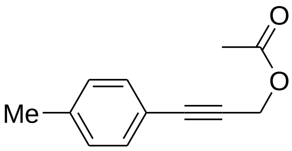


1-Methoxy-4-(2-phenylethynyl)benzene,[1] White crystalline solid, mp 56-58 ^{o}C (Lit. mp 58-60 ^{o}C)

IR (in KBr): ν_{max} 2216 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 3.82 (s, 3H, OCH_3), 6.86-6.89 (m, 2H, ArH), 7.31-7.33 (m, 3H, ArH), 7.45-7.53 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 55.3, 88.0, 89.3, 114.0, 115.4, 123.6, 127.9, 128.3, 131.4, 133.0, 159.6.

Table 2, entry 2

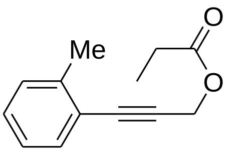


3-*p*-Tolylprop-2-ynyl acetate, colourless liquid.

IR (neat) ν_{max} 2237, 1747 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 2.13 (s, 3H, C<u>H</u>$_3$CO), 2.35 (s, 3H, ArC<u>H</u>$_3$), 4.90 (s, 2H, CH_2), 7.12 (d, *J* = 8.1 Hz, 2H, ArH), 7.34 (d, *J* = 8.1 Hz, 2H, ArH); ^{13}C NMR ($CDCl_{3,}$ 75 MHz): δ/ppm 20.8, 21.5, 52.9, 82.1, 86.6, 119.0, 129.0,131.8, 139.0, 170.4.

Table 1, entry 3

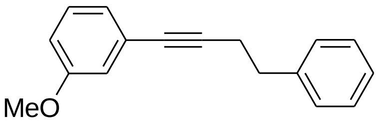


3-*o*-Tolylprop-2-ynyl propionate, colourless liquid.

IR (neat): ν_{max} 2229, 1743 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 1.19 (t, *J* = 7.5 Hz, 3H, CH_3), 2.38-2.45 (m, 5H, ArC<u>H</u>$_3$, C<u>H</u>$_2$), 4.95 (s, 2H, O-CH_2), 7.10-7.26 (m, 3H, ArH), 7.41 (d, *J* = 7.5 Hz, 1H, ArH); ^{13}C NMR ($CDCl_{3,}$ 75 MHz): δ/ppm 9.0, 20.6, 27.4, 52.8, 85.3, 86.8, 121.9, 125.5, 128.7, 129.4, 132.2, 140.5, 173.8.

Table 1, entry 4

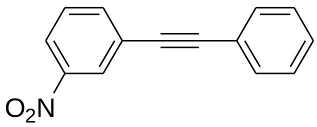


1-Methoxy-3-(4-phenylbut-1-ynyl)benzene,[2] Colourless liquid.

IR (neat): ν_{max} 2227 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 2.69 (t, *J* = 7.5 Hz, 2H, CH_2), 2.92 (t, *J* = 7.5 Hz, 2H, CH_2-Ar), 3.78 (s, 3H, O-CH_3), 6.82-6.85 (m, 1H, ArH), 6.90-6.91 (m, 1H, ArH), 6.95-6.98 (m, 1H, ArH), 7.16-7.32 (m, 6H, ArH); ^{13}C NMR ($CDCl_{3,}$ 75 MHz): 21.7, 35.1, 55.2, 81.2, 89.4, 114.2, 116.4, 124.0, 124.8, 126.3, 128.4, 128.5, 129.2, 140.7, 159.2.

Table 1, entry 5

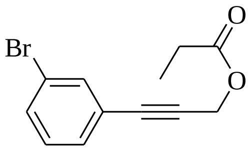


1-(2-(3-nitrophenyl)ethynyl)benzene, yellow solid, 69-71 °C (Lit.[1] mp 67-69 °C)

IR (in KBr): ν_{max} 2207 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 7.38-7.39 (m, 3H, ArH), 7.50-7.57 (m, 3H, ArH), 7.80-7.84 (m, 1H, ArH), 8.15-8.19 (m, 1H, ArH), 8.37-8.38 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 86.7, 91.9, 122.2, 122.9, 125.2, 126.4, 128.5, 129.0, 129.3, 131.8, 137.2, 148.2.

Table 1, entry 6

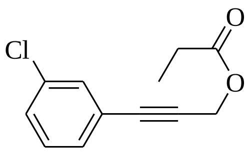


3-(3-Bromophenyl)prop-2-ynyl propionate, colourless liquid.

IR (neat): ν_{max} 2229, 1743 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 1.18 (t, *J* = 7.5 Hz, 3H, CH_3), 2.41 (q, *J* = 7.5 Hz, 2H, C<u>H</u>$_2$-CH_3), 4.90 (s, 2H, O-C<u>H</u>$_2$), 7.15-7.21 (m, 1H, ArH), 7.36-7.39 (m, 1H, ArH), 7.45-7.48 (m, 1H, ArH), 7.60-7.61 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): 8.9, 27.3, 52.4, 84.4, 84.7, 122.1, 124.1, 129.7, 130.4, 131.9, 134.6, 173.7.

Table 1, entry 7

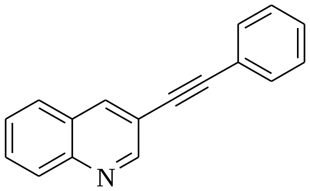


3-(3-Chlorophenyl)prop-2-ynyl propionate, colourless liquid.

IR (neat): ν_{max} 2229, 1743 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 1.18 (t, *J* = 7.2 Hz, 3H, CH_3), 2.40 (q, *J* = 7.5 Hz, 2H, C<u>H</u>$_2$-CH_3), 4.90 (s, 2H, O-C<u>H</u>$_2$), 7.21-7.34 (m, 3H, ArH), 7.44 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): 8.9, 27.3, 52.4, 84.3, 84.8, 123.8, 128.9, 129.5, 129.9, 131.7, 134.1, 173.6.

Table 1, entry 10

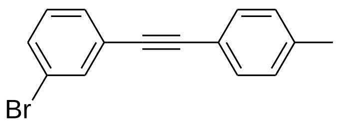


3-(2-Phenylethynyl)quinoline, yellow solid, 65-68 ^{o}C (Lit.[3] mp 67-70 ^{o}C).

IR (in KBr): ν_{max} 2218 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): 7.38-7.41 (m, 3H, ArH), 7.55-7.61 (m, 3H, ArH), 7.70-7.76 (m, 1H, ArH), 7.79-7.82 (m, 1H, ArH), 8.12 (d, J = 8.4 Hz, 1H, ArH), 8.32 (d, J = 1.8 Hz, 1H, ArH), 9.00 (d, 1H, J = 1.8 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): 86.4, 92.7, 117.5, 122.5, 127.3, 127.4, 127.6, 128.5, 128.8, 129.1, 130.2, 131.7, 138.5, 146.4, 151.9.

Table 1, entry 12A

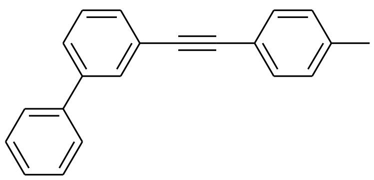


1-(2-(3-Bromophenyl)ethynyl)-4-methylbenzene,[4] White crystalline solid, mp 91-93 ^{o}C (Lit. mp 89-91 ^{o}C)

IR (in KBr): ν_{max} 2222 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 2.37 (s, 3H, OCH_3), 7.14-7.25 (m, 3H, ArH), 7.40-7.46 (m, 4H, ArH), 7.67 (t, J = 1.8 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 21.5, 87.1, 90.9, 119.6, 122.1, 125.5, 129.1, 129.7, 130.0, 131.1, 131.5, 134.2, 138.8.

Table 1, entry 12B



1-(2-(3-Biphenyl)ethynyl)-4-methylbenzene, White Solid, mp 69-71 ^{o}C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm 2.37 (s, 3H, OCH_3), 7.16 (d, J = 8.1 Hz, 2H, ArH), 7.36-7.53 (m, 8H, ArH), 7.59-7.62 (m, 2H, ArH), 7.76-7.77 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm 21.5, 88.7, 89.7, 120.2, 124.0, 126.9, 127.1, 127.6, 128.7, 128.8, 129.1, 130.3, 131.5, 138.4, 140.4, 141.4.

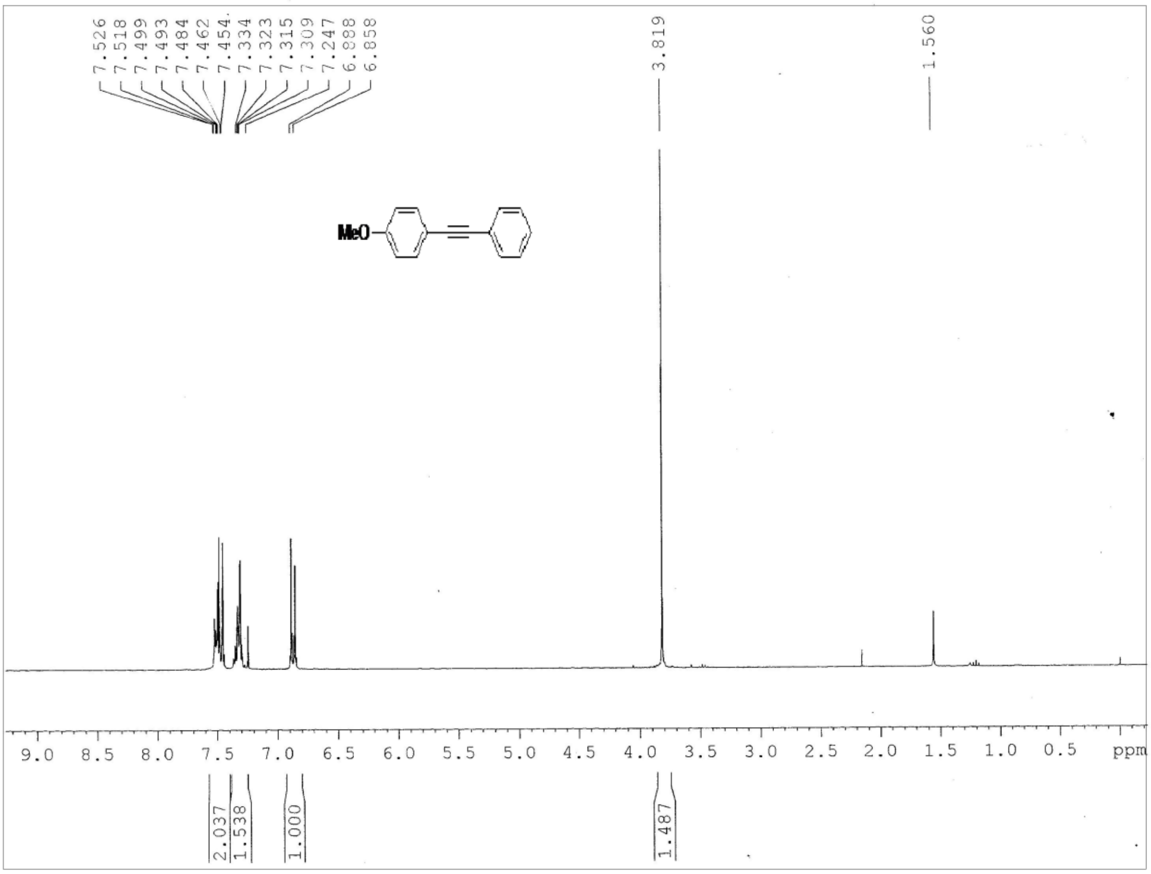
5. References

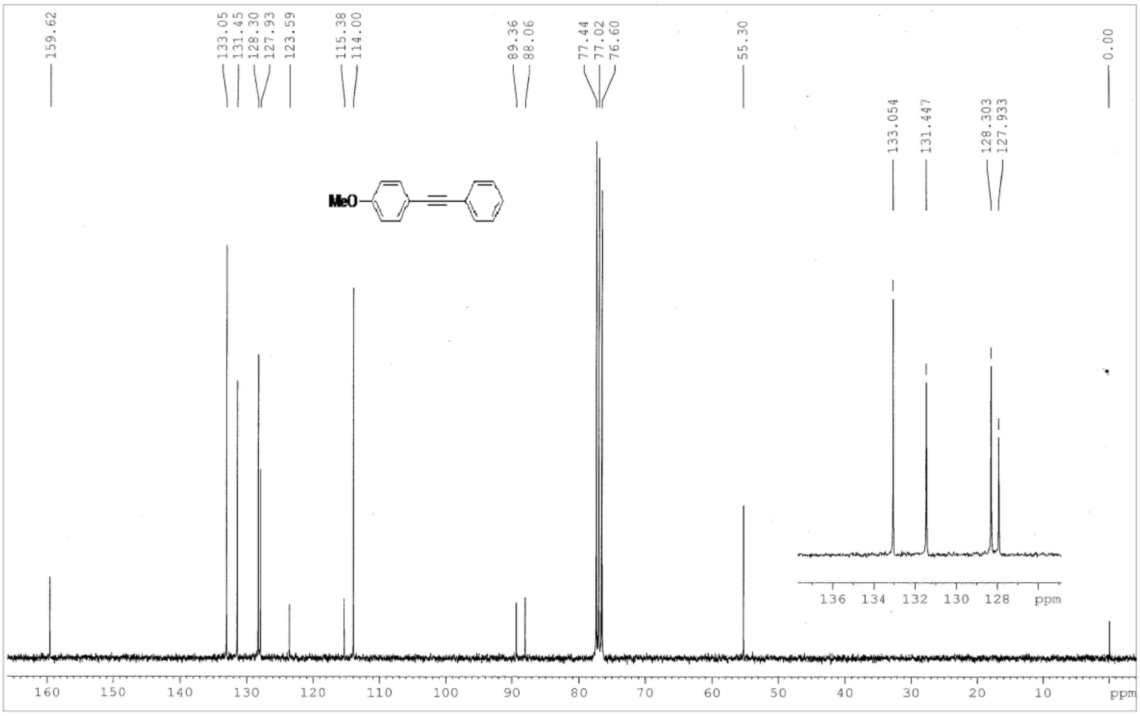
1. P. Li, L. Wangand and H. Li, *Tetrahedron*, 2005, **61**, 8633.

2. B. Basu, S. Das, P. Das, B. Mandal, D. Banerjee and F. Almqvist, *Synthesis*, 2009, 1137.
3. U. S. Sorensen and E. P. Villar, *Tetrahedron*, 2005, **61**, 2697.
4. O. Akihiro, T. Hisataka and O. Junzo, *Chem. Asian J.*, 2006, **1**, 430.

6. Scanned NMR Spectra

Table 1, entry 1





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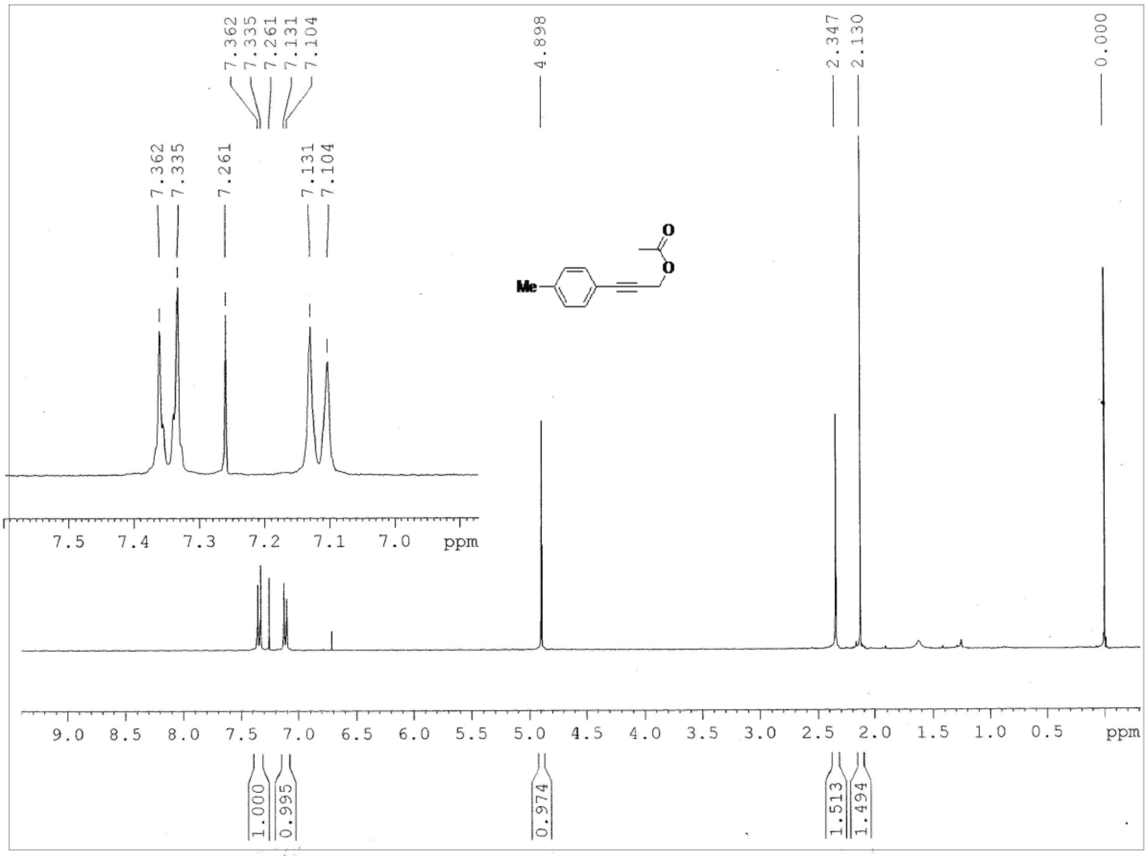

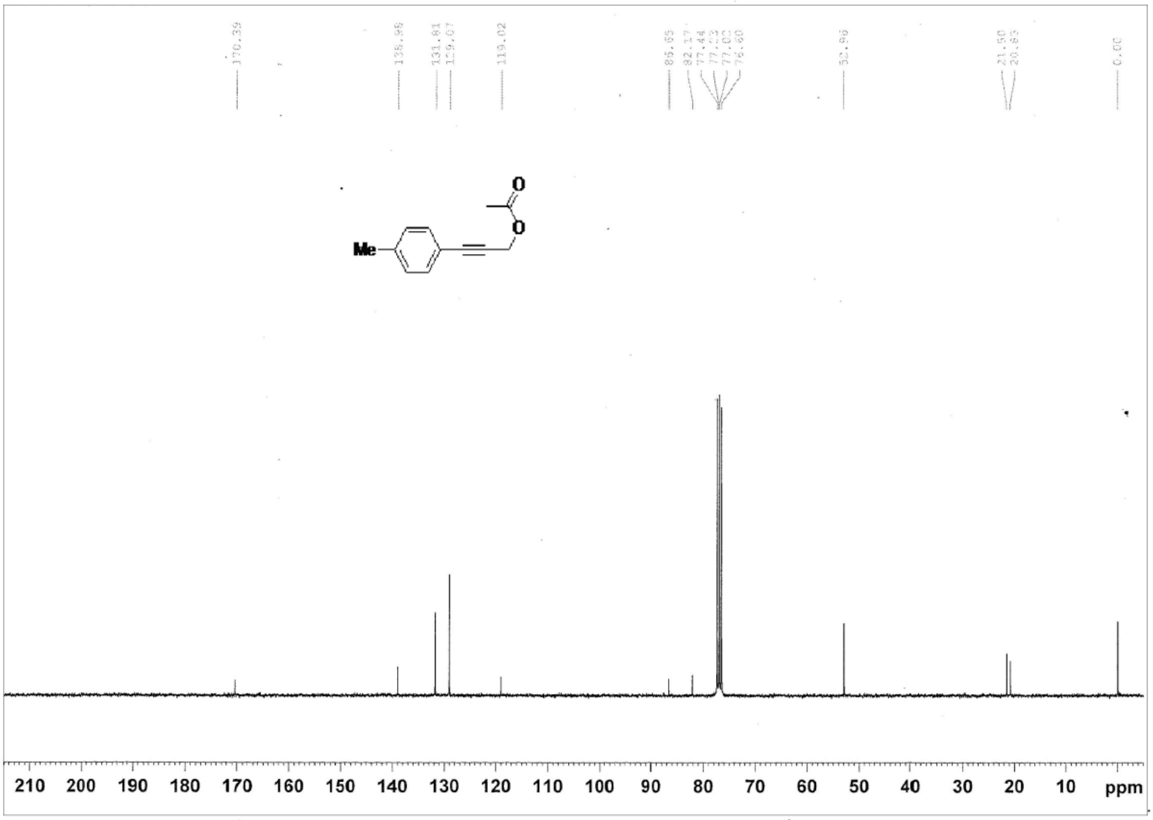

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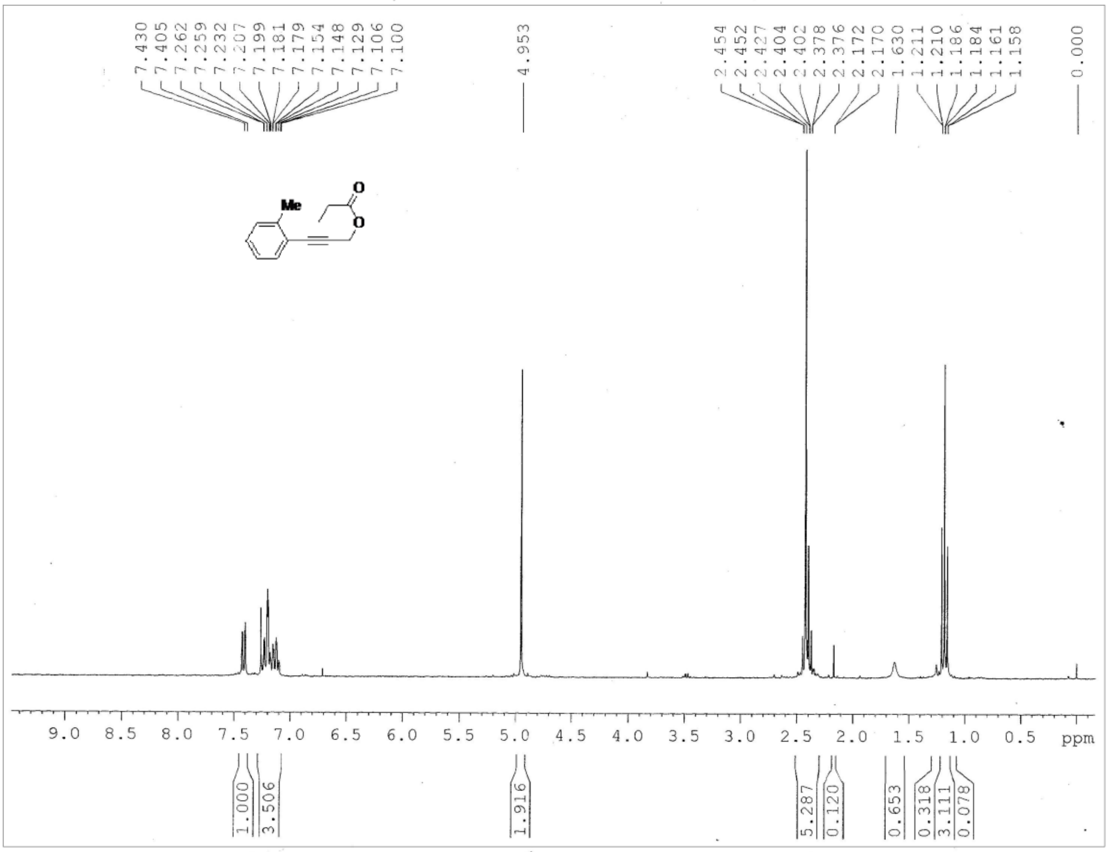

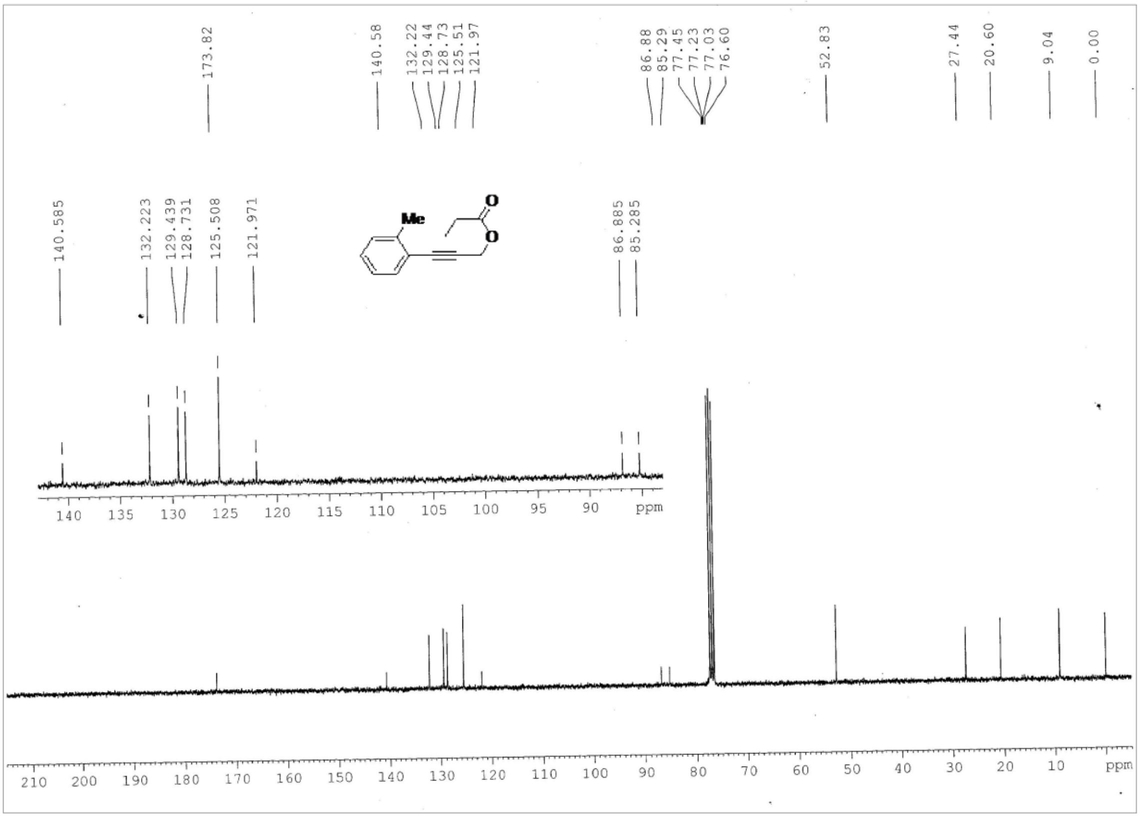

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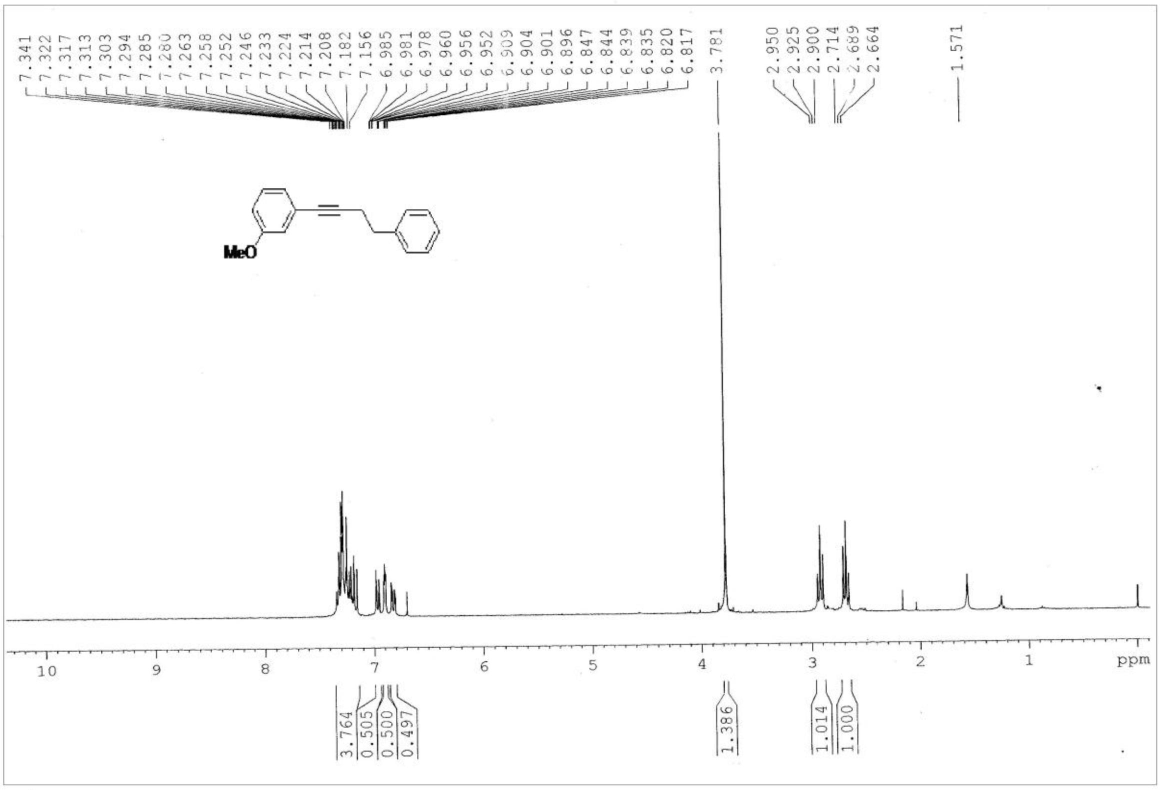

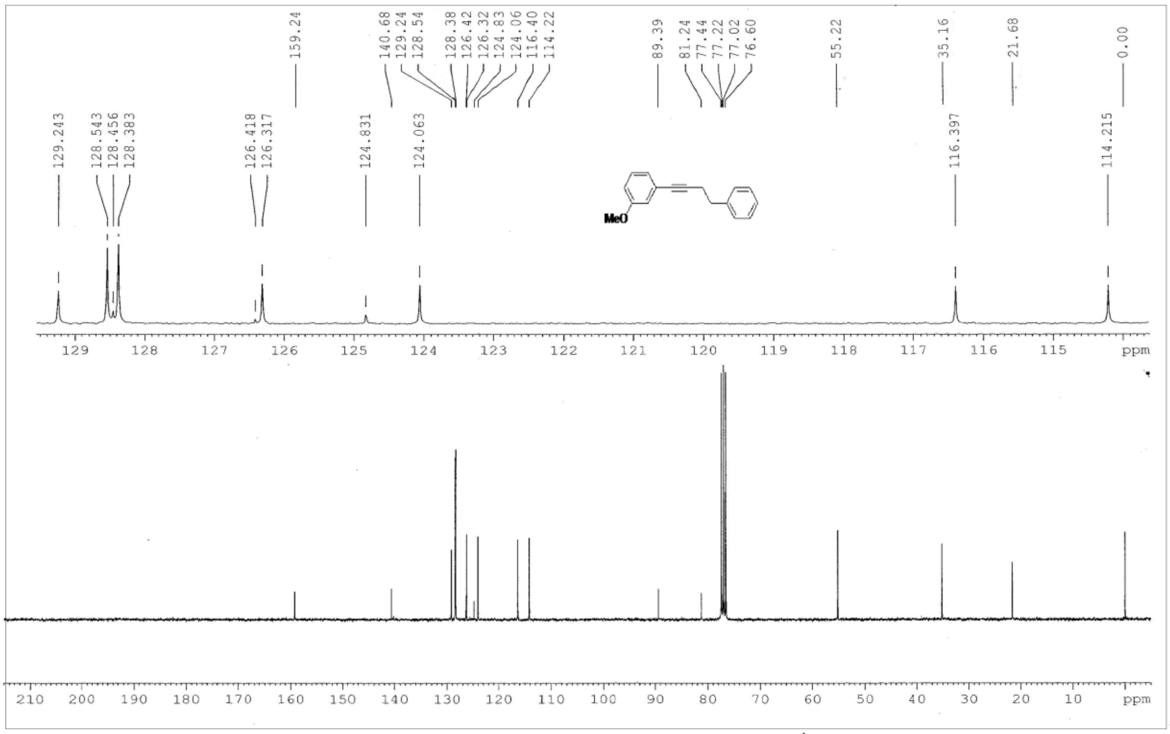

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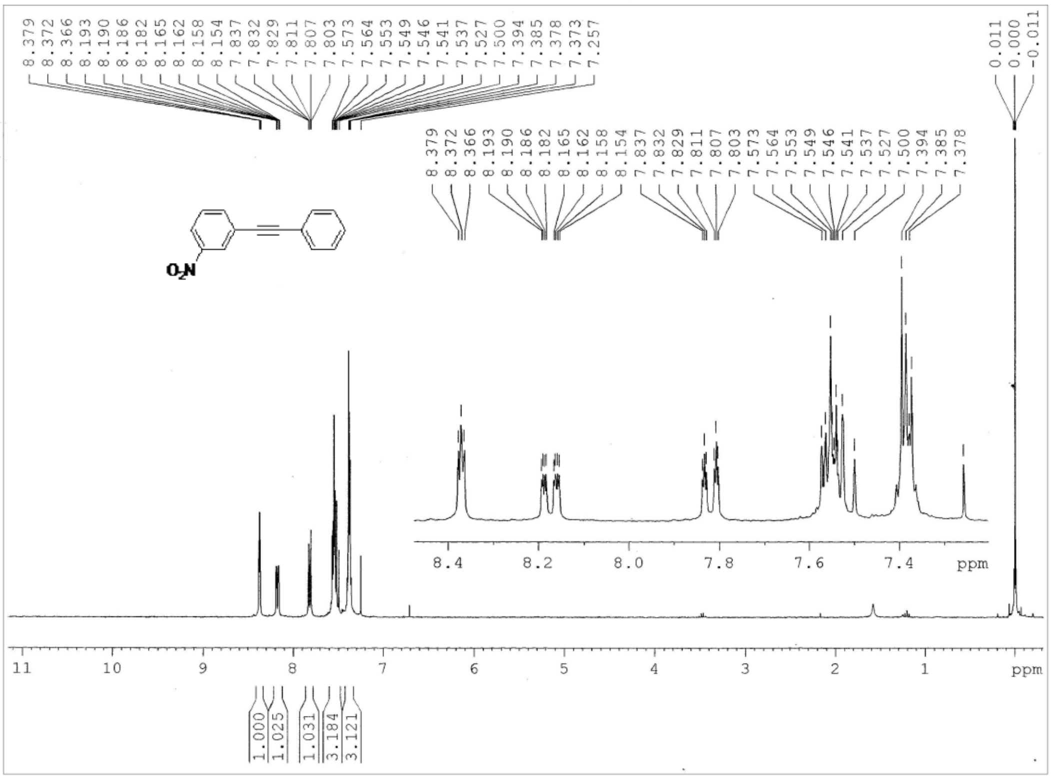

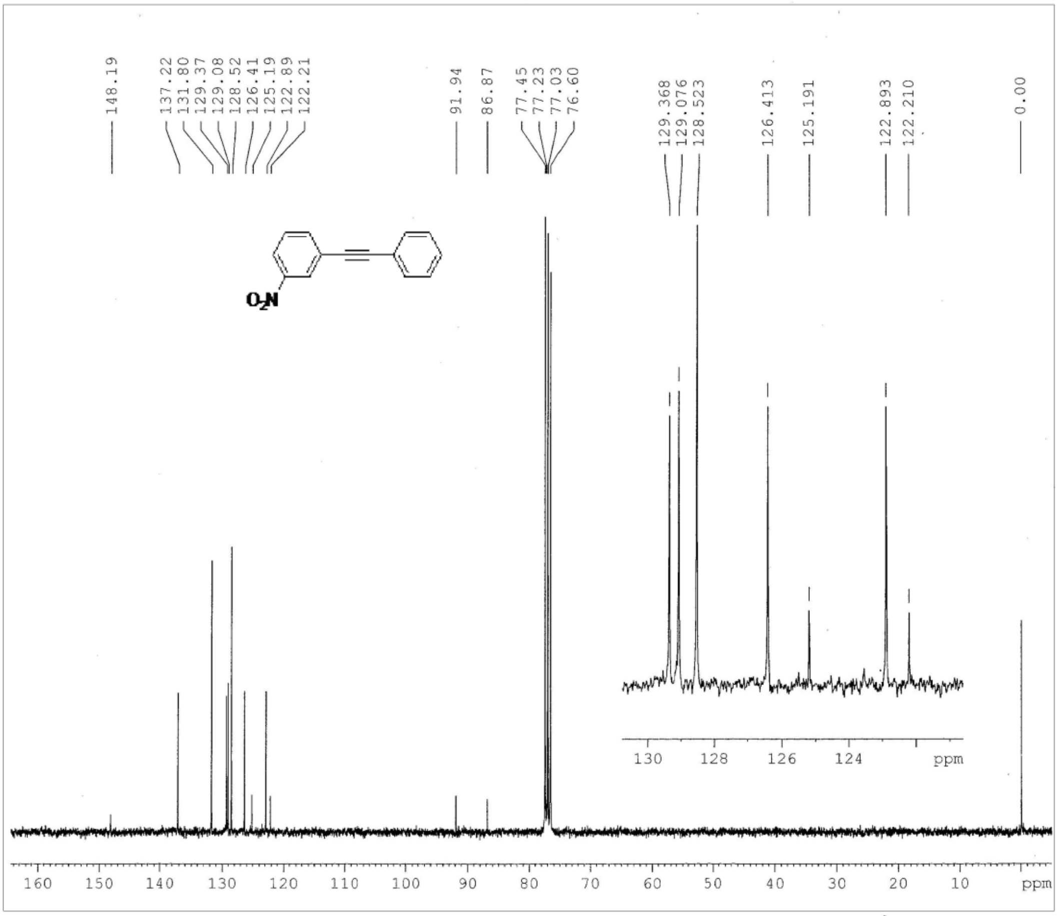

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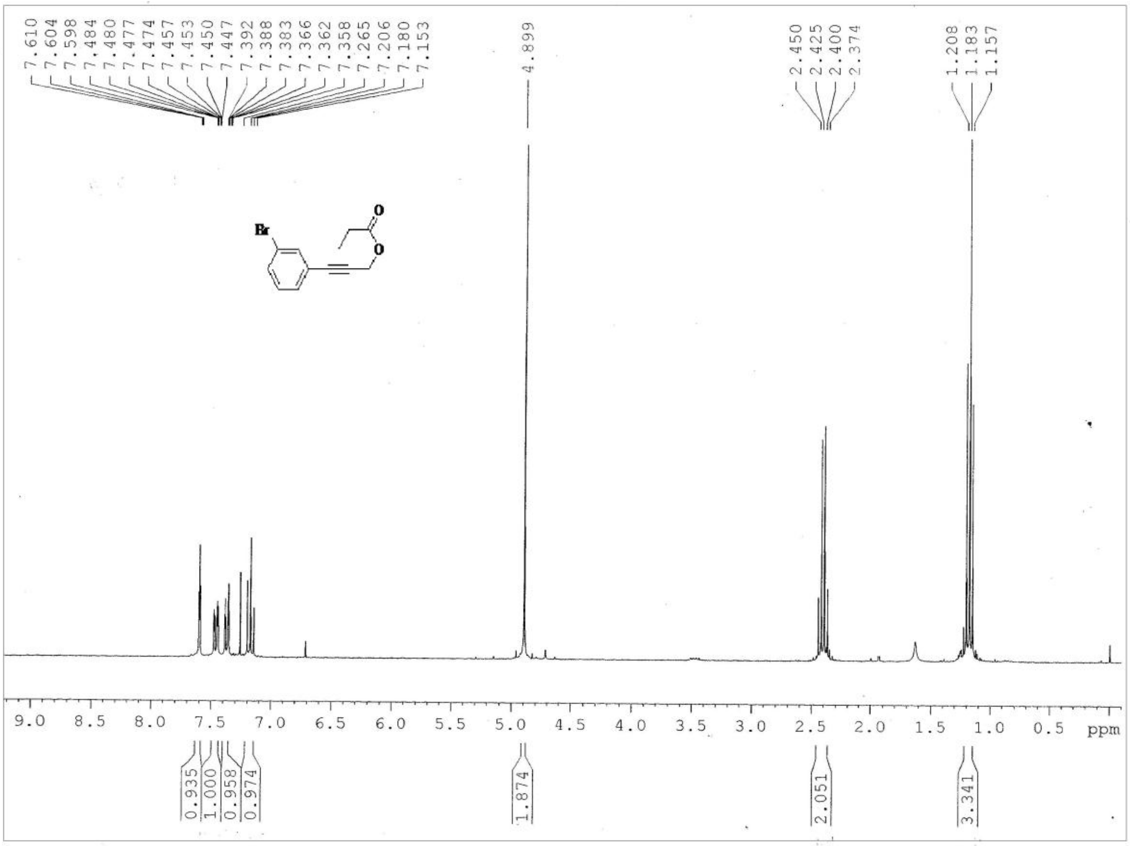

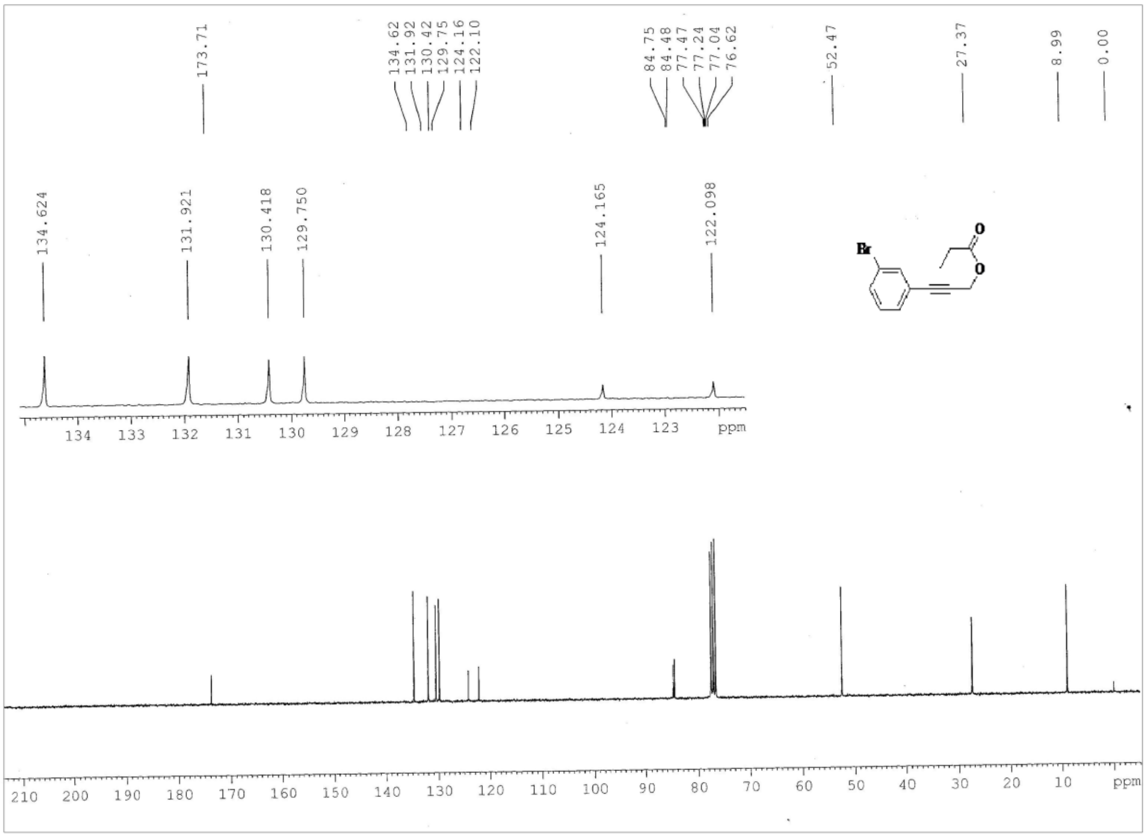

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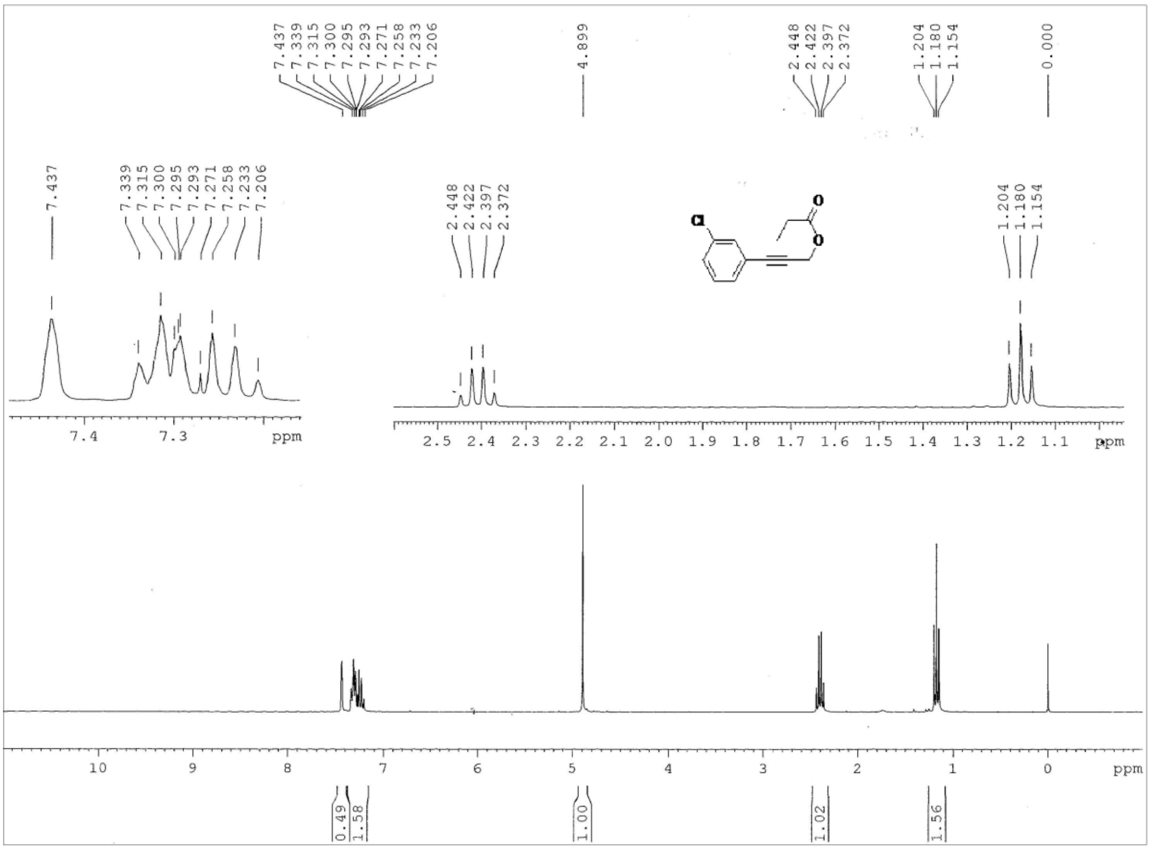

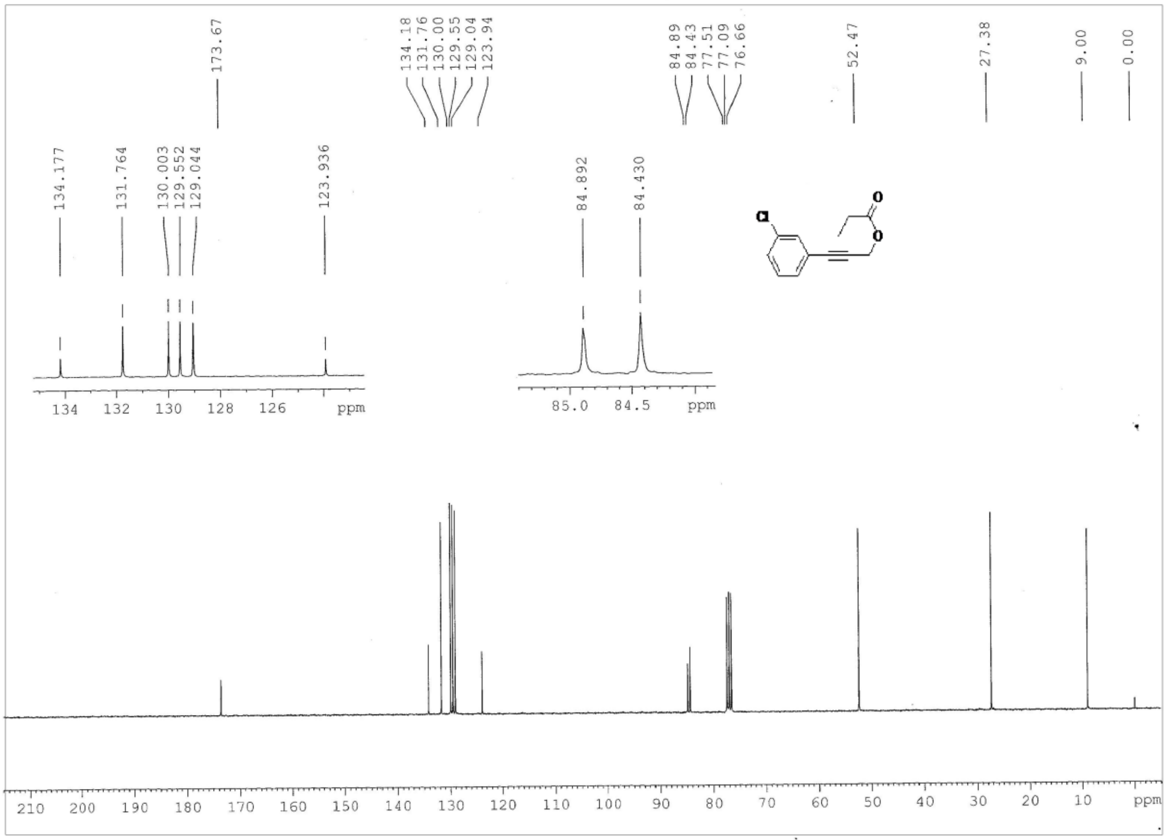

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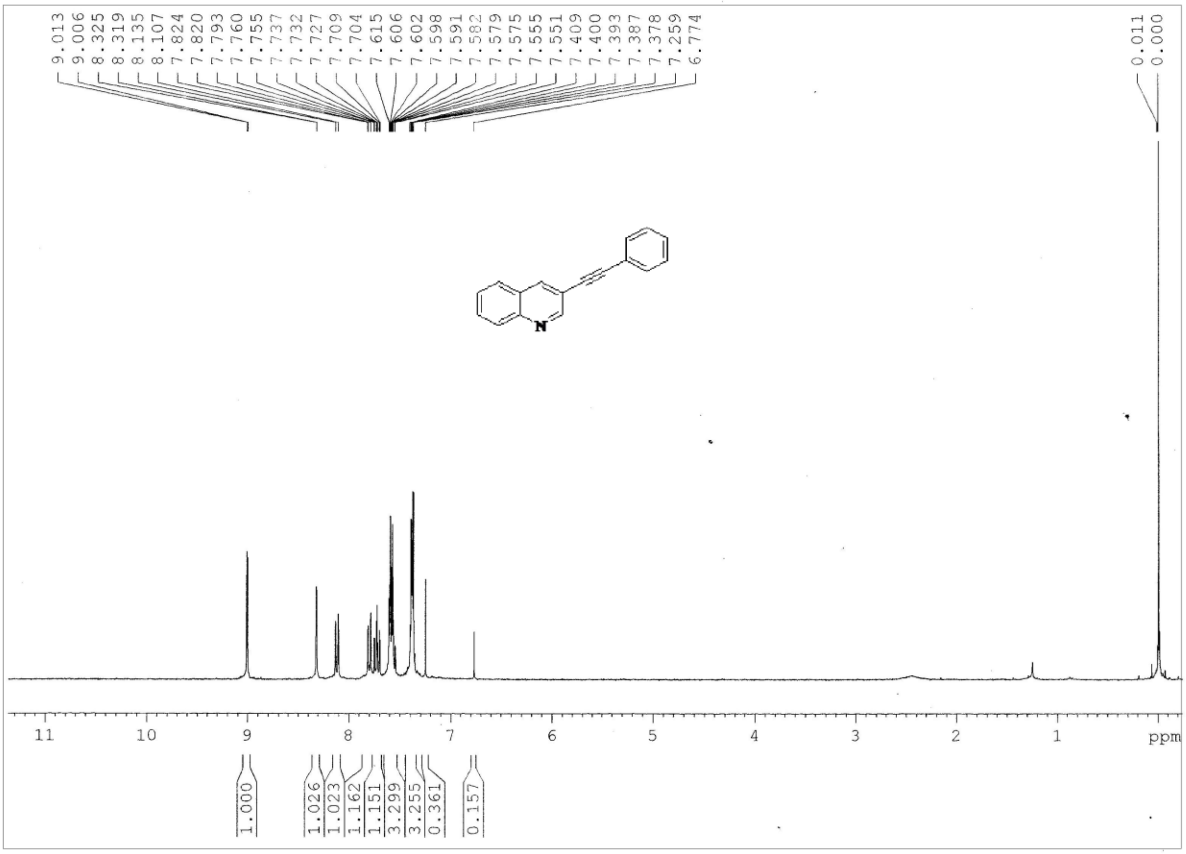
Table 1, entry 10



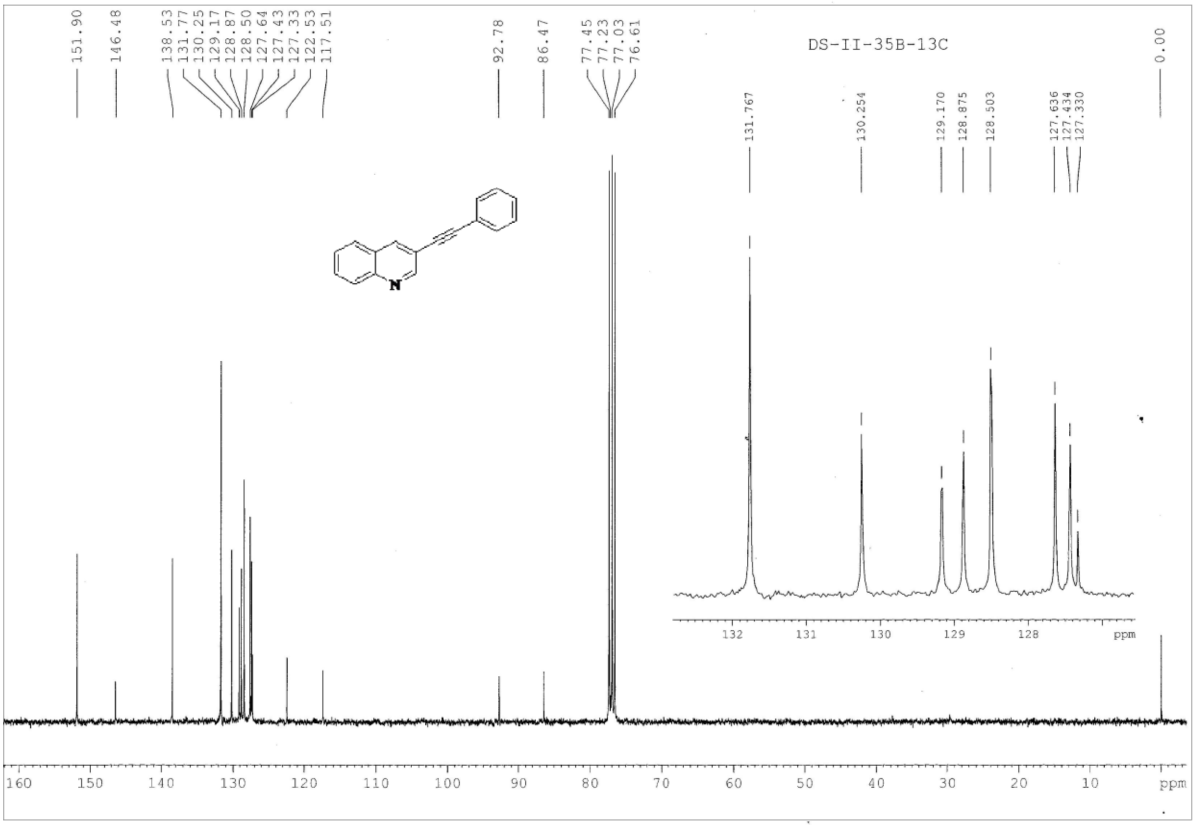
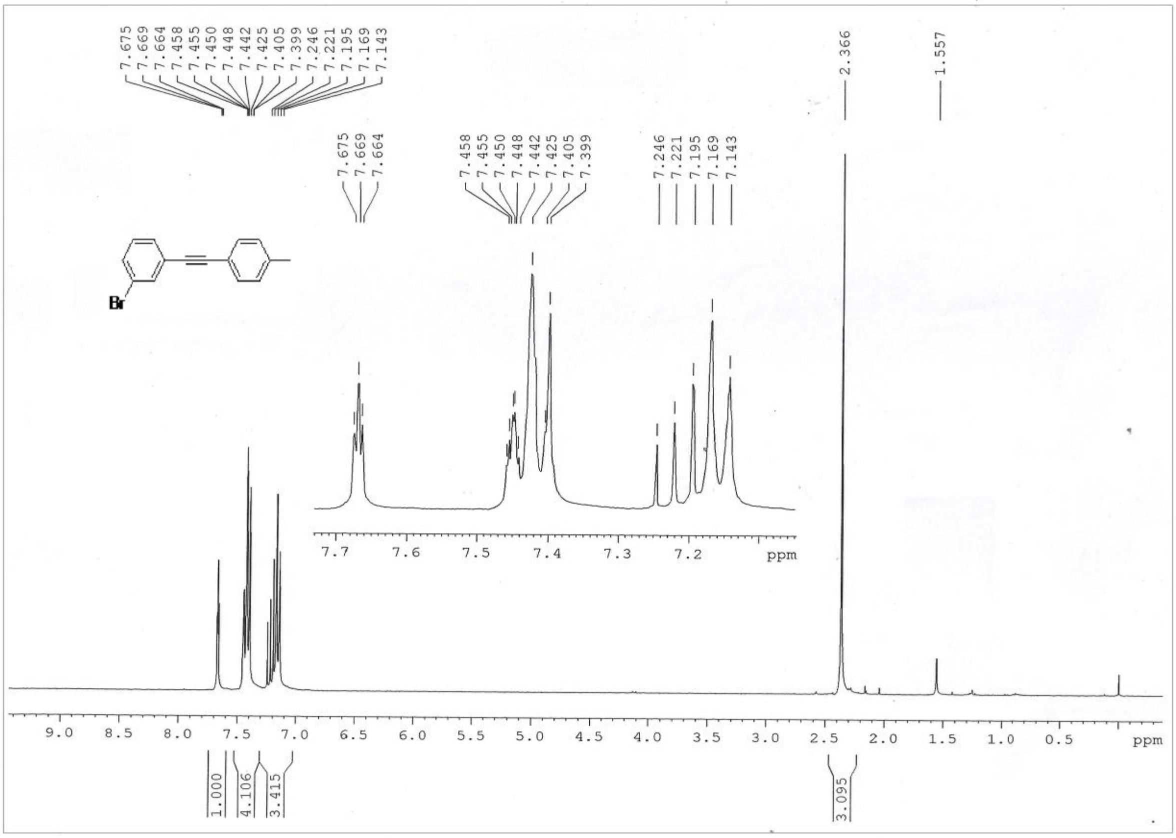


Table 1, entry 12A



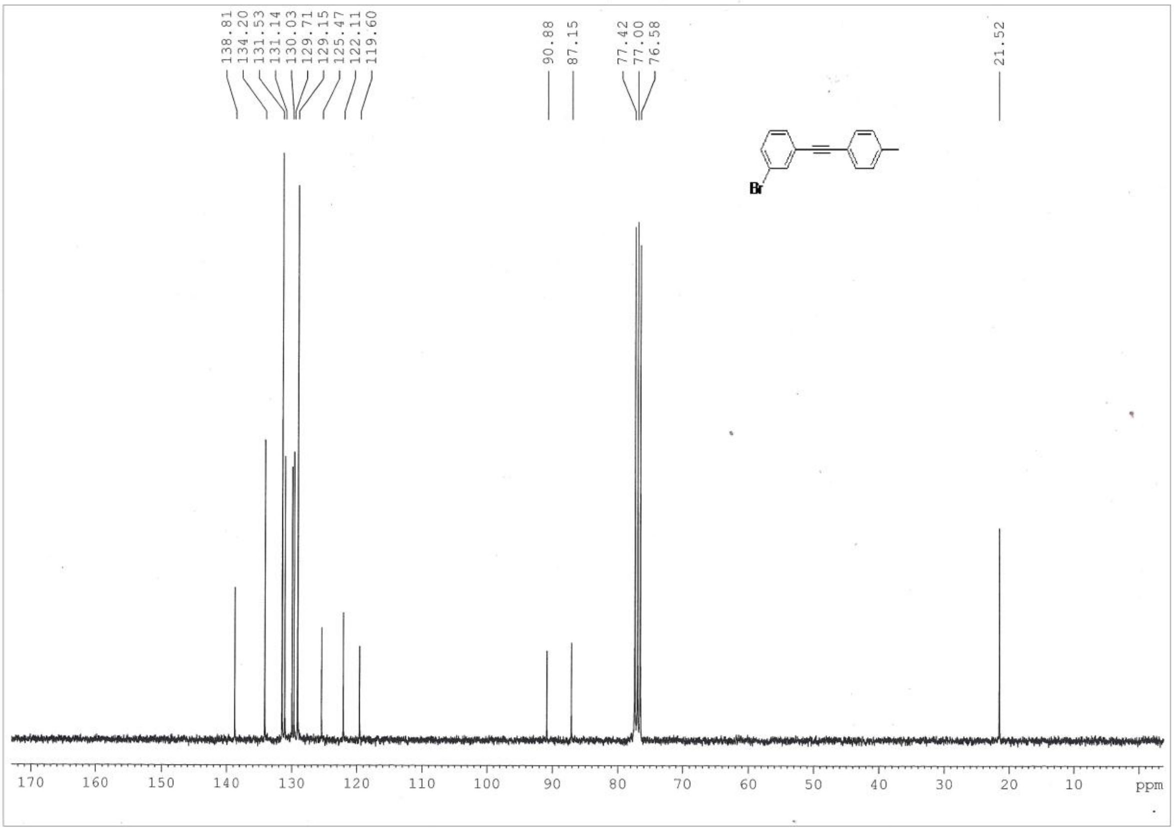


Table 1, entry 12B