Electronic Supplementary Material (ESI) for Catalysis Science & Technology


# Supporting Information

## Synthesis of Palladium Nanocatalysts with Cucurbit[n]uril as Both Protecting Agent and Support for Suzuki and Heck Reactions

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## *Table of contents*



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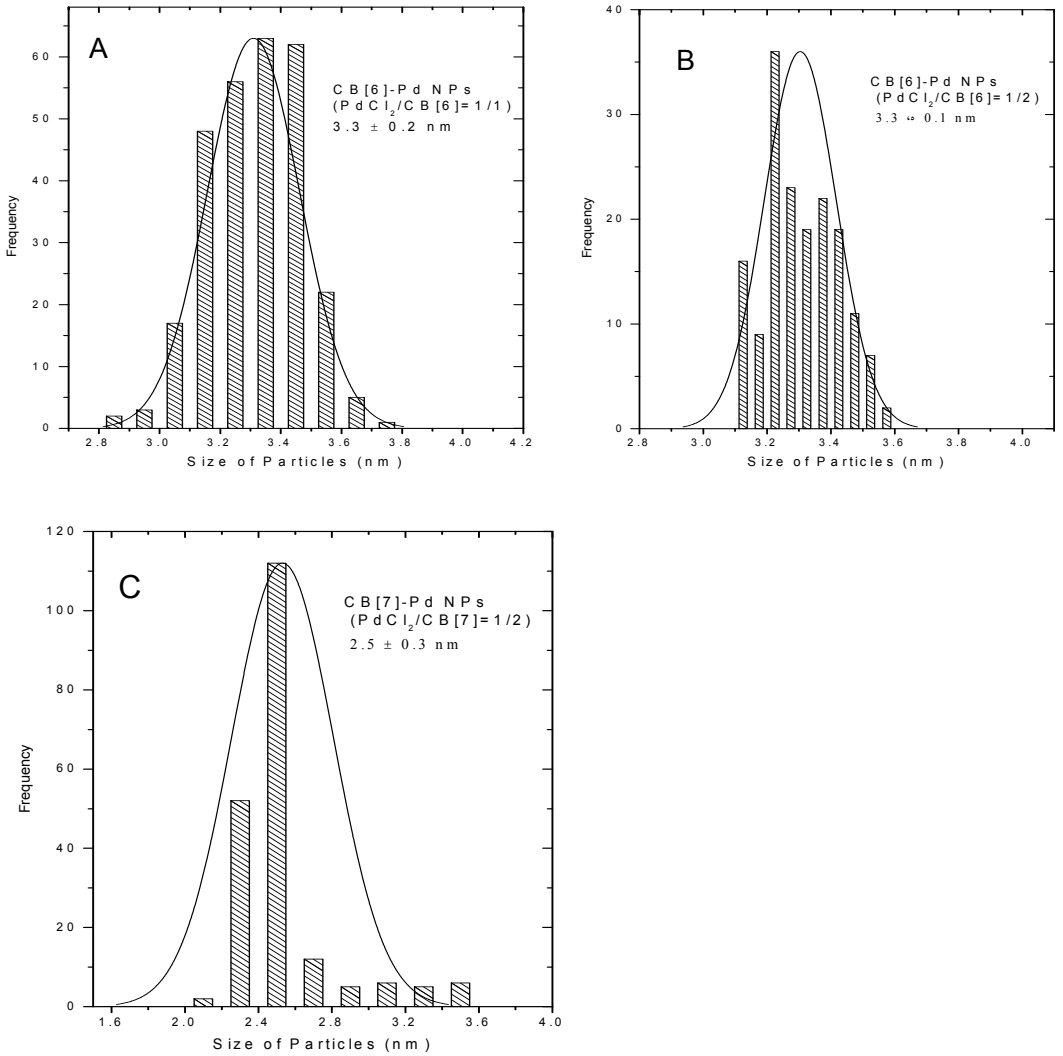



***Figure S1.*** Size distribution of CB[6]-Pd NPs 1 with the ratio of $PdCl_2$ to CB[6] is 1:1(A) and 1:2(B); CB[7]-Pd NPs (C)

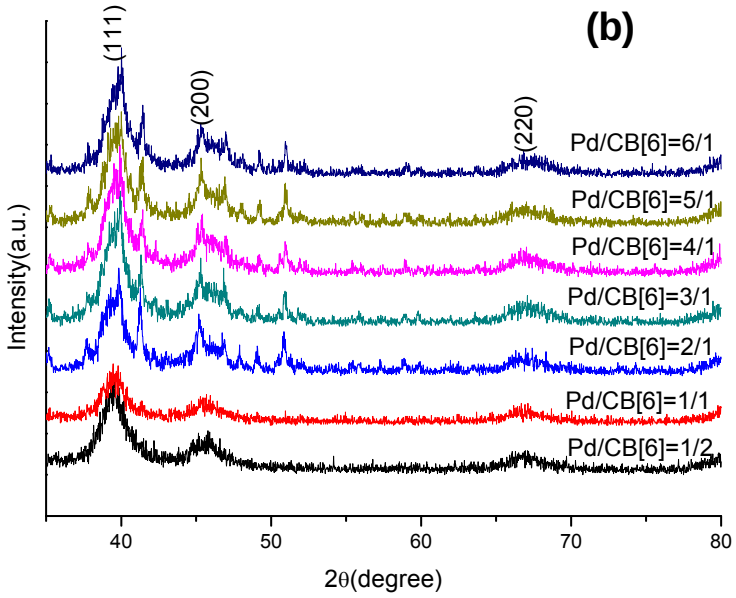



***Figure S2***. PXRD patterns of CB[6]-Pd NPs with the molar ratio of $PdCl_2$ to CB[6] of (a) 1:1 (b) between 1:2 and 6:1. The four main peaks correspond to (111), (200), (220) and (311) Bragg reflection of face-centered cubic (fcc) Pd.

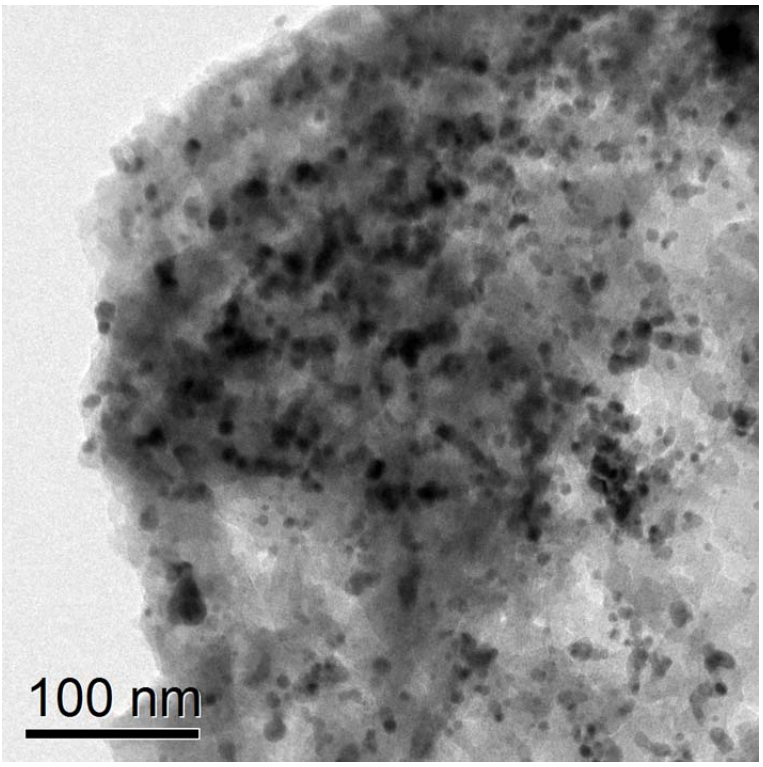
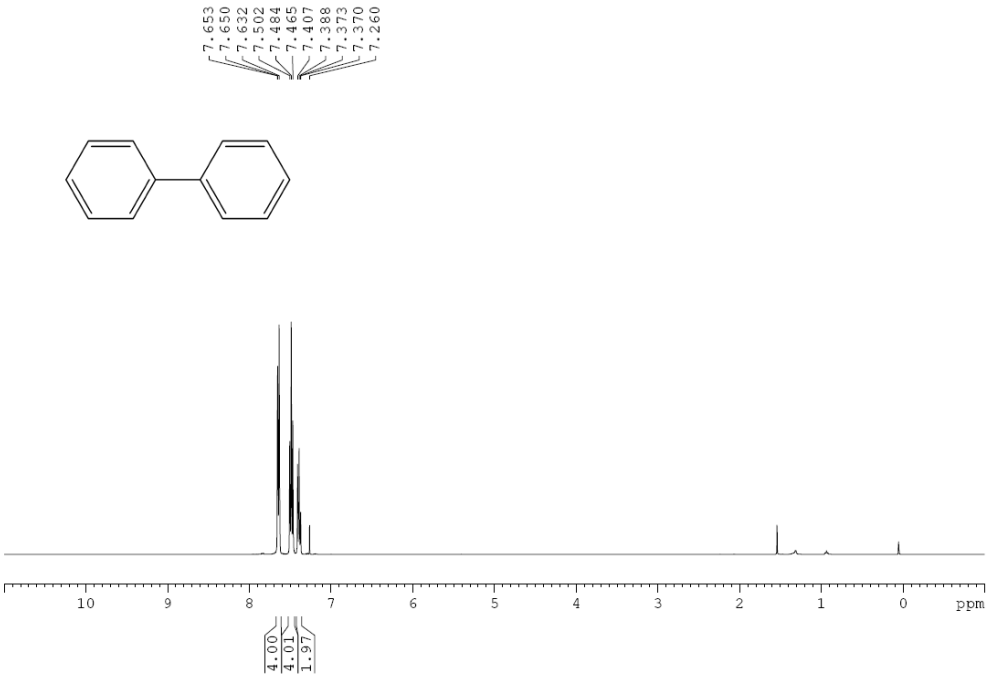
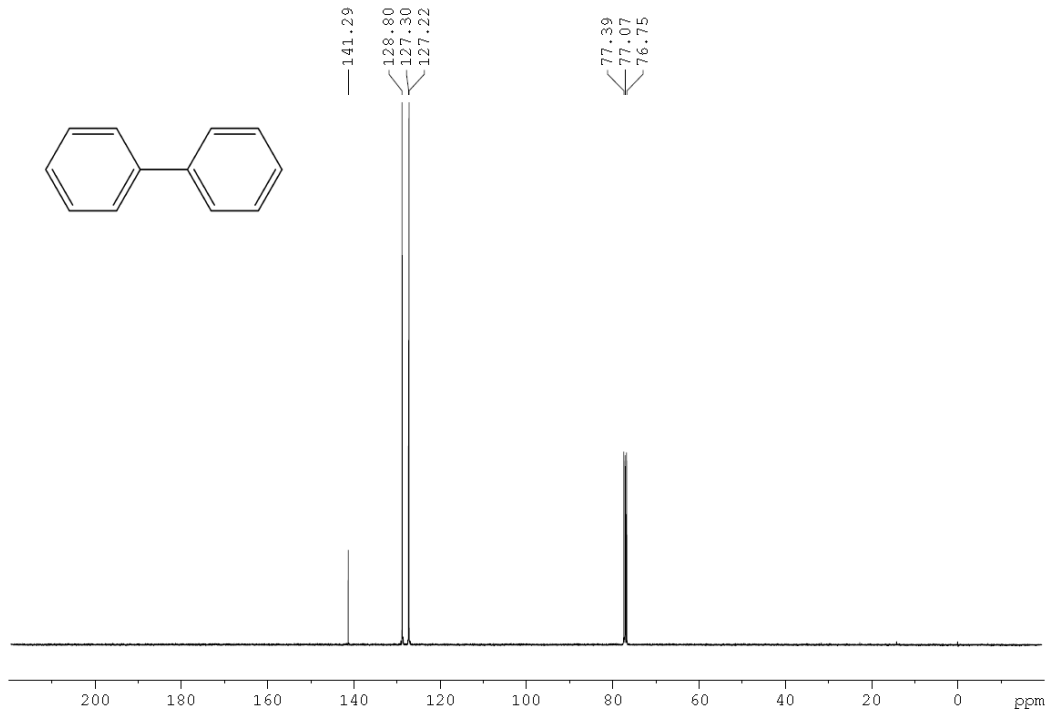



***Figure S3.*** TEM images of CB[6]-Pd NPs **1** after catalyzed Heck coupling reaction with high catalyst loading up to 3 mol% (table 2, entry 3)

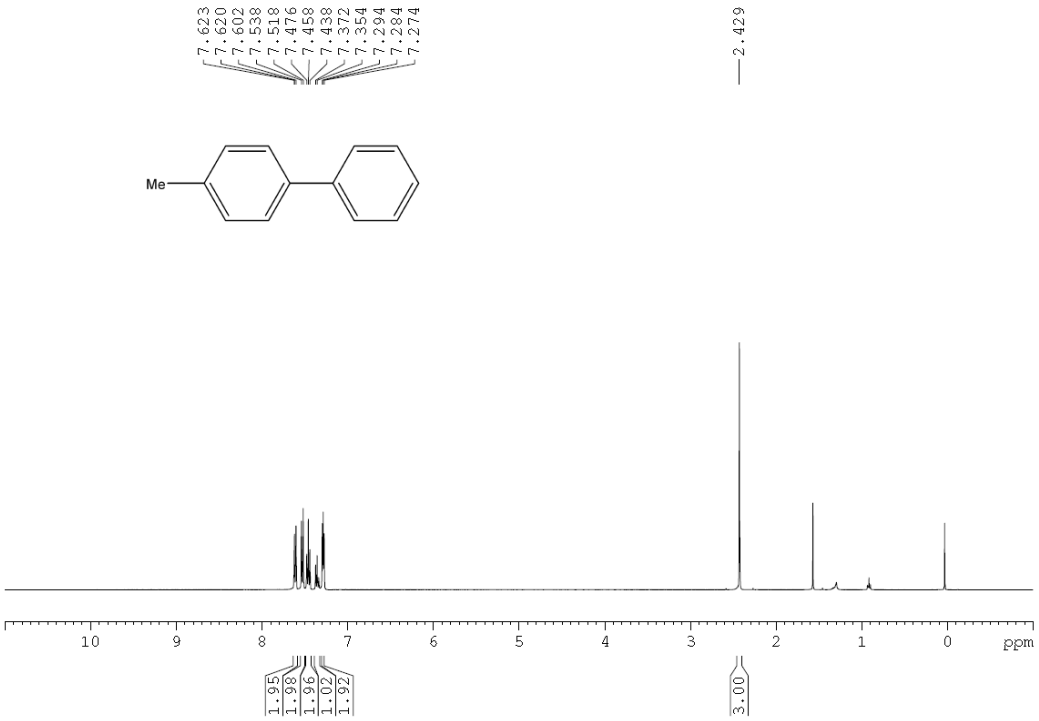
## 3. characterization for the products of Suzuki coupling reactions：

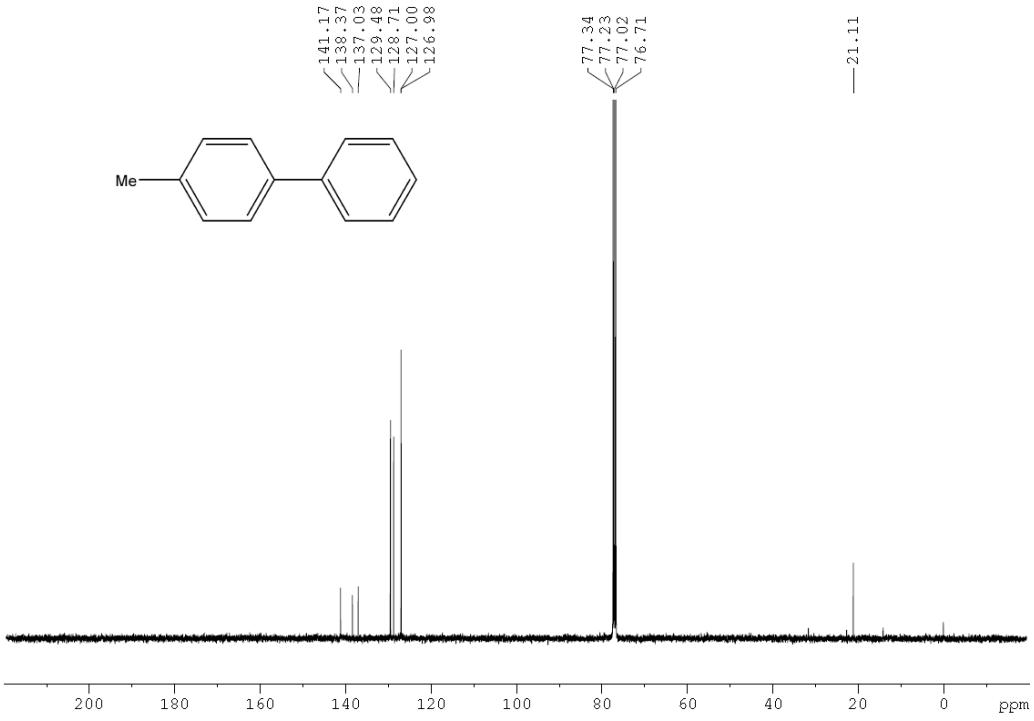
### ( 1 ) $^{1}$H NMR and $^{13}$C NMR of Biphenyl



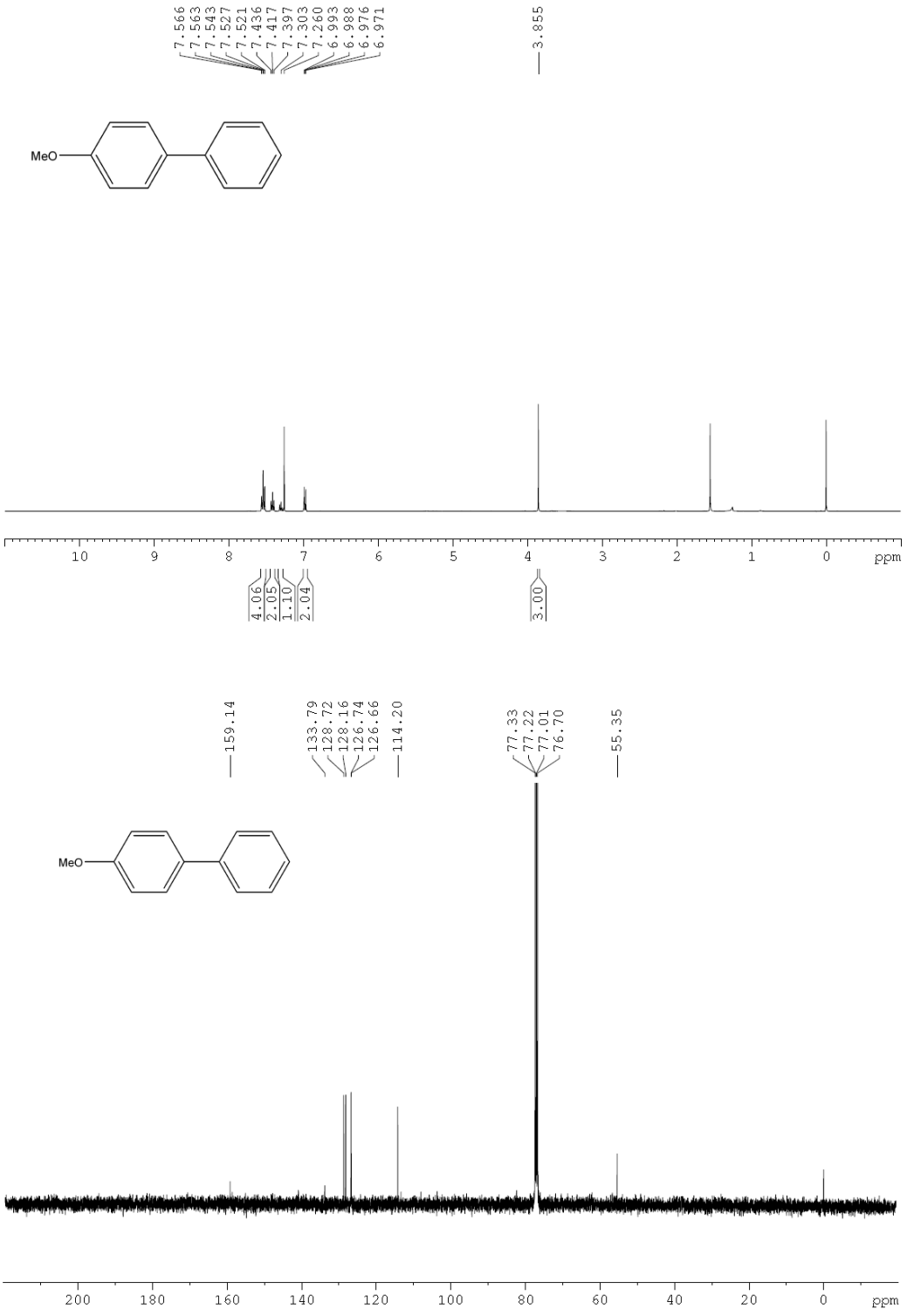



## (2) $^{1}$H NMR and $^{13}$C NMR Ethylbiphenyl

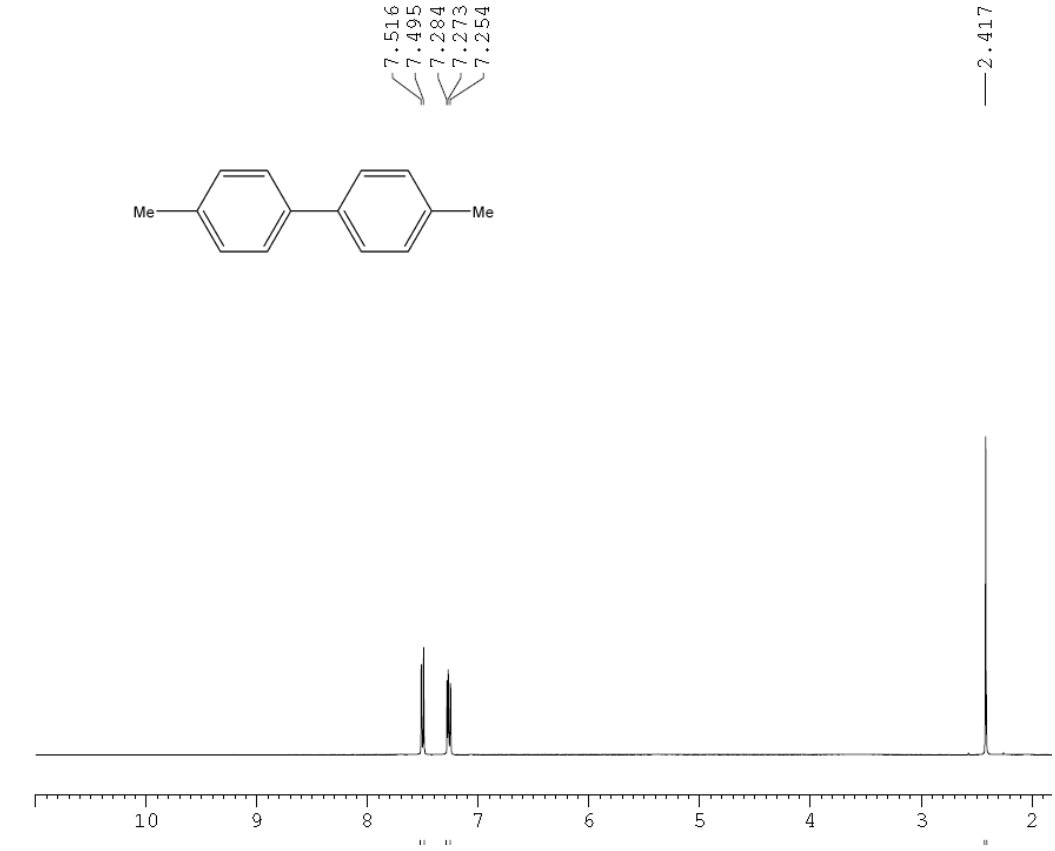


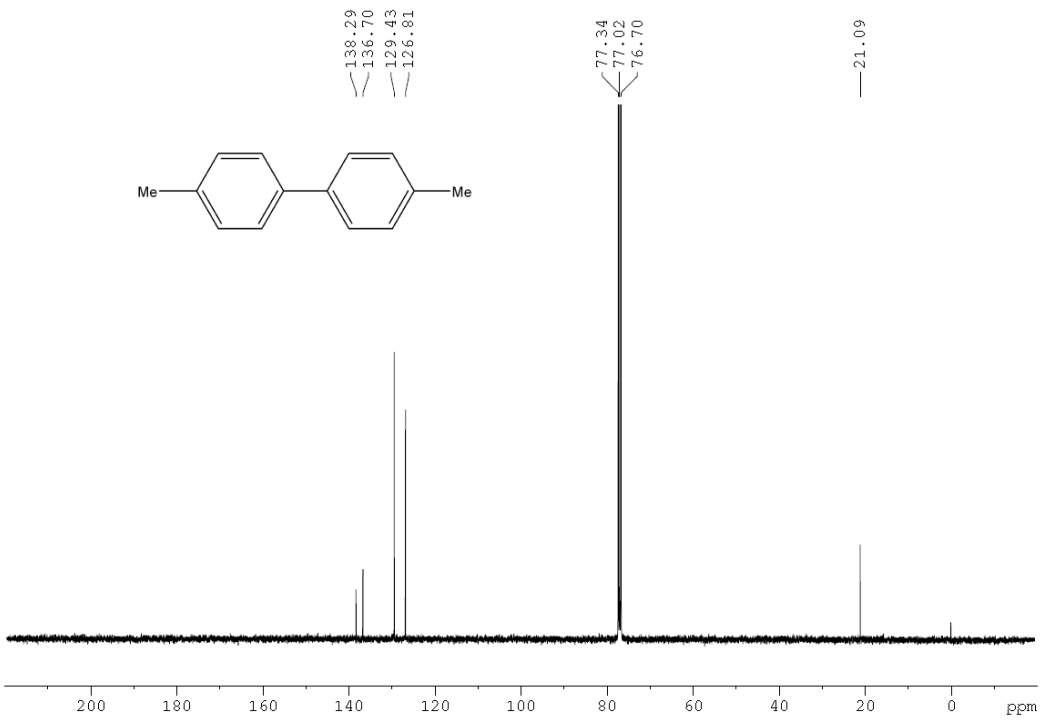



## (3) $^{1}$H NMR and $^{13}$C NMR 4-Methoxybiphenyl

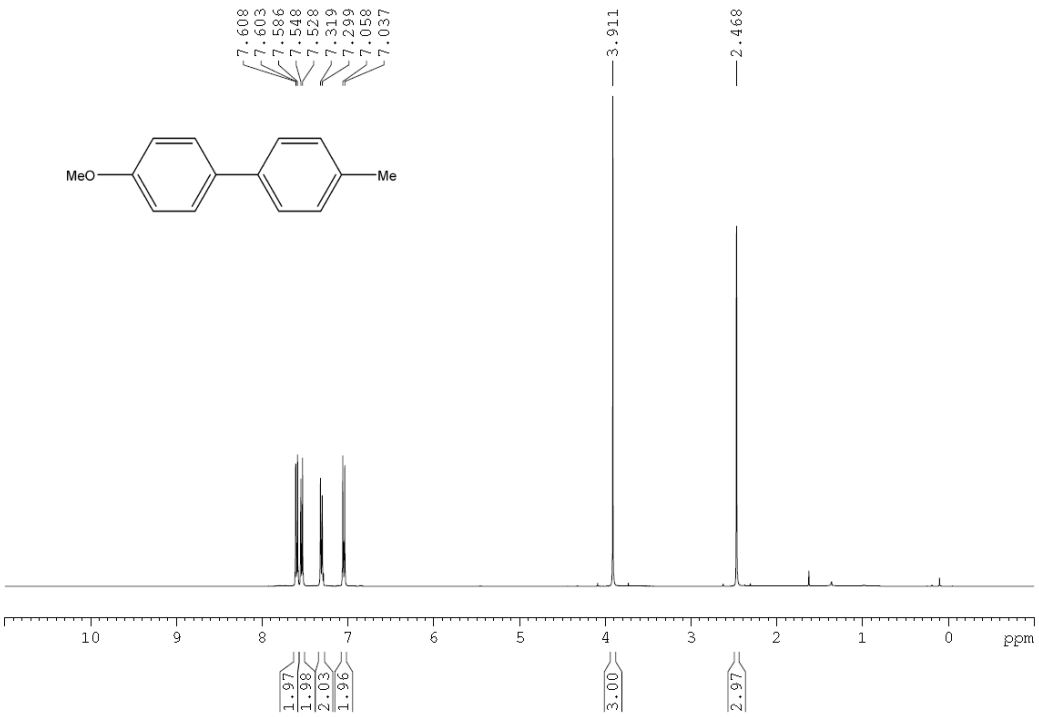


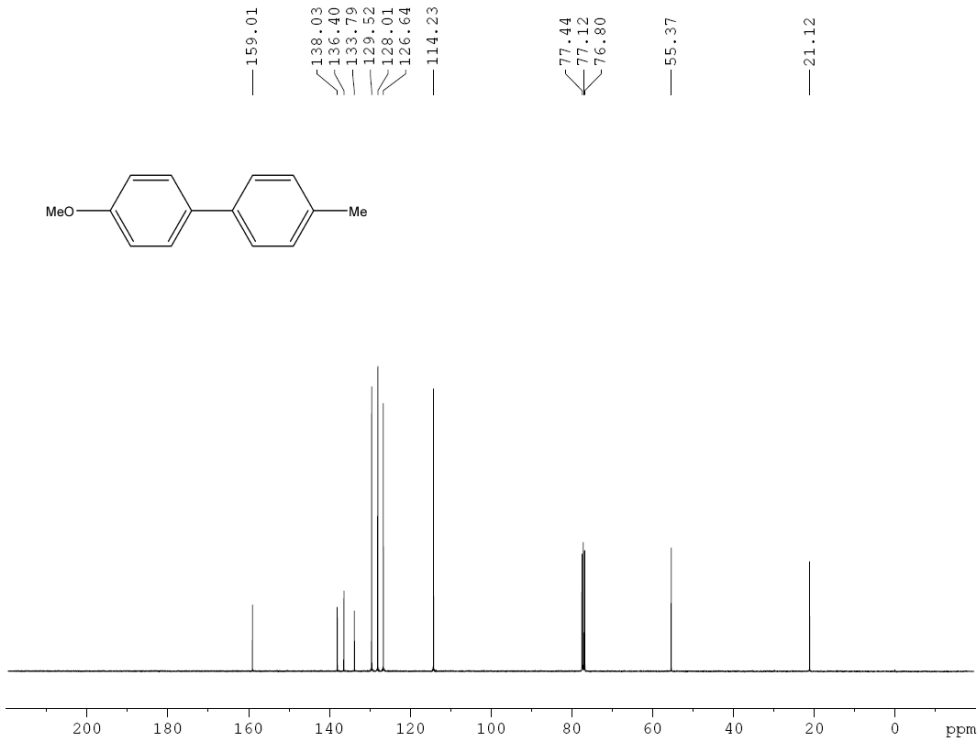
## (4) $^{1}$H NMR and $^{13}$C NMR 4,4'-Dimethylbiphenyl



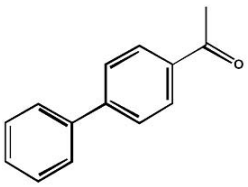
## (5) $^{1}$H NMR and $^{13}$C NMR 4-Methoxy -4'-methylbiphenyl



## (6) $^{1}$H NMR and $^{13}$C NMR 4-Acetylbiphenyl

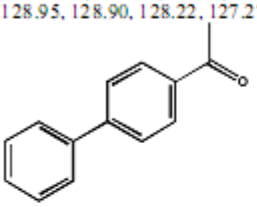
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, $J$ = 8.5 Hz, 1H), 7.72 (d, $J$ = 8.5 Hz, 1H), 7.66 (d, $J$ = 7.1 Hz, 1H), 7.50 (t, $J$ = 7.4 Hz, 1H), 7.43 (t, $J$ = 7.3 Hz, 1H), 2.67 (s, 2H).



4-Acetylbiphenyl




$^{13}$C NMR (77 MHz, $CDCl_3$) δ 197.71, 145.79, 139.89, 135.88, 128.95, 128.90, 128.22, 127.27, 127.22, 26.65 (s).



4-Acetylbiphenyl

The $^{1}H$ and $^{13}C$ spectra were in accordance with those described in literature.

**1) Biphenyl**

Z. Tang, Q. Hu, *J. Am. Chem. Soc.*, 2004, **126,** 3058

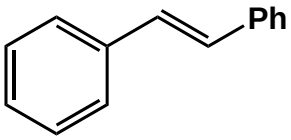
**2) 4,4'-Dimethylbiphenyl**

L. Wu, B. Li, Y. Huang, H. Zhou, Y. He, Q. Fan, *Org. Lett.* 2006, **8,** 3605.

**3) 4-Methylbiphenyl, 4-Methoxybiphenyl and 4-Methoxy-4'-methylbiphenyl**

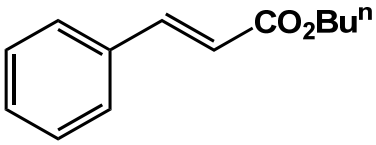
N. Yoshikai, H. Mashima and E. Nakamura, *J. Am. Chem. Soc.*, 2005, **127,** 17978.

## 2. characterization for the products of Heck coupling reactions：



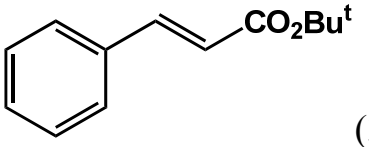

(1)

***trans*-stibene[1]:** $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 4H), 7.35 (t, *J* = 7.6 Hz, 4H), 7.27 – 7.21 (m, 2H), 7.10 (s, 2H). $^{13}C$ NMR (77 MHz, $CDCl_3$) δ 137.35, 128.69, 127.61, 126.51.



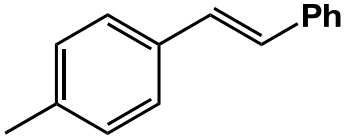

(2)

***trans*-cinnamic acid *n*-butyl ester[2]:** $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.62 – 7.45 (m, 2H), 7.43 – 7.17 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.83 – 1.59 (m, 2H), 1.61 – 1.21 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). $^{13}C$ NMR (77 MHz, $CDCl_3$) δ 167.02, 144.51, 134.50, 130.18, 128.85, 128.03, 118.33, 64.39, 30.81, 19.21, 13.75.



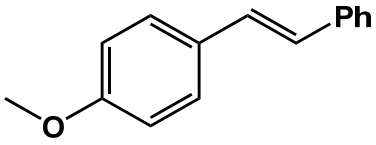

(3)

***trans*-cinnamic acid *t*-butyl ester[3]:** $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.38 – 7.25 (m, 3H), 6.36 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 9H). $^{13}C$ NMR (77 MHz, $CDCl_3$) δ 166.30, 143.53, 134.69, 129.94, 128.81, 127.94, 120.22, 80.46, 28.21 (s).



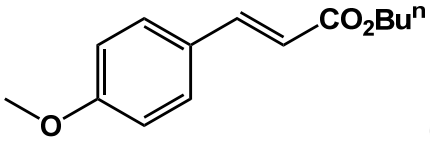

(4)

**4-methyl-*trans*-stilbene[1]:** $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.26-7.33 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 2.5 Hz, 2H), 2.41 (s, 3H). $^{13}C$ NMR (77 MHz, $CDCl_3$) δ 137.56, 134.53, 129.41, 128.66, 127.74, 127.42, 126.44, 21.27.



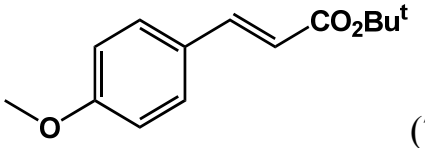

(5)

**4-methoxy-*trans*-stilbene[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 16.3 Hz, 1H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). $^{13}$C NMR (77 MHz, $CDCl_3$) δ 159.34, 137.69, 130.19, 128.66, 128.25, 127.74, 127.23, 126.66, 126.28, 114.17, 55.34.



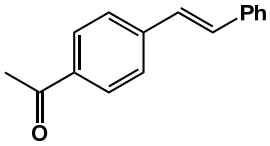

(6)

**4-methoxy-*trans*-cinnamic acid *n*-butyl ester[2]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.79 (s, 3H), 1.67 (m, *J* = 14.6, 6.9 Hz, 2H), 1.43 (m, *J* = 15.0, 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (77 MHz, $CDCl_3$) δ 167.29, 161.32, 144.13, 129.63, 127.17, 115.74, 114.27, 64.16, 55.24, 30.82, 19.20, 13.72.



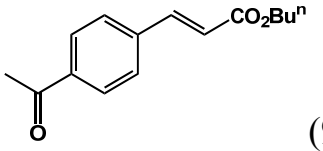

(7)

**4-methoxy-*trans*-cinnamic acid *t*-butyl ester[4]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 15.9 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.26 (d, *J* = 15.9 Hz, 1H), 3.84 (s, 3H), 1.55 (s, 9H). $^{13}$C NMR (77 MHz, $CDCl_3$) δ 166.65, 161.12, 143.18, 129.52, 127.40, 117.72, 114.25, 80.18, 55.31, 28.23.



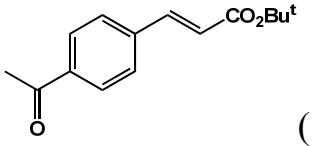

(8)

**4-acetyl-*trans*-stilbene[5]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.30 (m, 3H), 7.26 (d, *J* = 16.4 Hz, 1H), 7.16 (d, *J* = 16.3 Hz, 1H), 2.63 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.43, 142.01, 136.71, 135.98, 131.47, 128.87, 128.80, 128.31, 127.46 , 126.82, 126.50, 26.57.




(9)

**4-acetryl-*trans*-cinnamic acid *n*-butyl ester[6]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.22 (t, *J* = 7.0 Hz, 2H), 2.61 (s, 3H), 1.74 – 1.65 (m, 1H), 1.44-1.51 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (77 MHz, $CDCl_3$) δ 197.19, 166.50, 142.91, 138.79, 137.96, 128.80, 128.0, 120.83, 64.63, 30.72, 26.62, 19.16, 13.70.




(10)

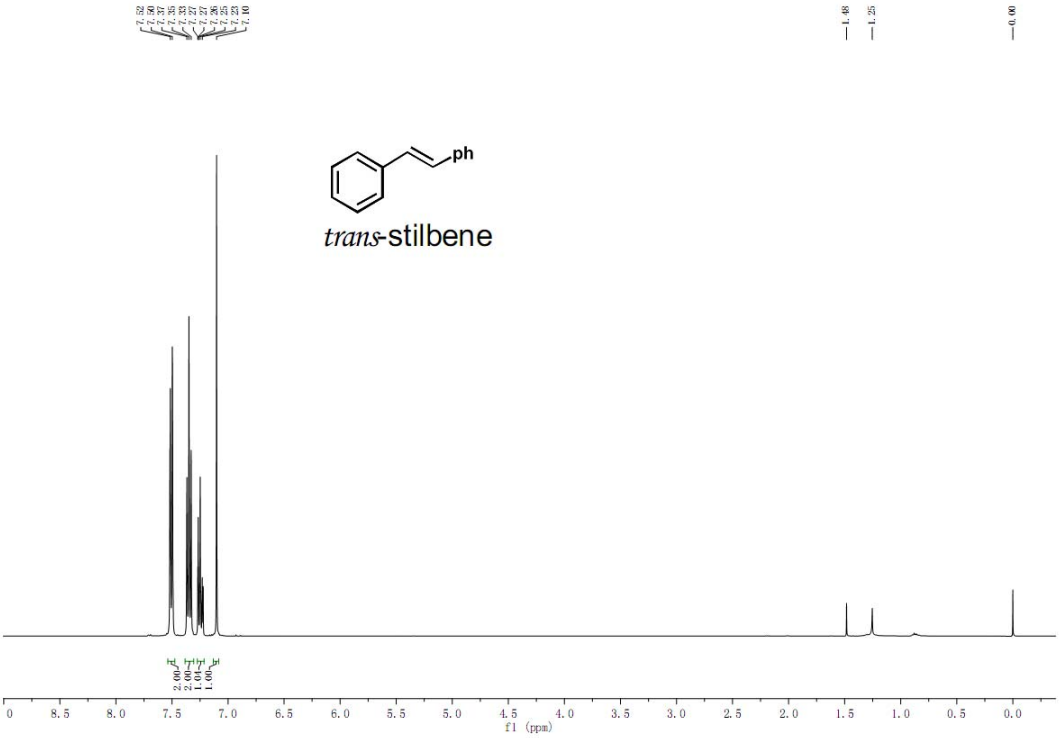
**4-acetryl-*trans*-cinnamic acid *t*-butyl ester[7]:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.53 (m,3H), 6.46 (d, *J* = 16.1 Hz, 1H), 2.61 (s, 3H), 1.55 (s, 9H). $^{13}$C NMR (77 MHz, $CDCl_3$) δ 197.26, 165.72, 141.93, 139.05, 137.79, 128.79, 127.98, 122.77, 80.89, 28.15, 26.62.

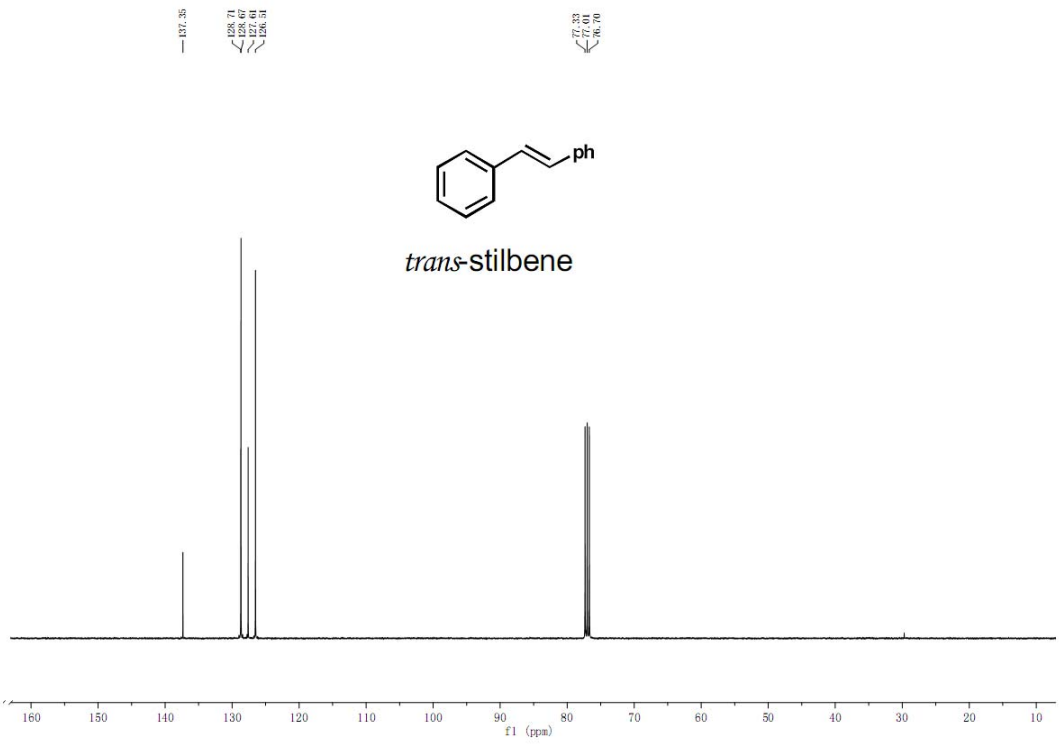
The $^{1}$H and $^{13}$C spectra were in accordance with those described in literature.

(1) Dai, M.-J.; Liang, B.; Wang, C.-H.; Chen, J.-H.; Yang, Z. *Org. Lett.* **2003**, *6*, 221. (products 1 and 4)
(2) Yao, Q.-W.; Elizabeth, P. K.; Zheng, C. *Org. Lett.* **2004**, *6*, 2997. (products 2, 5 and 6)
(3) Erathodiyil, N.; Ooi, S.; Seayad, A. M.; Han, Y.; Lee, S. S.; Ying, J. Y. Chem. Eur. J. **2008**, *14*, 3118. (product 3)
(4) Kantchev, E. A. B.; Peh, G.-R.; Zhang, C.; Ying, J. Y. *Org. Lett.* **2008**, *10,* 3949. (product 4 and 7)
(5) Lucas, R. M.; Kevin, H. S. *Org. Lett.* **2004**, 6, 225. (product 8)
(6) Dams, M.; Drijkoningen, L.; Panwels, B.; Tendeloo, G. V.,; Vos, D. E.; Jacobs, P. A. *J. Catal.* **2002**, *209,* 225. (product 9)
(7) Haneda, S.; Ueba, C.; Eda, K.; Hayashi, M. *Adv. Synth. Catal.* **2007**, *349,* 833. (product 10)

# Original $^{1}H$ and $^{13}C$ NMR Spectra for the products of Heck coupling reactions:

## (1) *trans-stibene:*



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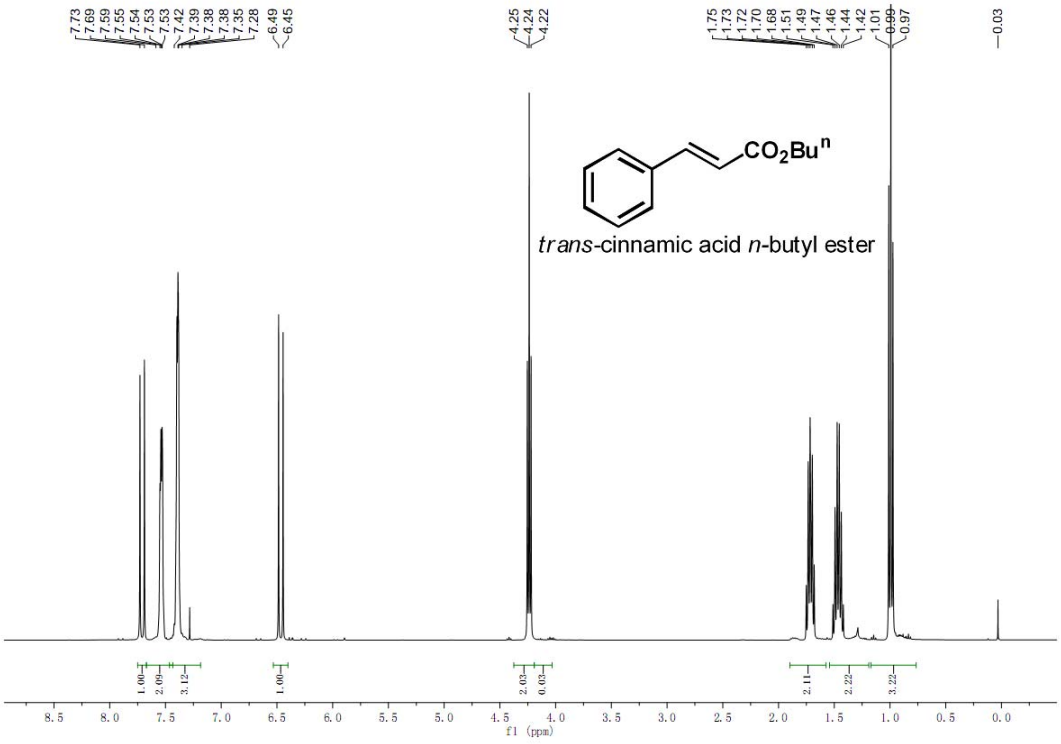
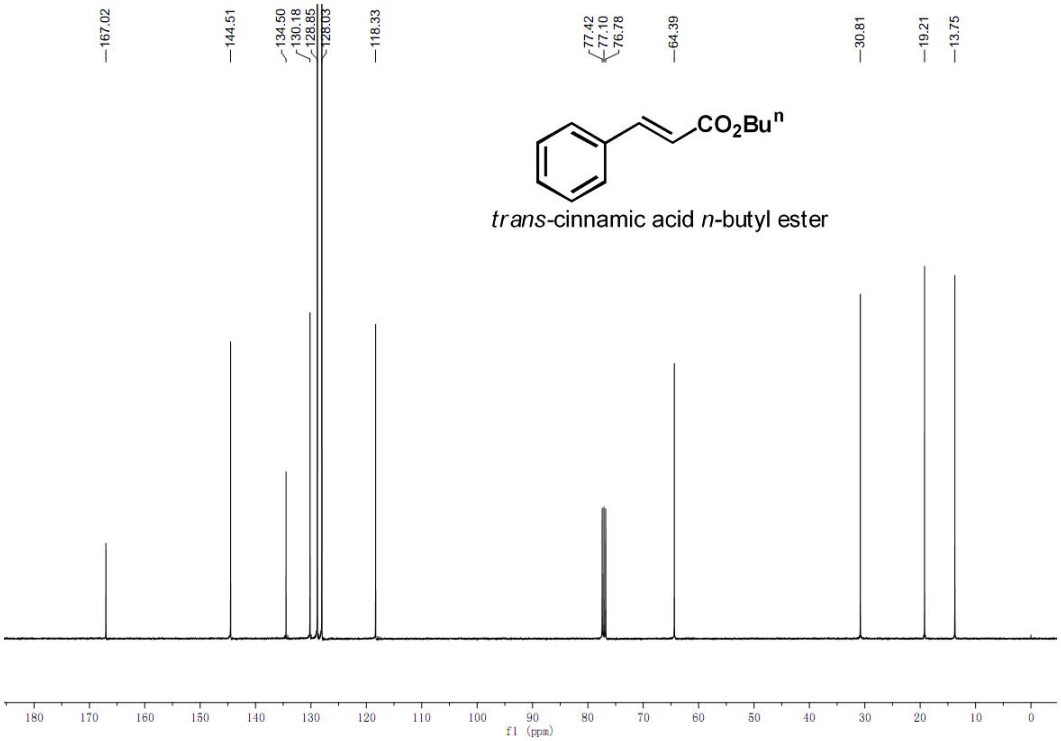
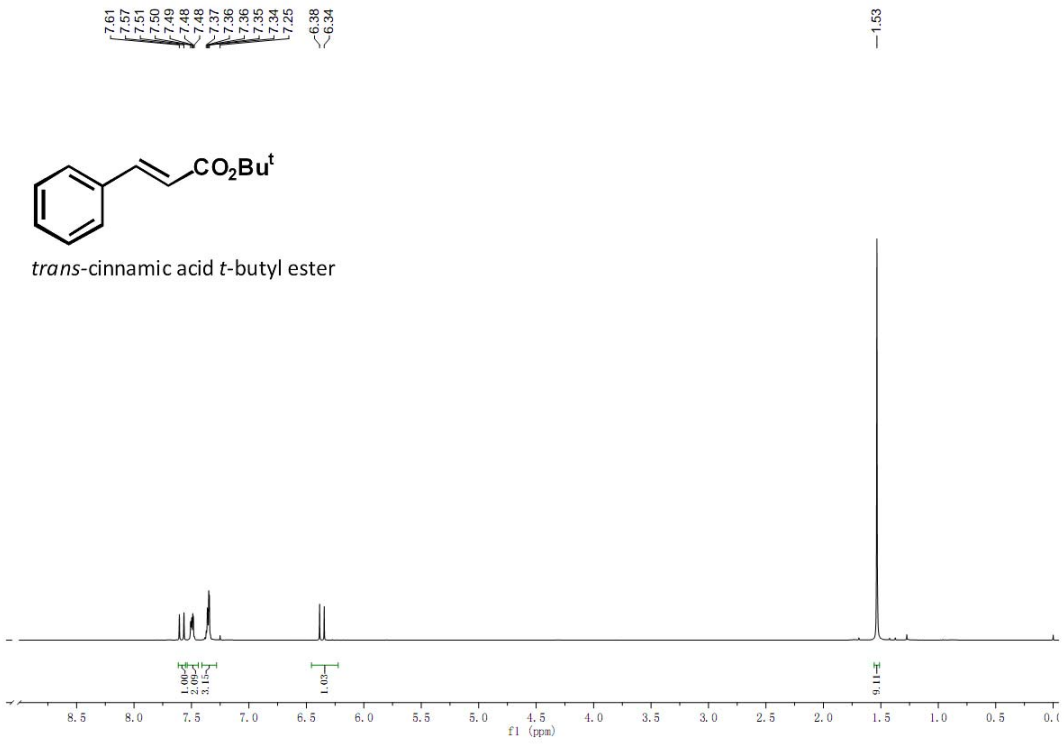
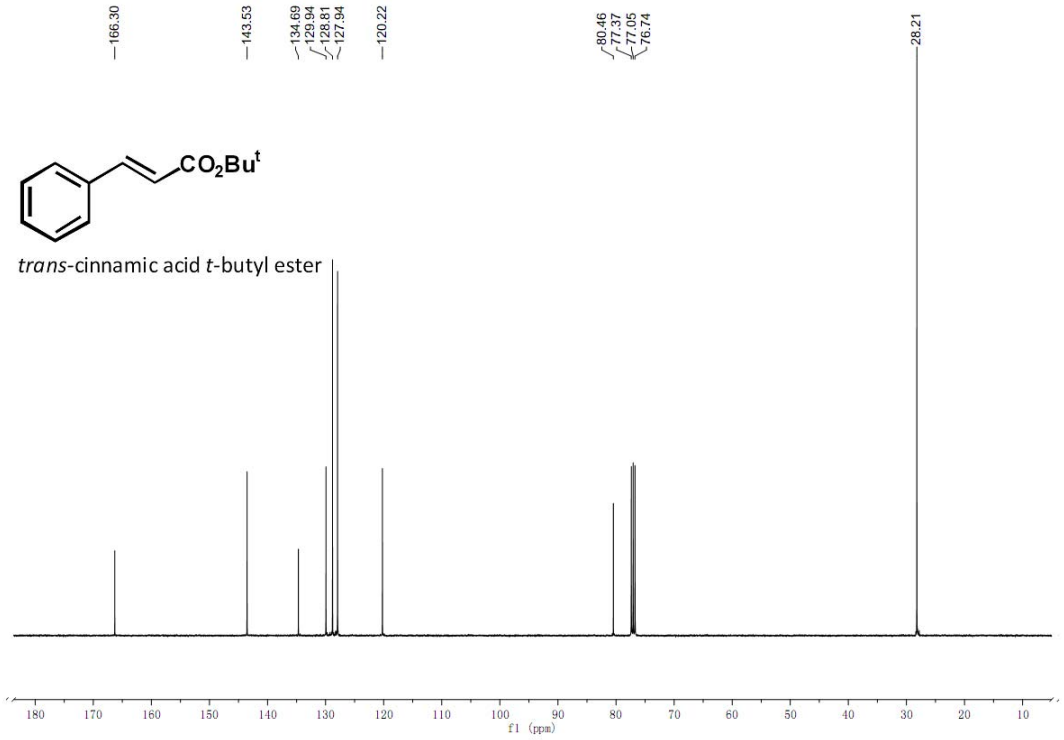


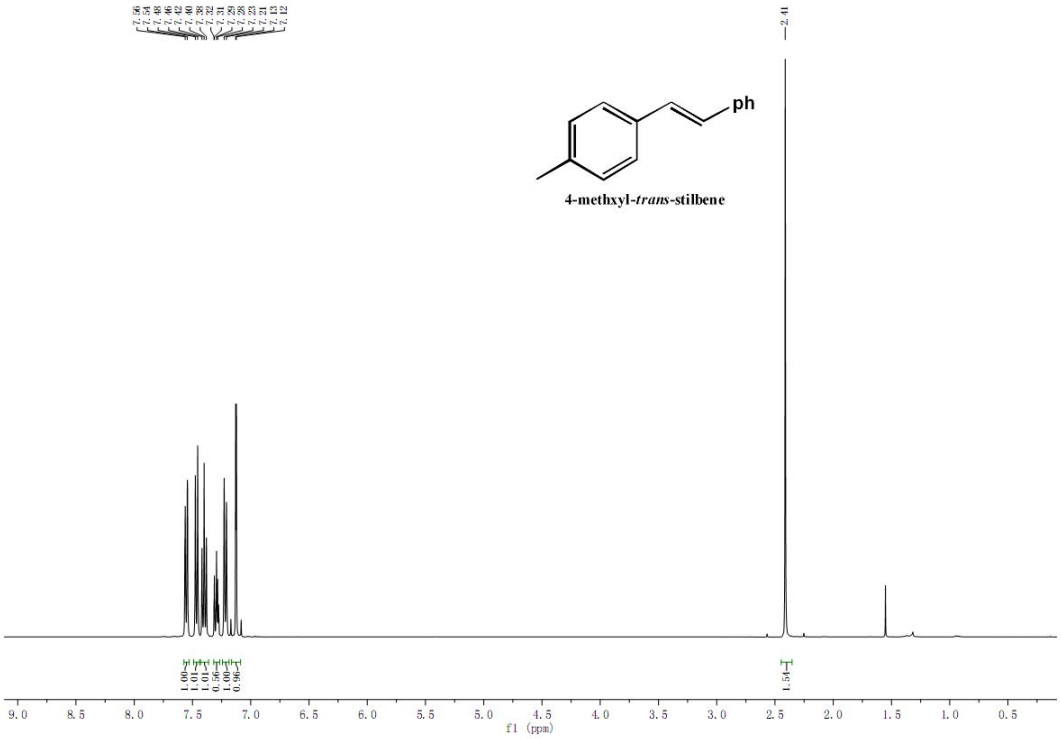



## (3) *trans*-cinnamic acid *t*-butyl ester

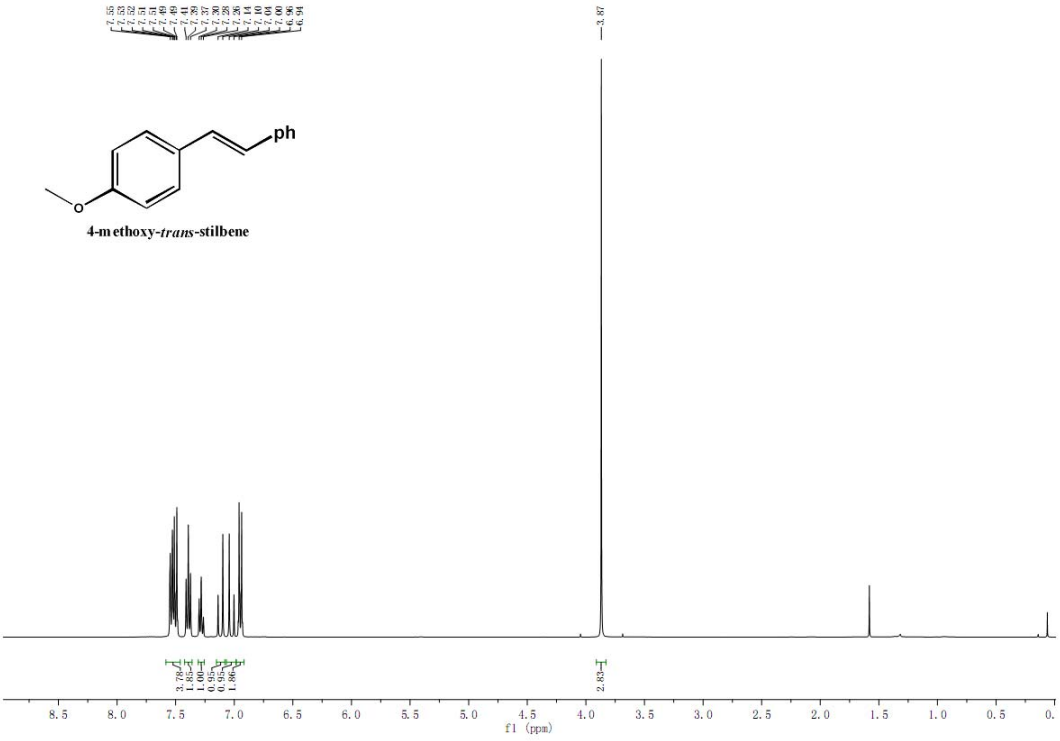


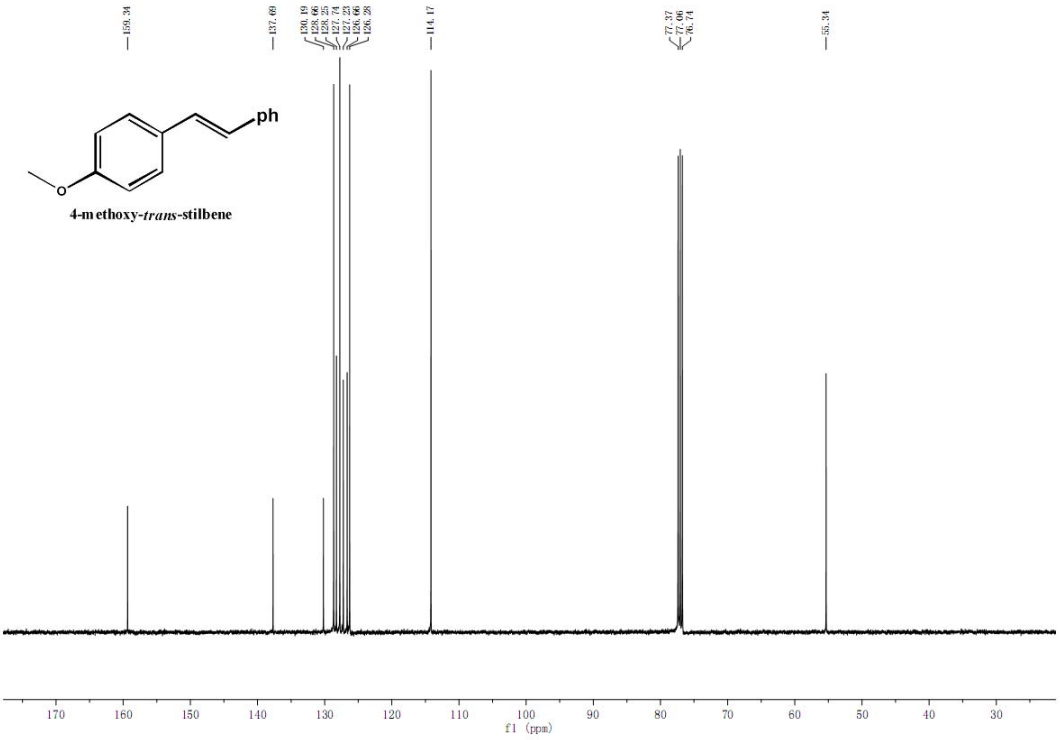



## (4) 4-methyl-*trans*-stilbene

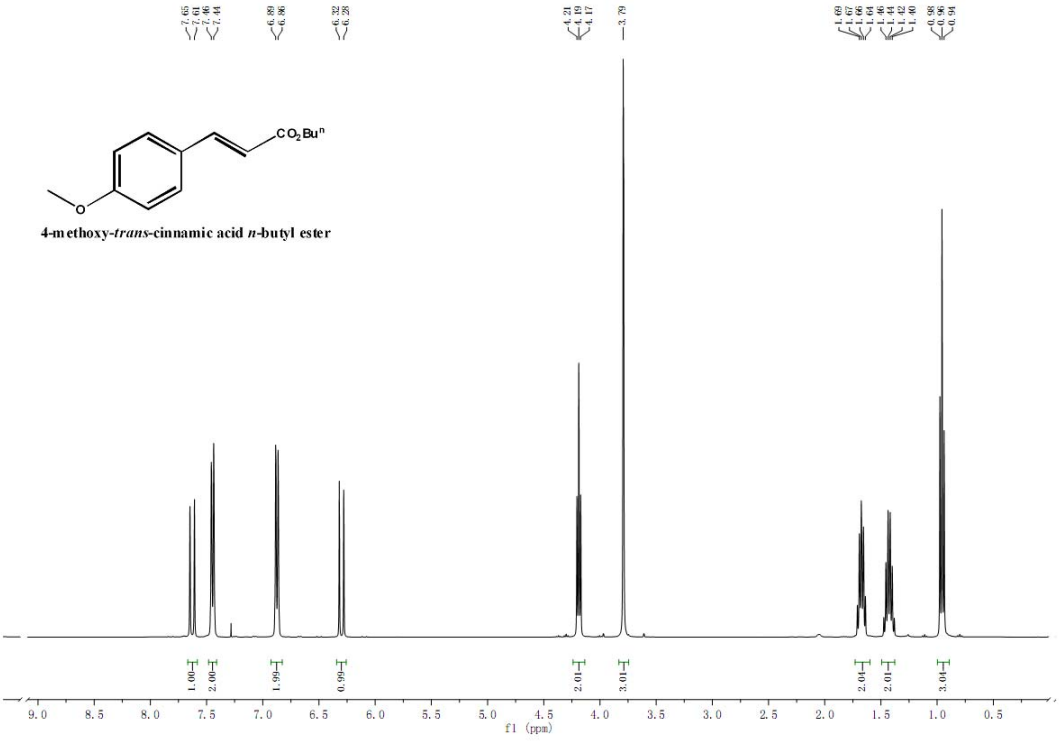


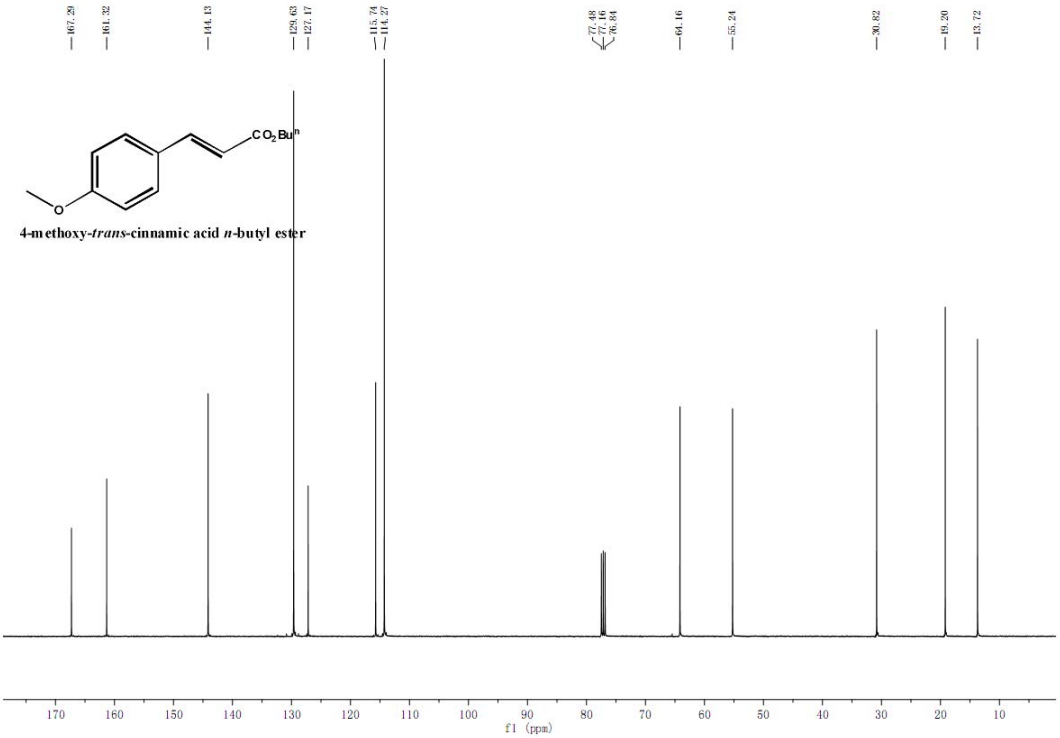

## (5) 4-methoxy-*trans*-stilbene



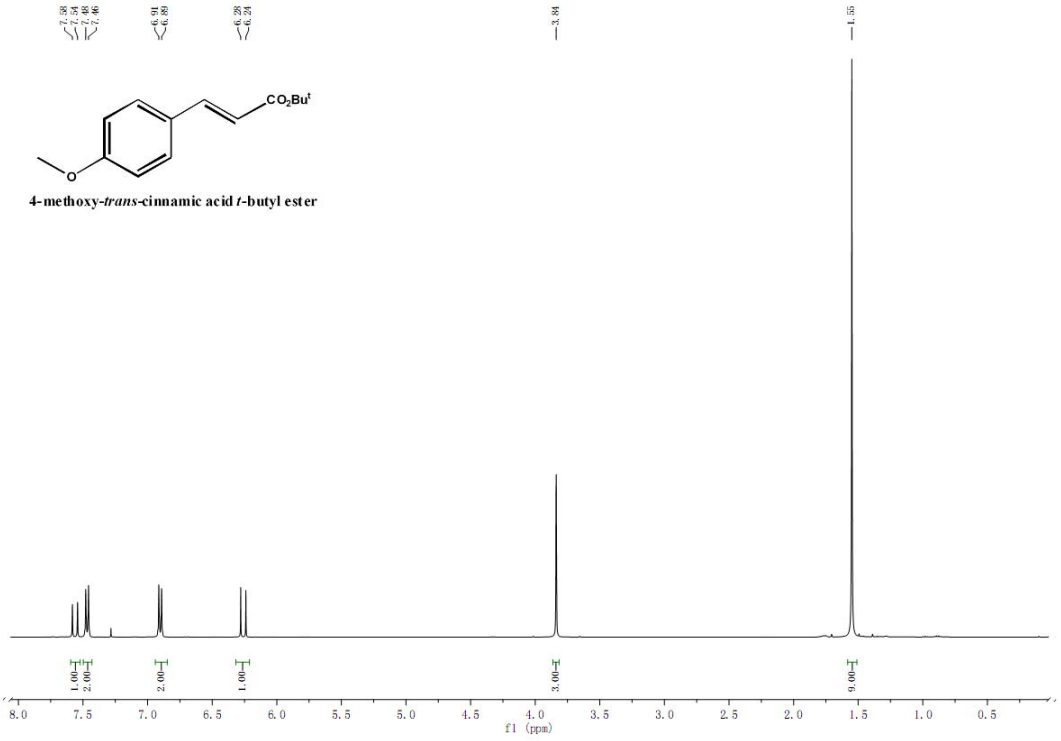



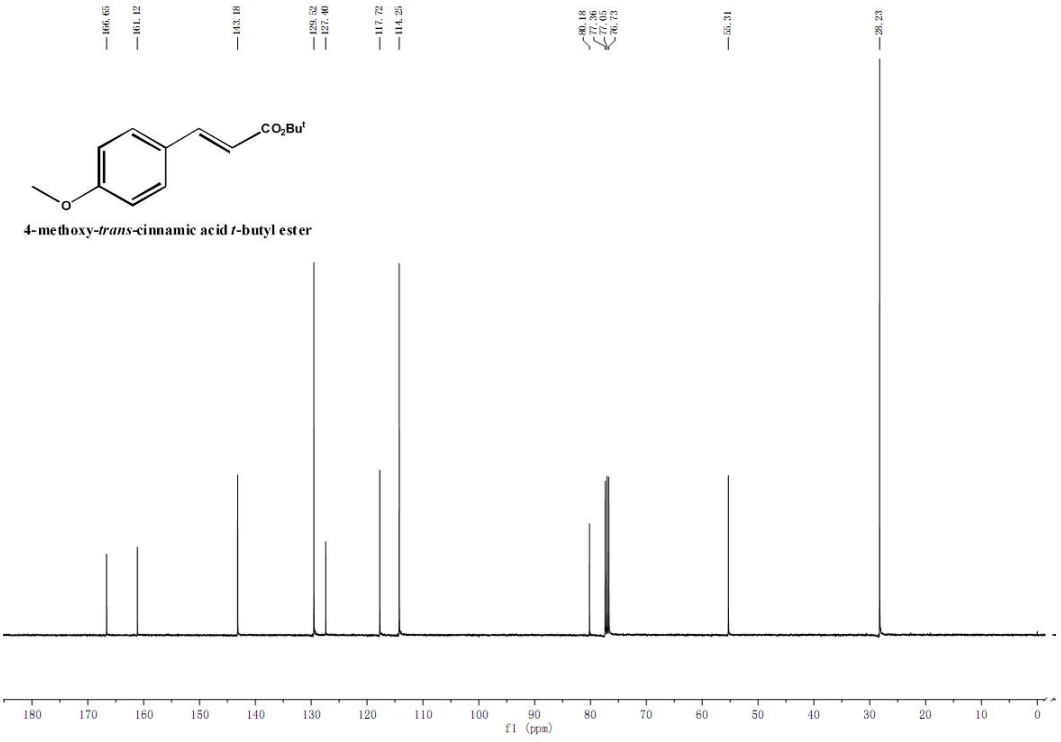
## (6) 4-methoxy-*trans*-cinnamic acid *n*-butyl ester



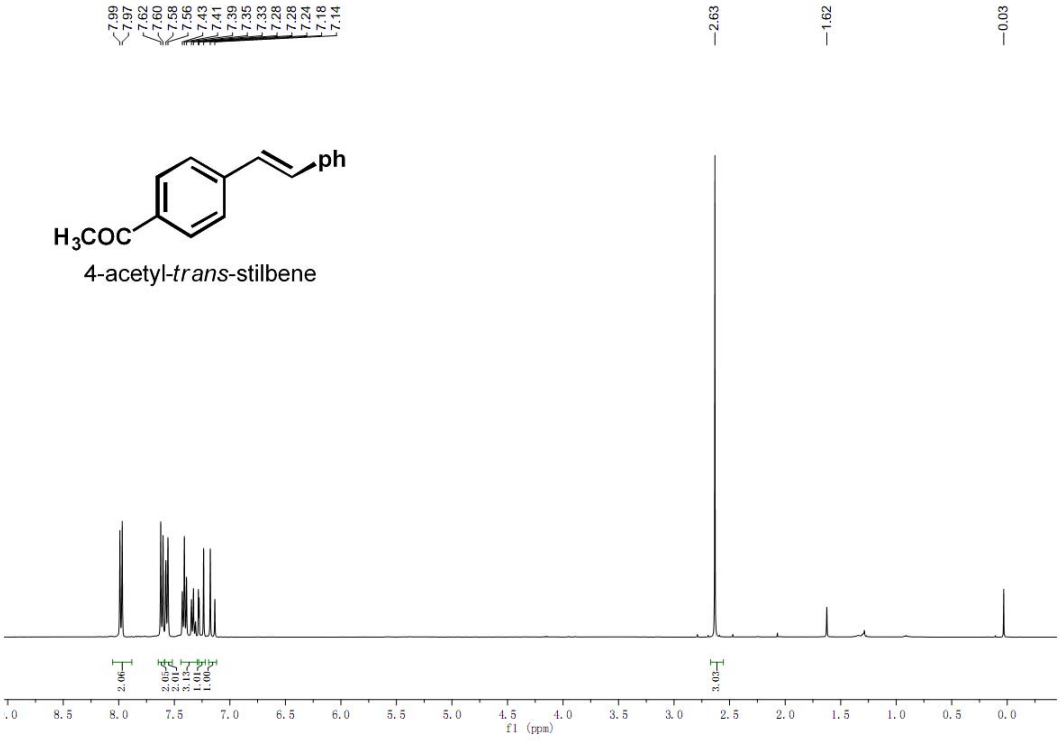



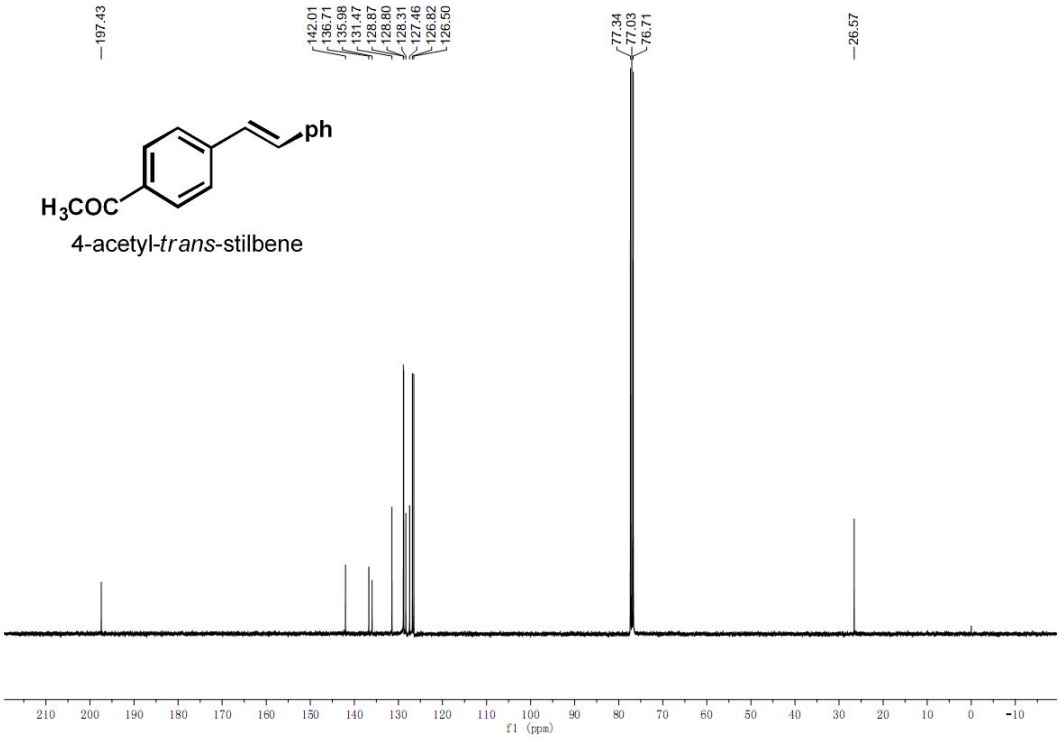
## (7) 4-methoxy-*trans*-cinnamic acid *t*-butyl ester



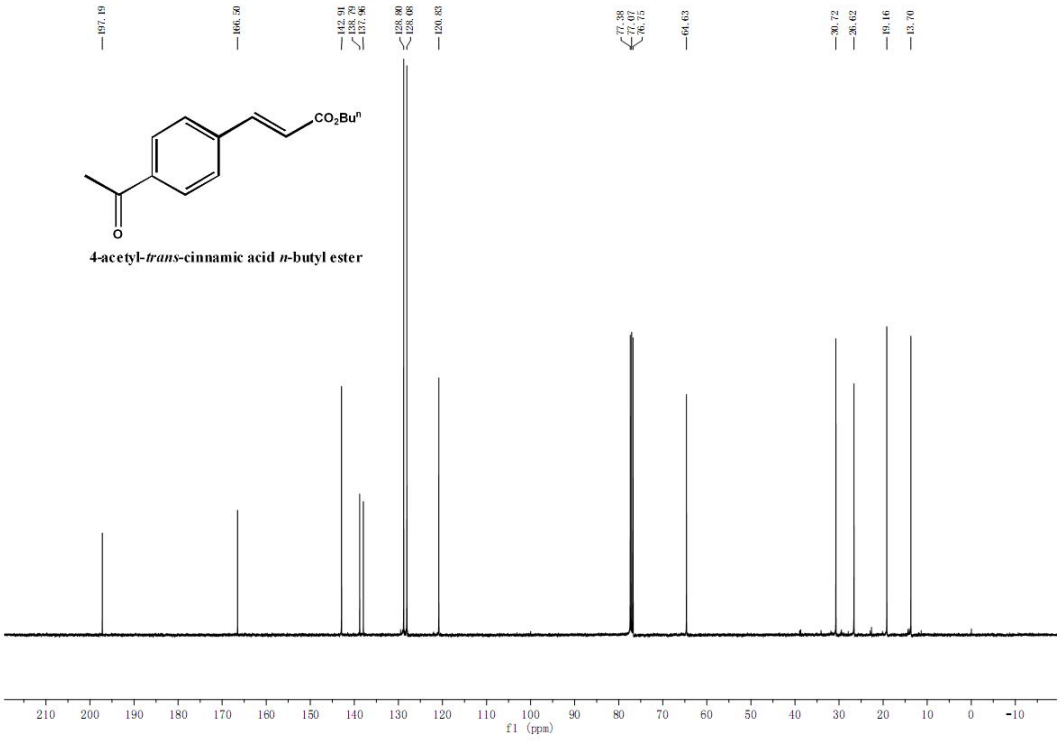



## (8) 4-acetyl-*trans*-stilbene



## (9) 4-acetyl-*trans*-cinnamic acid *n*-butyl ester

## (10) 4-acetyl-*trans*-cinnamic acid *t*-butyl ester