Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Palladium nanoparticles immobilized on a magnetic Chitosan-anchored Schiff base: Application in Suzuki-Miyaura and Heck-Mizoroki coupling reactions

Anuradha[a], Shweta Kumari[b], Samaresh Layek[a], and Devendra D. Pathak[a*]

[a]Department of Applied Chemistry, Indian Institute of Technology (ISM), Dhanbad-826004, India

[b]Department of Chemical Engineering, Indian Institute of Technology, Gandhinagar-382355, India

Email: anuradhakumar3107@gmail.com (Anuradha), shweta@ac.ism.ac.in (Shweta Kumari), samareshchemist92@gmail.com (Samaresh Layek). ddpathak@yahoo.com*

*Phone number: +91 9431126250

Contents **Page No.**

Instrumentation

FT-IR spectra were recorded using KBr pellets on a Perkin Elmer Spectrometer in the range of 4000-400 cm^{-1}. The powder X-ray diffraction (XRD) analysis of catalyst was carried out using a Bruker D8 Advance diffractometer at 40 kV and 40 mA with CuKα radiation (λ=0.15418 nm). XPS spectrum of the catalyst was recorded using model PHI 5000 Versa Prob II, FEI Inc. The surface morphology was characterized by Field Emission Scanning Electron Microscope (FESEM) of model FESEM Supra 55 (Carl Zeiss, Germany) with the accelerating voltage of 20kv at liquid nitrogen atmosphere. The EDX analysis was carried out using Electron Backscatter Diffraction (Oxford Integrated Advanced Aztec HKL EBSD with Forescatter system with 4 diodes for Nordlys Analysis. TEM of a nanocatalyst was carried out using model Jeol/JEM 2100. Thermo gravimetric analyses (TGA) were performed on a NETZSCH, STA 449 F3 Jupiter in the temperature range of 0-600℃ with heating ramp of 10℃ min^{-1} under nitrogen flow. Palladium content in the nanocatalyst was determined by using ICP-AES (Thermo slectron IRIS Intrepid). ^{1}H and ^{13}C NMR spectra of the isolated products were recorded on a Bruker Avance-II HD-400 MHz spectrometer in $CDCl_3$ using TMS as the internal Standard.

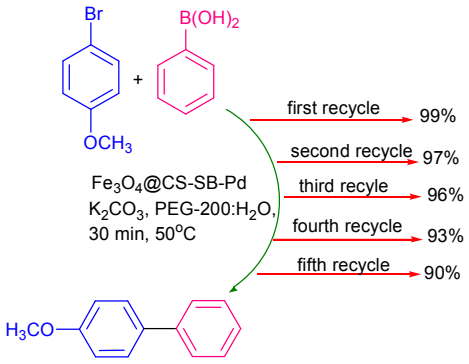


Fig. S1: Recyclability of Suzuki-Miyaura coupling reaction.

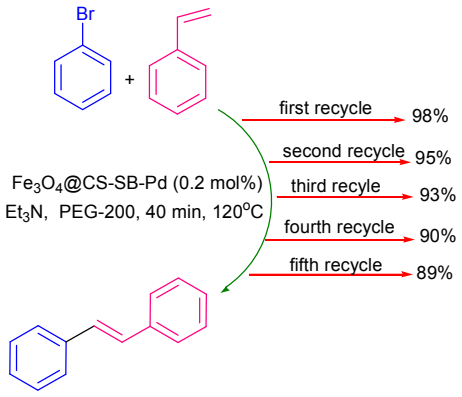


Fig. S2: Recyclability of Heck-Mizoroki coupling reaction.

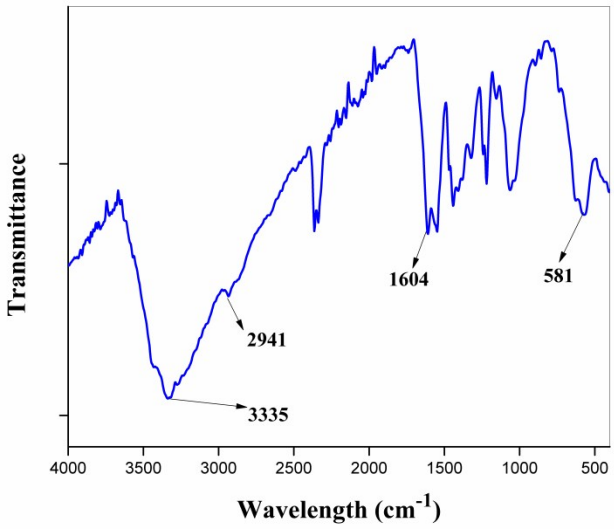


Fig. S3. FT-IR of reusable Fe_3O_4@CS-SB-Pd nanocatalyst after 5th cycle.

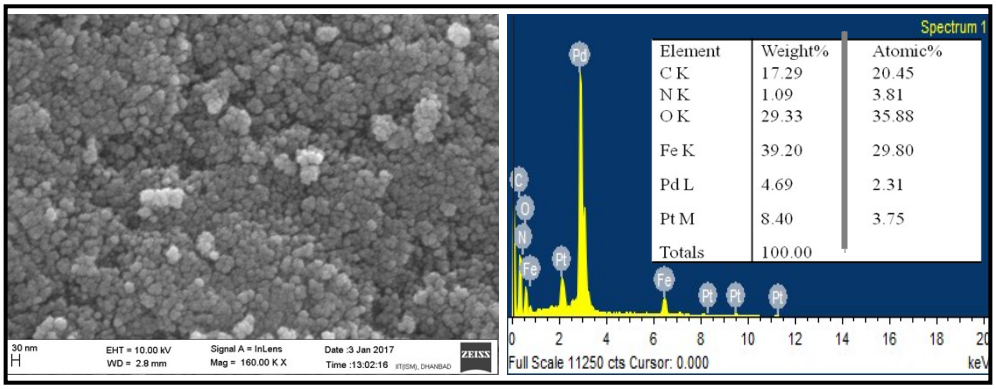
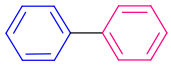
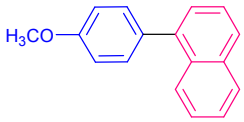


Fig. S4. FESEM image and EDX analysis of Fe_3O_4@CS-SB-Pd nanocatalyst after 5th cycle.

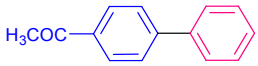
Spectral data (^{1}H and ^{13}C NMR) of Isolated Suzuki coupling product:



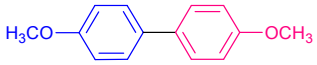
Biphenyl (3a): **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.60-7.58 (d, 2H), 7.44-7.46 (d, 2H), 7.35-7.42 (m, 1H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 141.26, 128.82, 127.26, 127.18, 77.34, 77.02, 76.70.



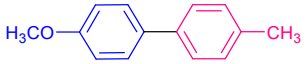
4-methoxy phenyl napthalene (3b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 7.90-7.84 (m, 3H), 7.73-7.70 (d, 1H), 7.67-7.66 (m, 2H), 7.53-7.44 (m, 2H), 7.04-7.01 (2H, m), 3.88 (s, 3H).



4-acetyl biphenyl (3c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-8.02 (d, 2H), 7.70-7.68 (d, 2H), 7.64-7.62 (d, 2H), 7.49-7.47 (d, 2H), 7.38-7.45 (m, 1H), 2.64 (s, 1H).

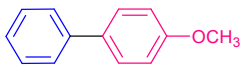


4,4-dimethoxy biphenyl (3e): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.46 (d, 2H), 6.95-6.93(d, 2H), 3.80 (s, 1H).

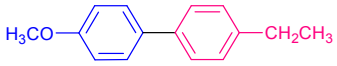


4-methoxy-4-methyl biphenyl (3f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.51 (d, 2H), 7.40-7.28 (m, 3H), 7.13-7.11 (d, 1H), 6.98-6.96 (d, 2H), 3.85 (s, 3H), 2.41 (s, 3H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 159.79, 138.09, 136.36, 133.76, 129.50, 128.03, 126.59, 114.25, 77.33, 77.01, 76.70, 55.71, 21.07.

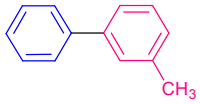
4-ethyl biphenyl (3g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.57 (d, 2H), 7.53-7.51 (d, 2H), 7.49-7.42 (m, 2H), 7.40-7.32 (m, 1H), 7.28-7.25 (m, 2h), 2.72-2.66 (m, 2H), 1.30-1.26 (t, 3H).



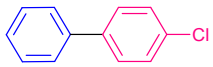
4-methoxy biphenyl (3h): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.43 (m, 4H), 7.42-7.40 (d, 2H), 7.32-7.28 (m, 1H), 6.99-6.97 (d, 2H), 3.88 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): 159.79, 133.80, 128.67, 128.09, 126.74, 126.66, 114.63, 77.33, 77.01, 76.69, 55.71.



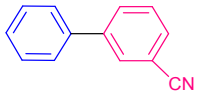
4-methoxy-4-ethyl biphenyl (3i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, 1H), 7.50 (d, 1H), 7.48 (d, 1H), 7.46 (d, 1H), 7.26 (d, 1H), 7.24 (d, 1H), 6.97 (d, 1H), 6.95 (d, 1H), 3.84 (s, 3H). 2.71-2.65 (m, 2H), 1.29-1.25 (t, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): 159.79, 133.80, 128.67, 128.09, 126.74, 126.66, 114.63, 77.33, 77.01, 76.69, 55.71.



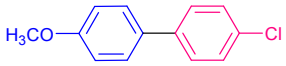
3-methyl biphenyl (3j): ^{1}H NMR (400 MHz, $CDCl_3$): 7.59-7.57 (d, 2H), 7.45-7.35 (m, 4H), 7.33-7.30 (m, 2H), 7.17-1.14 (t, 1H), 2.42 (s, 3H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 159.43, 140.98, 138.53, 133.91, 128.84, 128.12, 127.57, 127.23, 123.90, 77.33, 77.01, 76.70, 21.66.



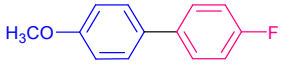
4-Chloro biphenyl (3k): ^{13}C NMR ($CDCl_3$, 100 MHz): 140.01, 139.73, 133.38, 128.95, 128.88, 128.39, 127.59, 126.99, 77.33, 77.01, 76.69.



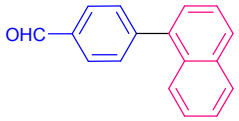
3-cyano biphenyl (3l): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.49 (d, 2H), 7.42-7.40 (d, 2H), 7.37-7.35 (d, 2H), 7.22-7.08 (m, 1H), 7.07-7.05 (d, 2H).



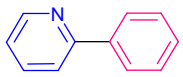
4-methoxy-4-chloro biphenyl (3m): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.45 (m, 4H), 7.38-7.36 (d, 2H), 6.98 (d, 1H), 6.96 (d, 1H), 3.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 159.43, 133.92, 128.84, 128.09, 126.74, 114.63, 77.46, 77.01, 76.69, 55.71.



4-methoxy-4-fluoro biphenyl (3n): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.45 (m, 4H), 7.11-7.09 (m, 2H), 6.97-6.95 (m, 2H), 3.84 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): 159.12, 137.08, 132.76, 128.26, 128.18, 128.04, 127.74, 114.26, 114.17, 77.34, 77.02, 76.70, 55.36.



4-formyl phenyl napthalene (3o): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (s, 1H), 8.03-8.01 (d, 2H), 7.94-7.91 (t, 2H), 7.85-7.83 (d, 1H), 7.69-7.67 (d, 2H), 7.57-7.51 (m, 2H), 7.46-7.43 (m, 2H).



2-phenyl pyridine (3q): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71-8.69 (d, 1H), 8.00-7.98 (2H, d), 7.75-7.72 (2H, m), 7.50-7.45 (2H, m), 7.43-7.40 (1H, m), 7.24-7.21 (1H, m)

^{1}H and ^{13}C NMR Spectra of Suzuki-Miyaura coupling product:

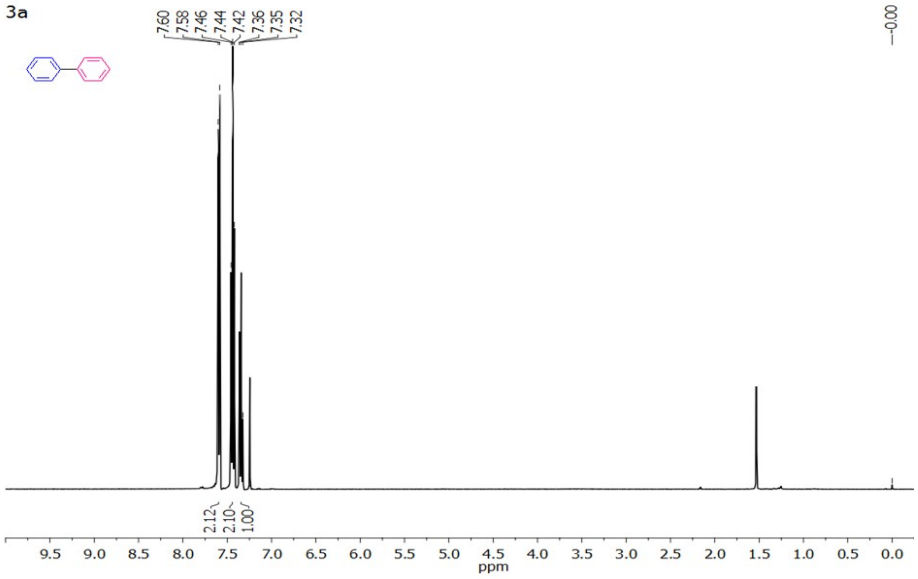


Fig. S5: ^{1}H NMR of Biphenyl (3a)

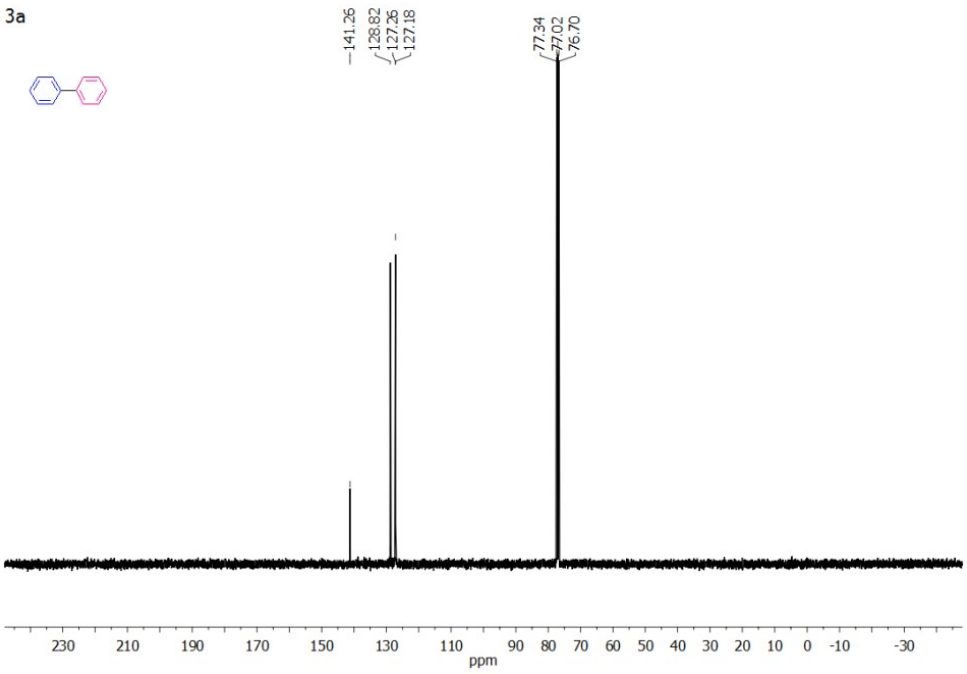


Fig. S6: ^{13}C NMR of Biphenyl (3a)

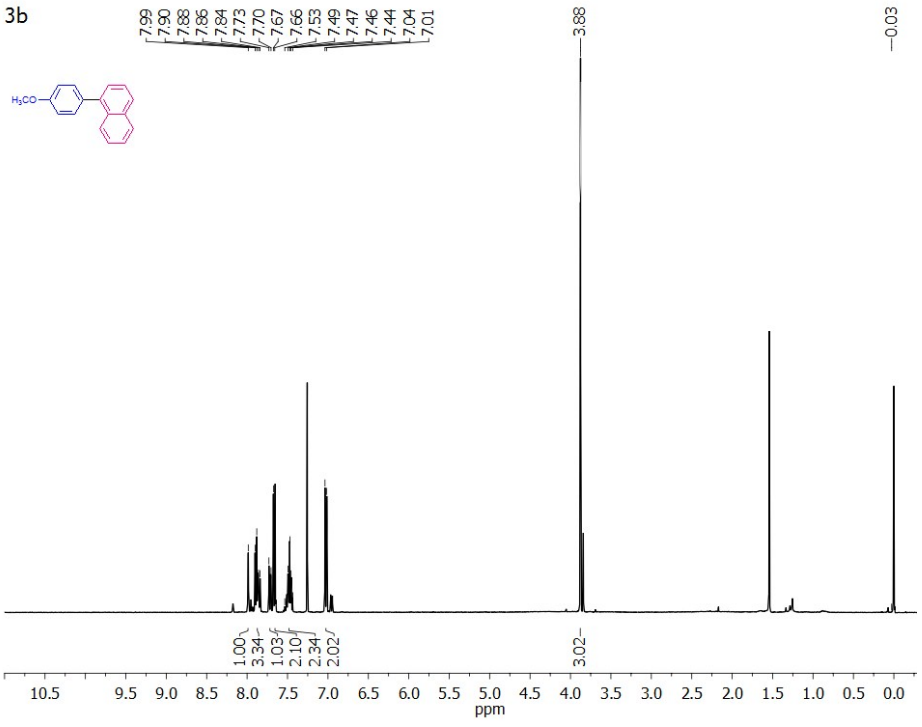


Fig. S7: ^{1}H NMR of 4-methoxy phenyl napthalene (3b)

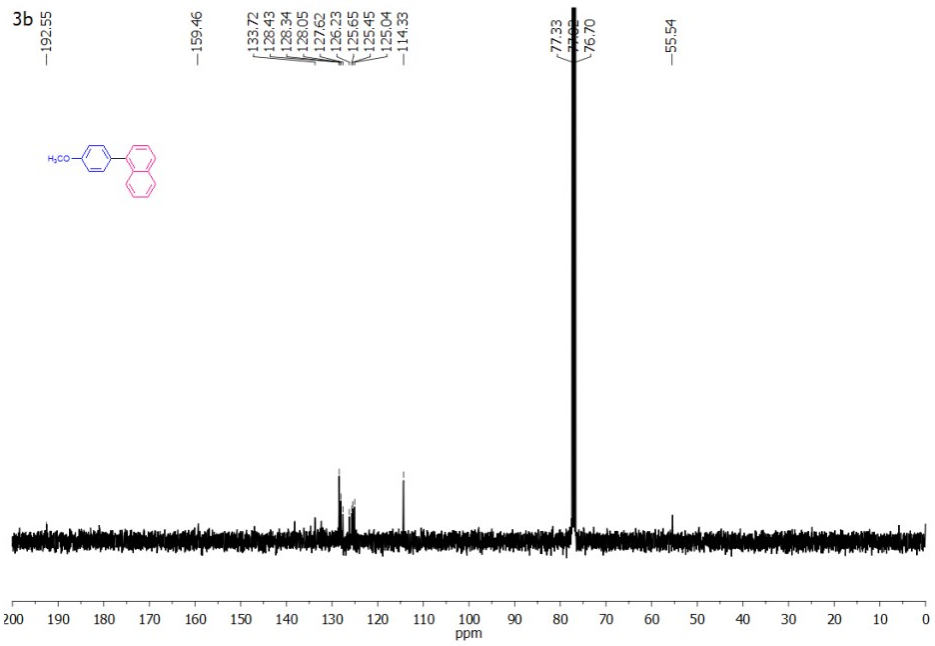


Fig. S8: ^{13}C NMR of 4-methoxy phenyl napthalene (3b)

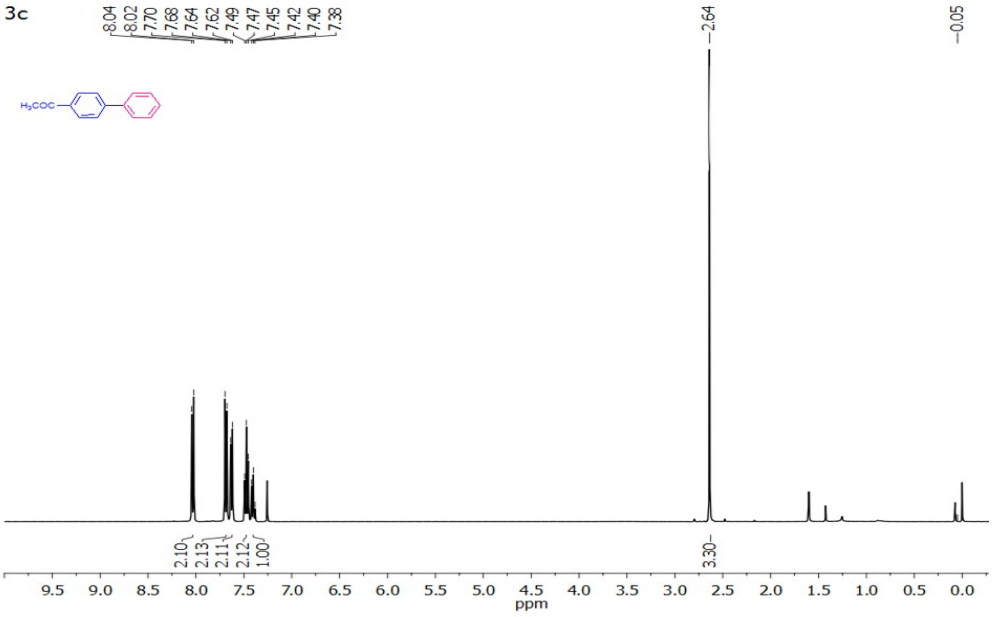


Fig. S9: ^{1}H NMR of 4-acetyl biphenyl (3c)

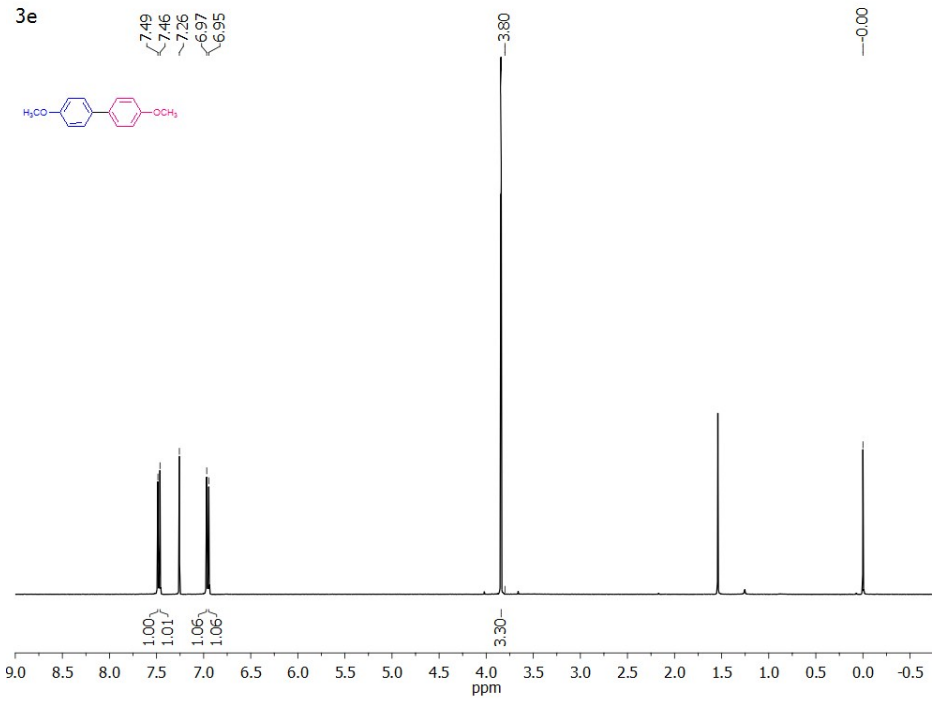


Fig. S10: ^{1}H NMR of of 4,4-dimethoxy biphenyl (3e)

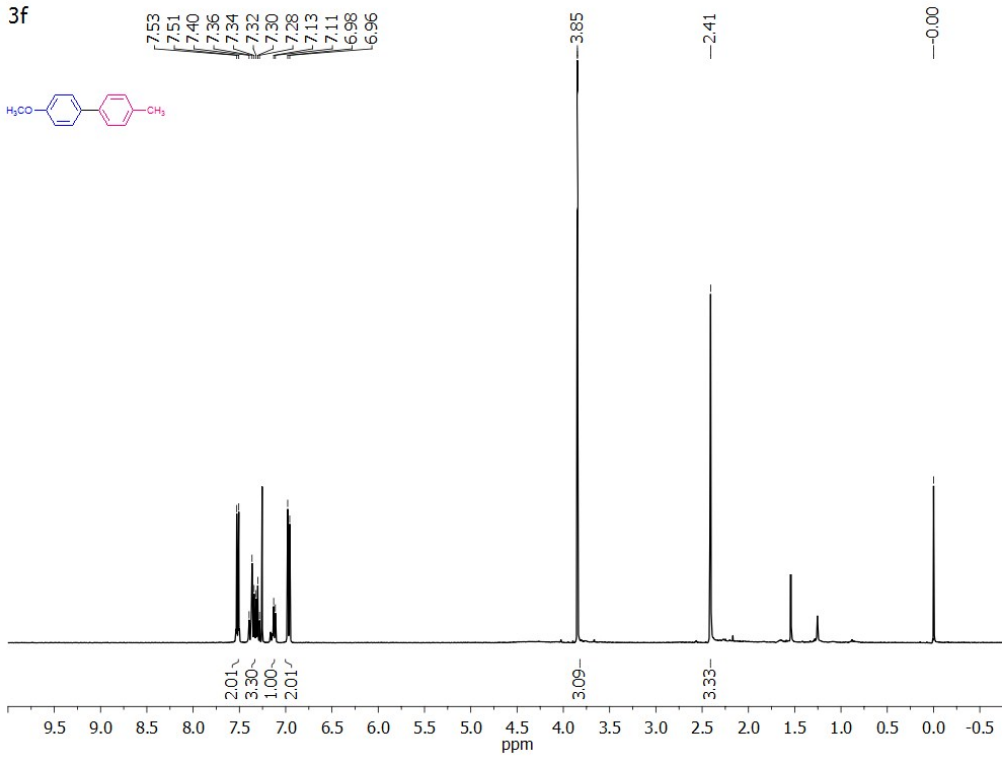


Fig. S11: ^{1}H NMR of 4-methoxy-4-methyl biphenyl (3f)

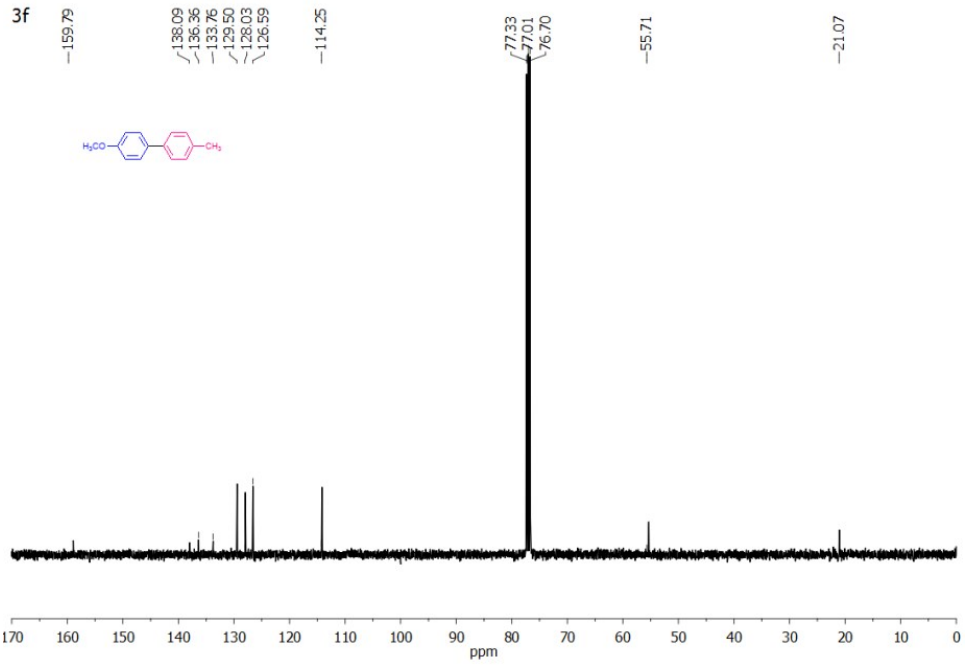


Fig. S12: ^{13}C NMR of 4-methoxy-4-methyl biphenyl (3f)

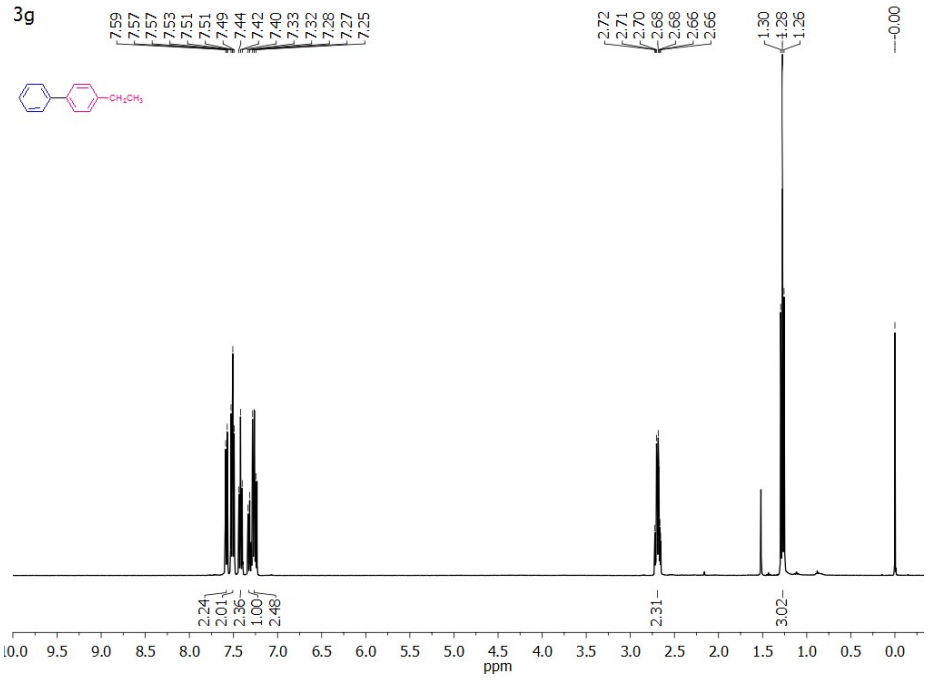


Fig. S13: ^{1}H NMR of 4-ethyl biphenyl (3g)

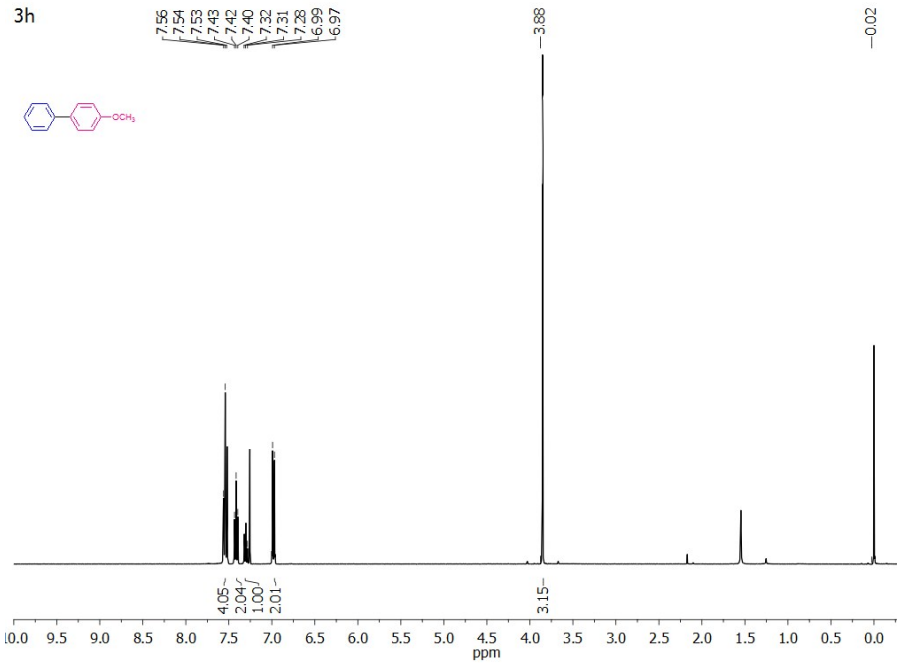


Fig. S14: ^{1}H NMR of 4-methoxy biphenyl (3h)

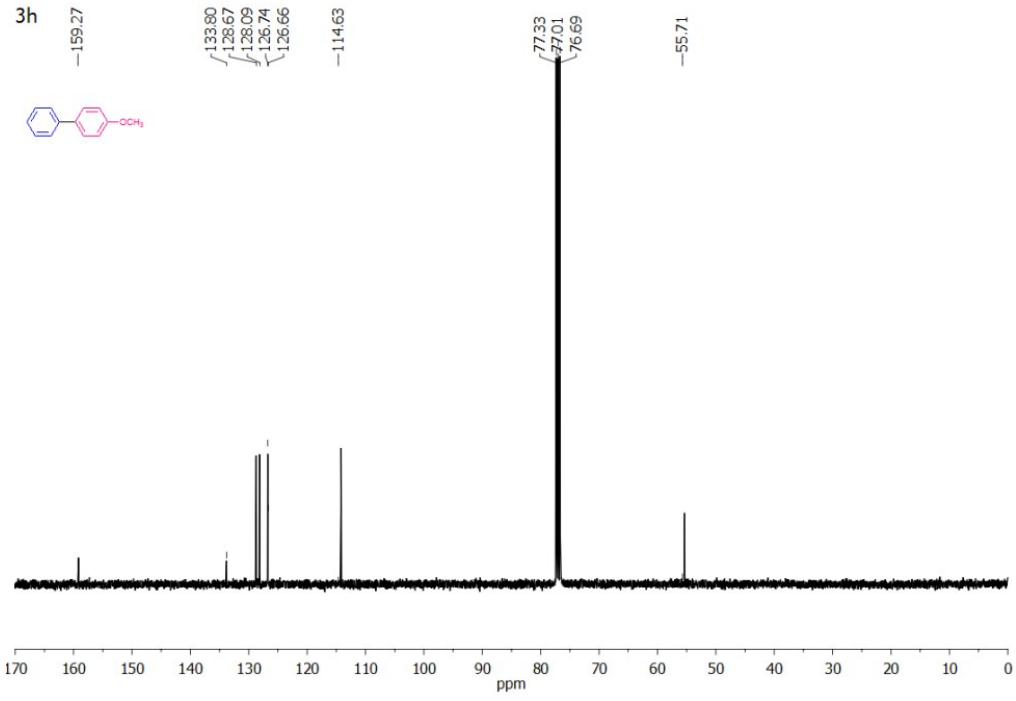


Fig. S15: ^{13}C NMR of 4-methoxy biphenyl (3h)

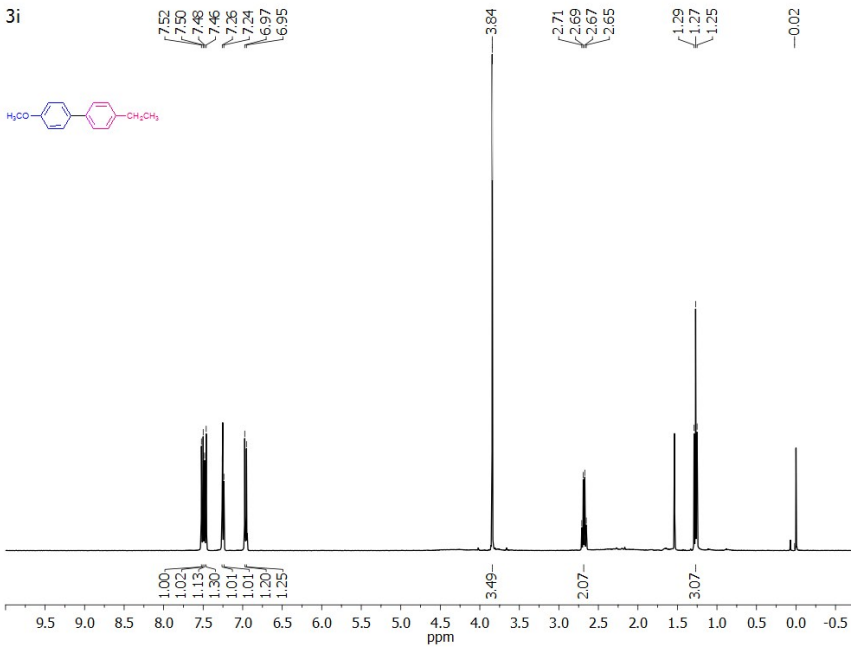


Fig. S16: ^{1}H NMR of 4-methoxy-4-ethyl biphenyl (3i)

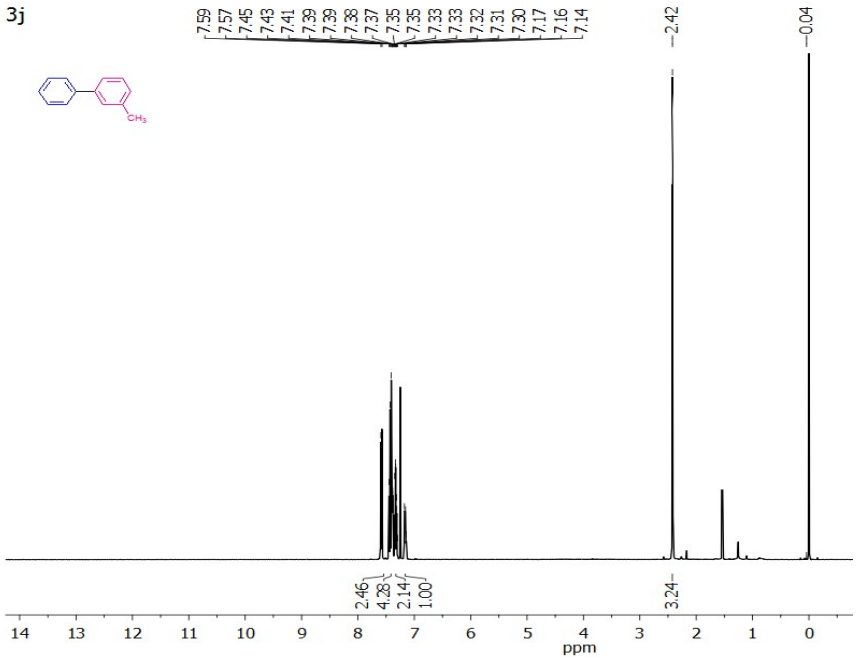


Fig. S17: ^{1}H NMR of 3-methyl biphenyl (3j)

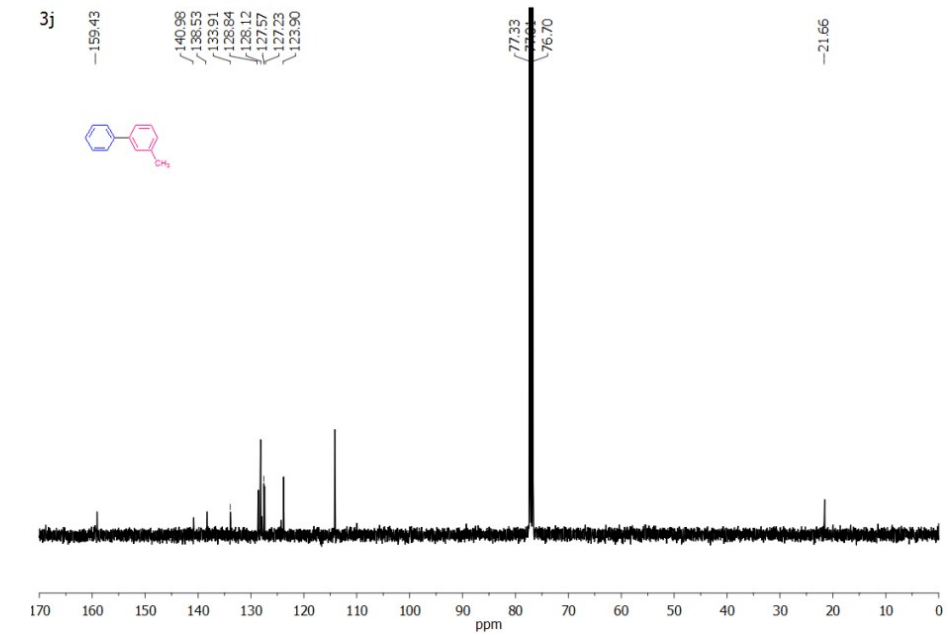


Fig. S18: ^{13}C NMR of 3-methyl biphenyl (3j)

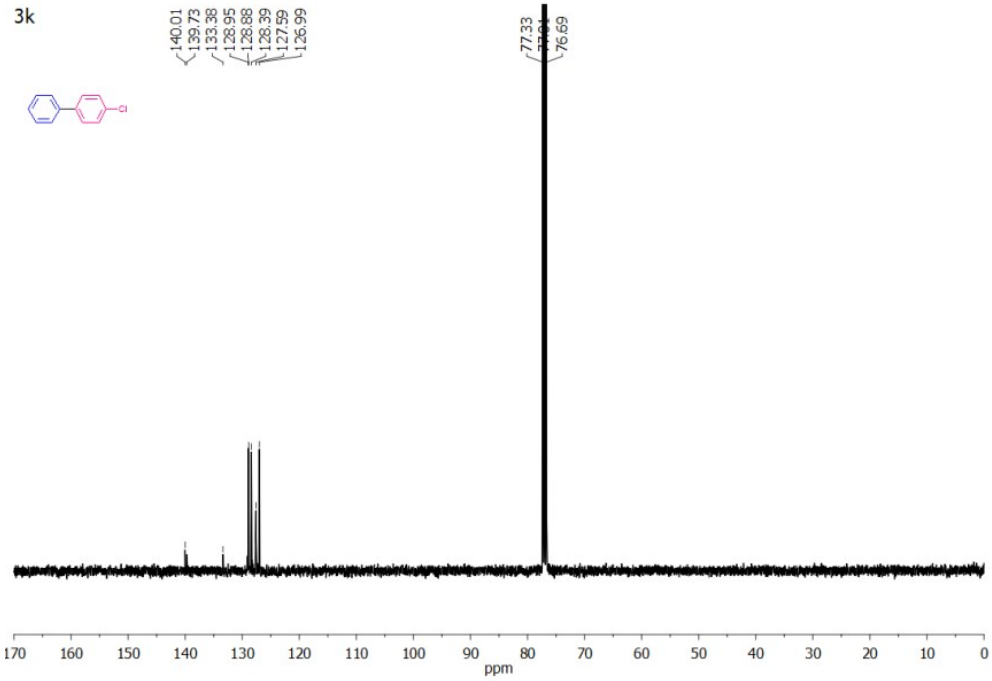


Fig. S19: ^{13}C NMR of 4-Chloro biphenyl (3k)

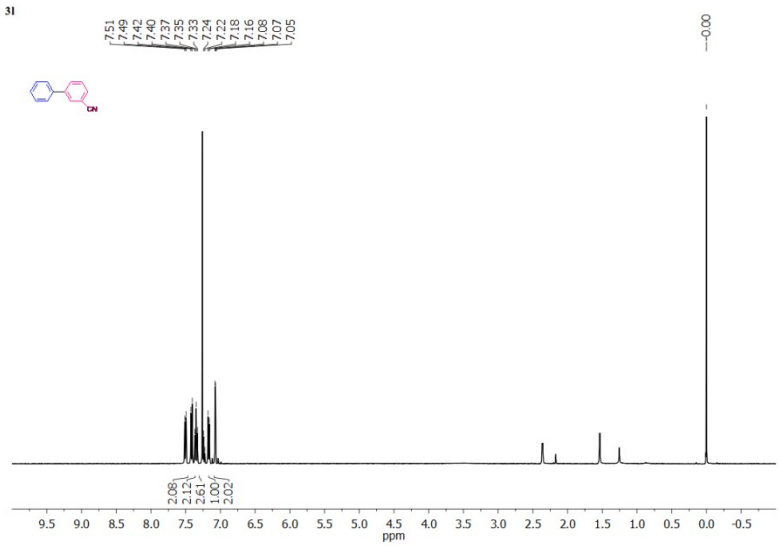


Fig. S20: ^{1}H NMR of 4-cyano biphenyl (3l)

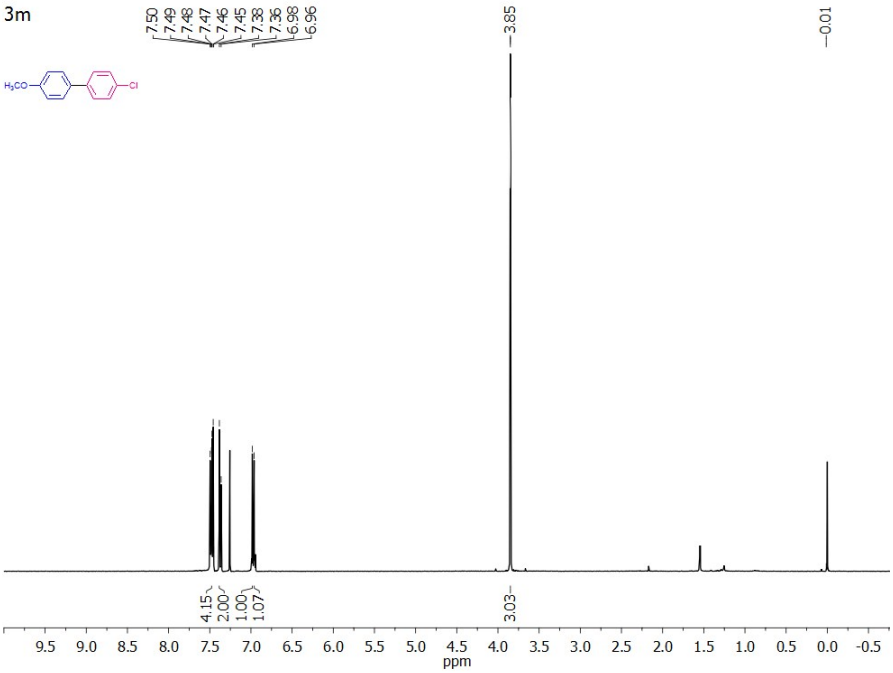


Fig. S21: ^{1}H NMR of 4-methoxy-4-chloro biphenyl (3m)

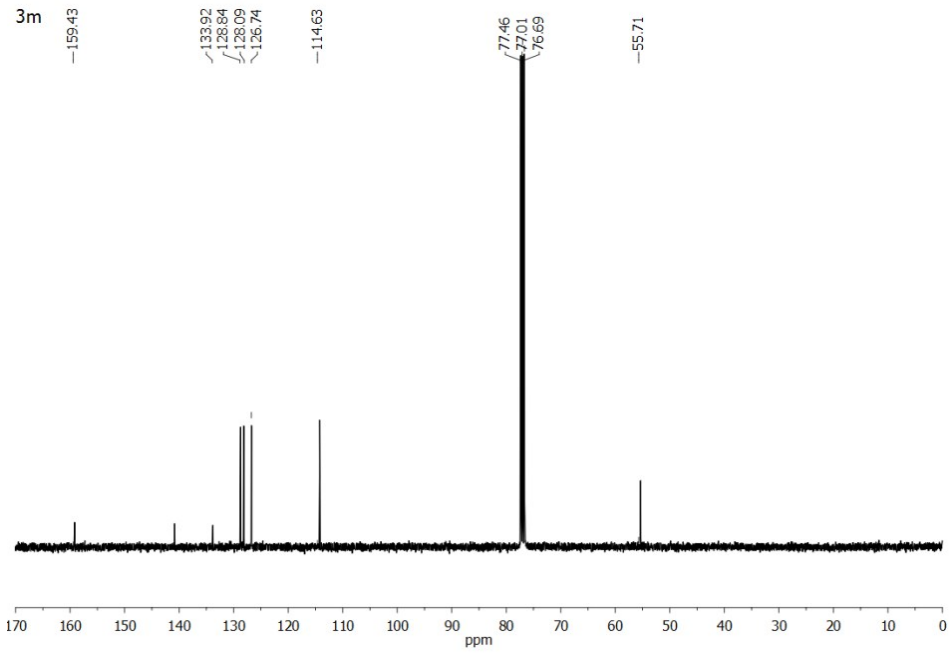


Fig. S22: ^{13}C NMR of 4-methoxy-4-chloro biphenyl (3m)

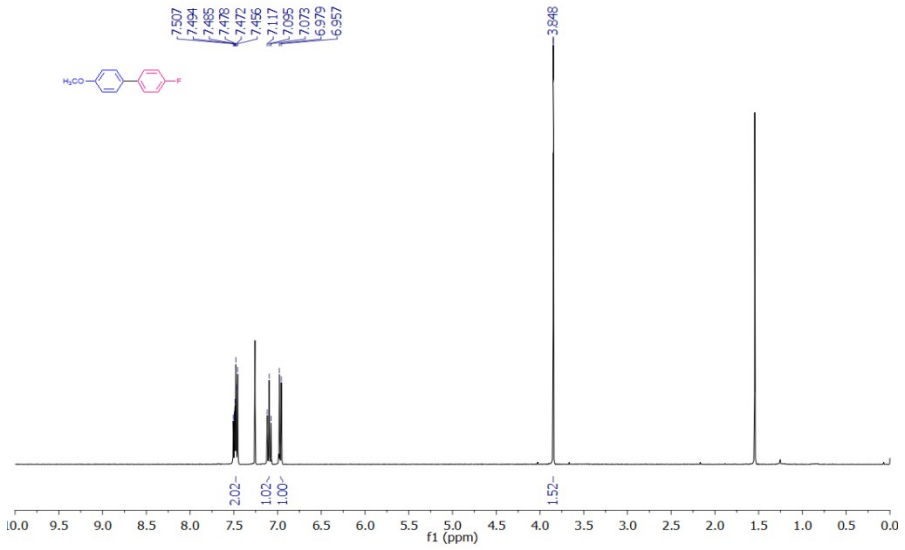


Fig. S23: ^{1}H NMR of 4-methoxy-4-flouro biphenyl (3n)

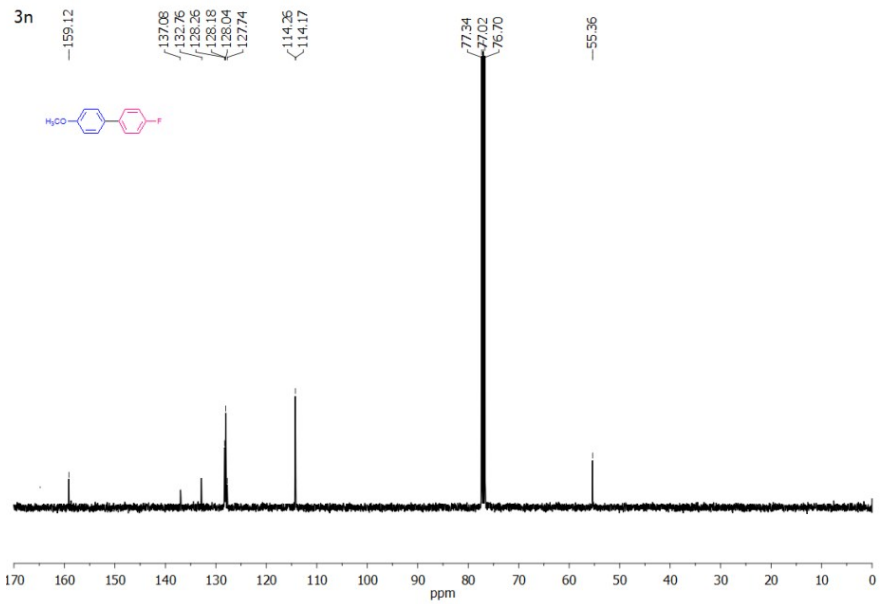


Fig. S24: ^{13}C NMR of 4-methoxy-4-flouro biphenyl (3n)

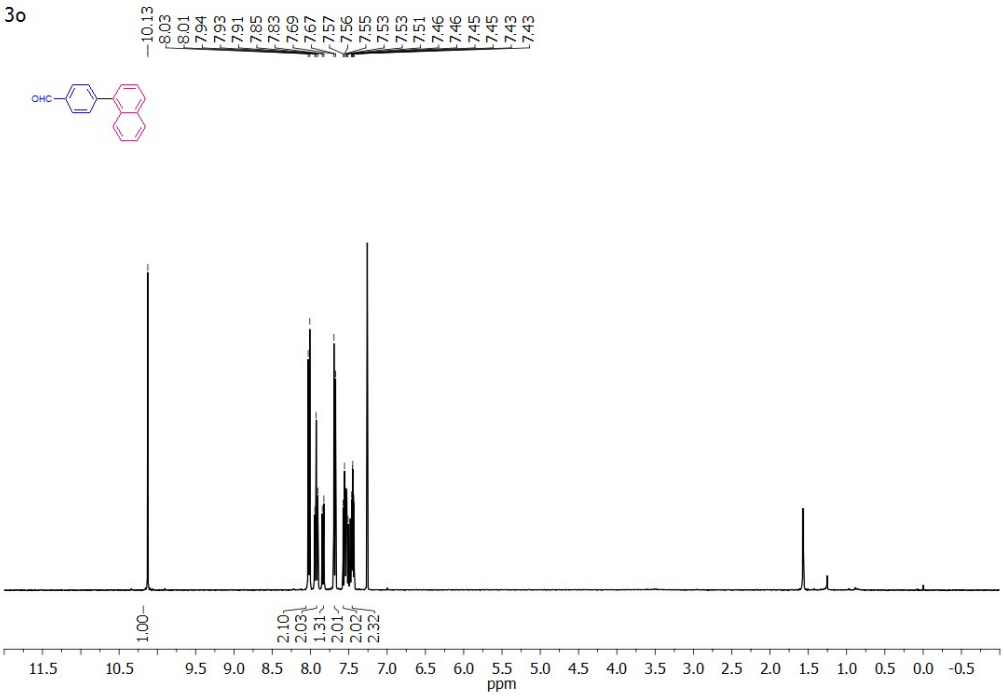


Fig. S25: ^{1}H NMR of 4-formyl phenyl napthalene (3o)

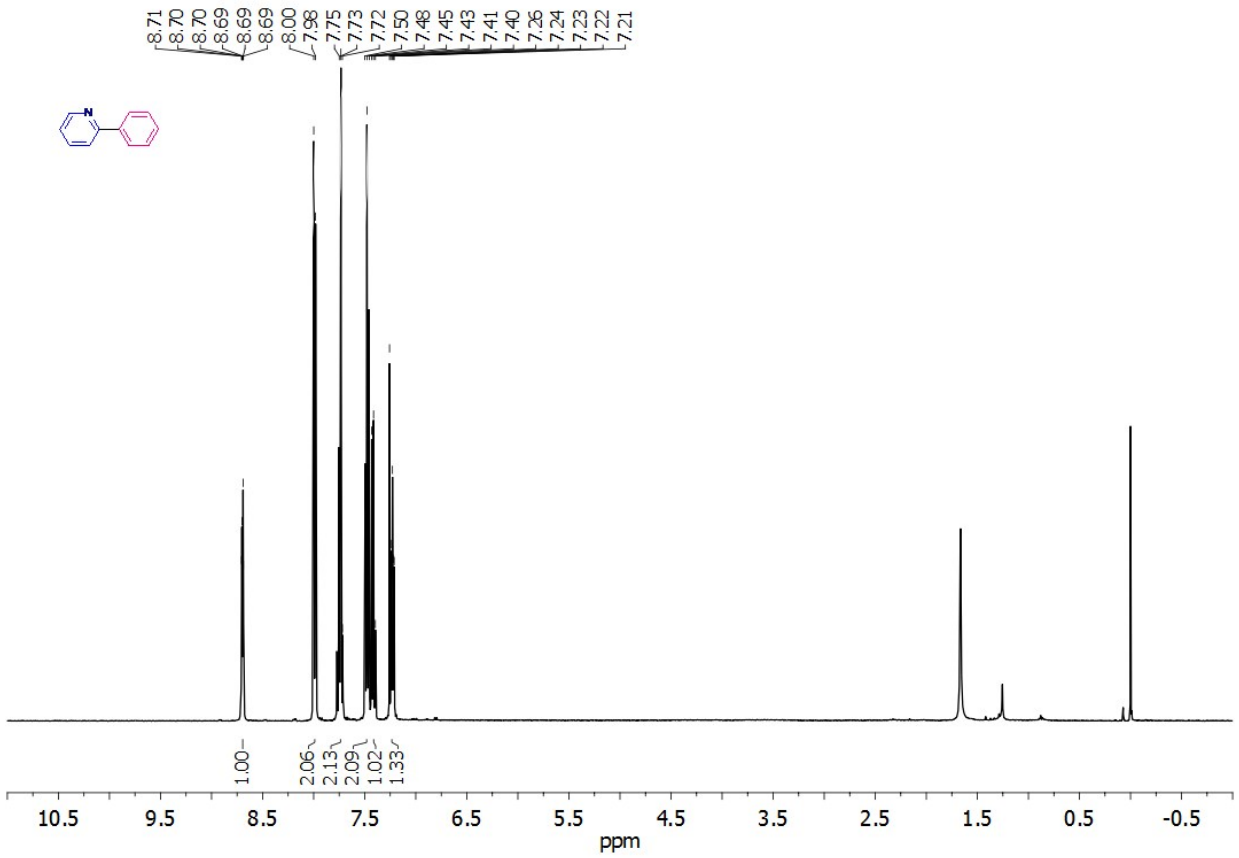
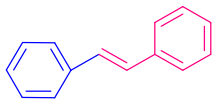
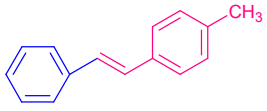


Fig. S26: ^{1}H NMR of 2-phenyl pyridine (3q)

Spectral data (^{1}H and ^{13}C NMR) of Heck-Mizoroki coupling product

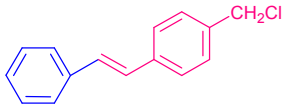


trans-stilbene (3a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.51 (d, 2H), 7.37-7.35 (d, 2H), 7.28-7.24 (m, 1H), 7.12 (s, 1H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 137.35, 128.69, 127.62, 126.52, 77.33, 77.02, 76.70.

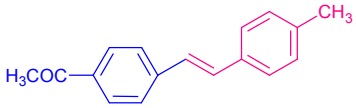


4-methyl-trans-stilbene (3b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.42 (d, 2H), 7.35-7.33 (d, 2H), 7.29-7.27 (d, 2H), 7.19-7.15 (m, 1H), 7.10-7.08 (d, 2H), 7.00-6.99 (s, 2H), 2.28 (s, 3H), **^{13}C**

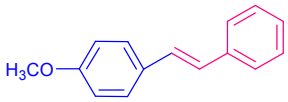
NMR ($CDCl_3$, 100 MHz): 137.53, 134.57, 129.48, 128.66, 128.64, 127.72, 127.41, 126.43, 126.40, 77.33, 77.02, 76.70, 21.34.



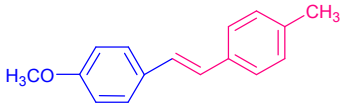
4-chloromethylene trans-stilbene (3c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.87 (d, 2H), 7.67-7.65 (d, 2H), 7.57-7.51 (m, 3H), 7.41-7.39 (d, 2H), 7.37-7.35 (d, 1H), 7.13-7.11 (d, 1H), 5.21 (s, 2H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 137.53, 134.57, 129.40, 128.66, 127.77, 127.41, 126.43, 77.33, 77.02, 76.70, 21.93.



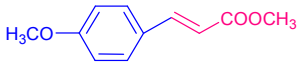
4-acetyl-4-methyl trans-stilbene (3d): ^{13}C NMR ($CDCl_3$, 100 MHz): 197.82, 142.29, 138.39, 135.78, 133.95, 131.45, 129.59, 128.88, 126.76, 126.52, 126.39, 77.33, 77.01, 76.99, 26.92, 21.44.



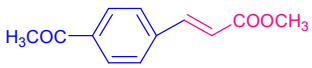
4-methoxy trans-stilbene (3e): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.43 (m, 3H), 7.35-7.33 (d, 2H), 7.31-7.20 (m, 2H), 7.08-7.04 (d, 1H), 6.98-6.94 (d, 1H), 6.90-6.88 (d, 2H), 3.82 (s, 3H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 159.46, 137.70, 128.72, 128.27, 127.58, 127.21, 126.64, 126.31, 114.20, 77.33, 77.01, 76.69, 55.44.



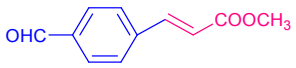
4-methoxy-4-methyl trans-stilbene (3f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.42 (d, 2H), 7.39-7.37 (d, 2H), 7.15-7.13 (d, 2H), 7.03-6.99 (d, 1H), 6.96-6.92 (d, 1H), 6.89-6.87 (d, 2H), 3.82 (s, 3H), 2.34 (s, 3H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 159.43, 137.22, 130.36, 129.36, 127.26, 126.59, 126.16, 114.12, 77.33, 77.01, 76.70, 55.36, 21.37.



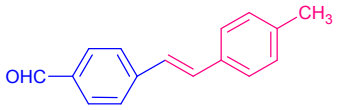
(E)-methyl 3-(4-methoxyphenyl) acrylate (3g): ^{13}C NMR ($CDCl_3$, 100 MHz): 168.18, 144.75, 133.45, 129.73, 127.23, 115.95, 114.25, 77.33, 77.01, 76.69.



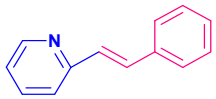
(E)-methyl 3-(4-acetylphenyl) acrylate (3h) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98-7.96 (d, 2H), 7.73-7.69 (d, 1H), 7.62-7.60 (d, 2H), 6.55-6.48 (d, 1H), 3.84 (s, 3H), 2.64 (s, 3H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 197.45, 167.31, 143.06, 139.29, 137.69, 129.31, 128.09, 126.57, 77.33, 77.01, 76.69, 51.95, 26.54.



(E)-methyl 3-(4-formylphenyl) acrylate (3i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04, (s, 1H), 7.92-7.90 (d, 2H), 7.74-7.67 (m, 3H), 6.58-6.54 (d, 1H), 3.86 (s, 3H), **^{13}C NMR** ($CDCl_3$, 100 MHz): 191.51, 167.35, 143.53, 139.76, 137.69, 130.54, 128.84, 121.40, 77.34, 77.02, 76.70, 51.96.



4-formyl-4-methyl trans-stilbene (3j): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97, (s, 1H), 7.86-7.84 (d, 2H), 7.647.62(d, 2H), 7.44-7.42 (d, 2H), 7.19-7.17 (d, 2H), 7.10-7.06 (d, 2H), 2.36 (s, 3H).



2-Styryl pyridine (3k): ^{1}H NMR (400 MHz, CDCl3): δ = 8.69-8.68 (d, 1H), 8.41-8.39 (d, 1H), 7.84-7.76 (m, 4H), 7.38-7.30 (m, 3H), 7.19-7.15 (m, 1H), 7.12-7.07 (m, 1H).

^{1}H and ^{13}C NMR Spectra of Heck-Mizoroki coupling product:

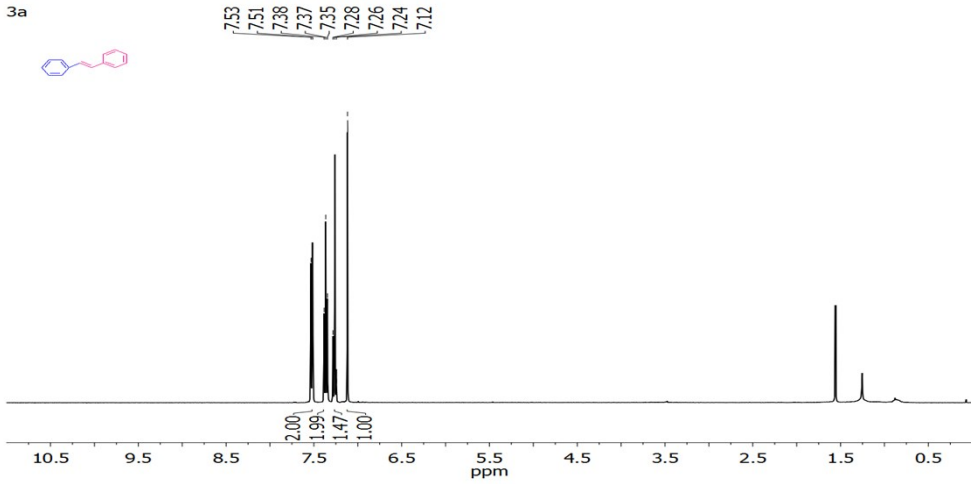


Fig. S27: ^{1}H NMR of trans-stilbene (3a)

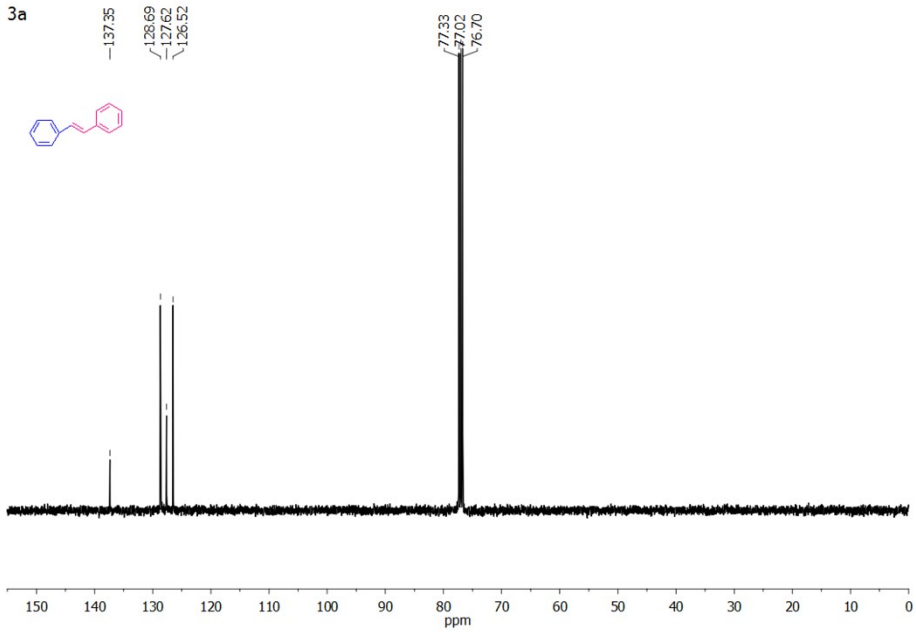


Fig. S28: ^{13}C NMR of trans-stilbene (3a)

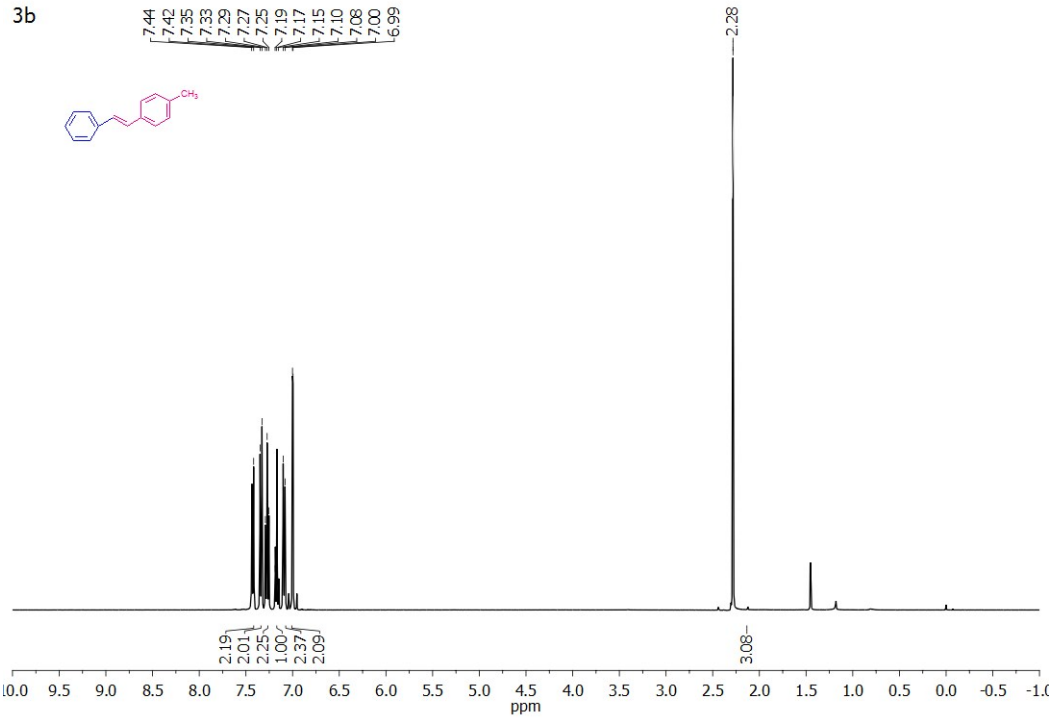


Fig. S29: ^{1}H NMR of 4-methyl trans-stilbene (3b)

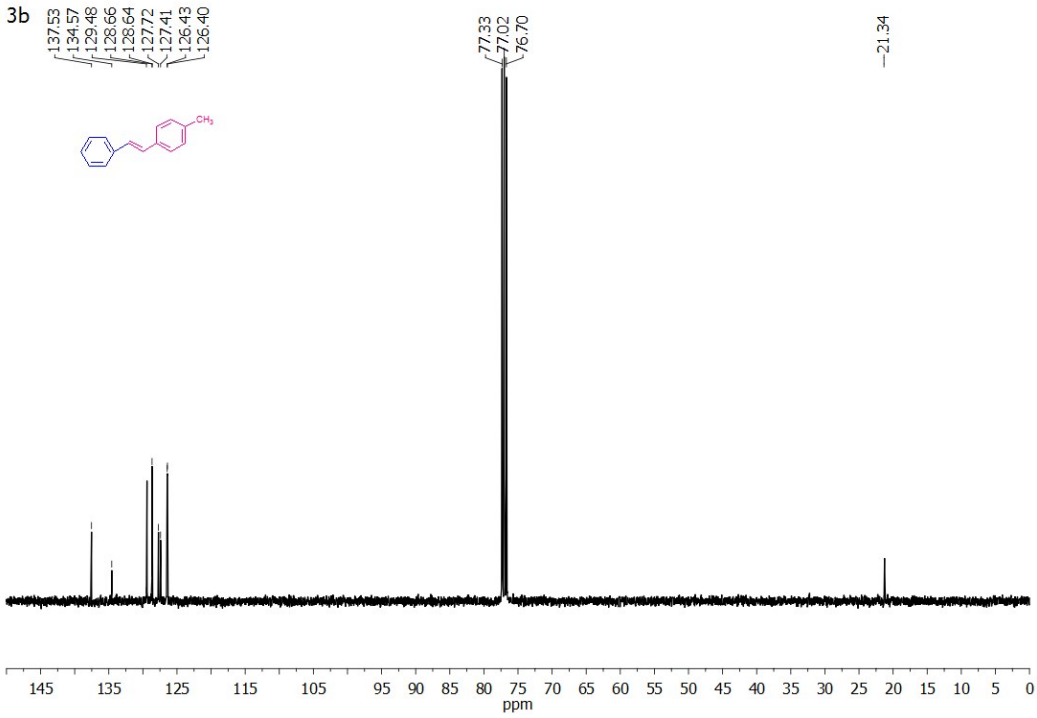


Fig. S30: ^{13}C NMR of 4-methyl trans-stilbene (3b)

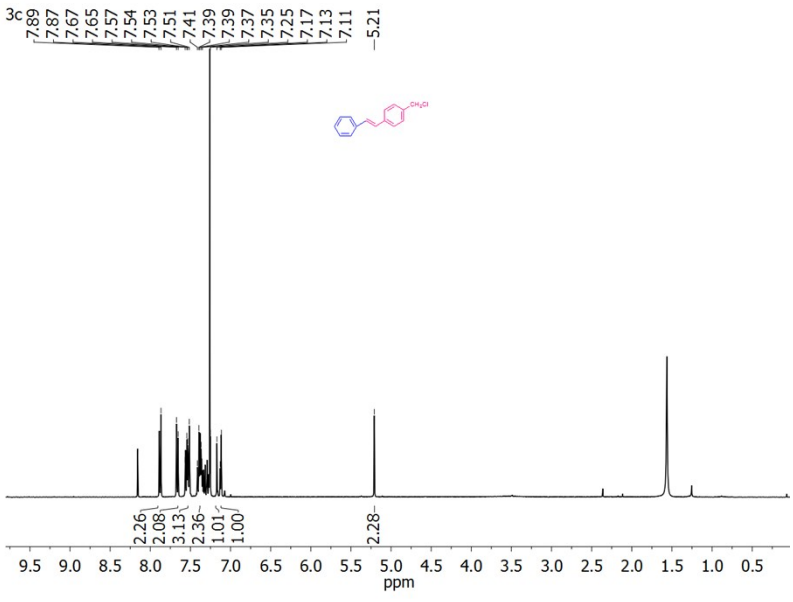


Fig. S31: ^{1}H NMR of 4-chloromethylene trans-stilbene (3c)

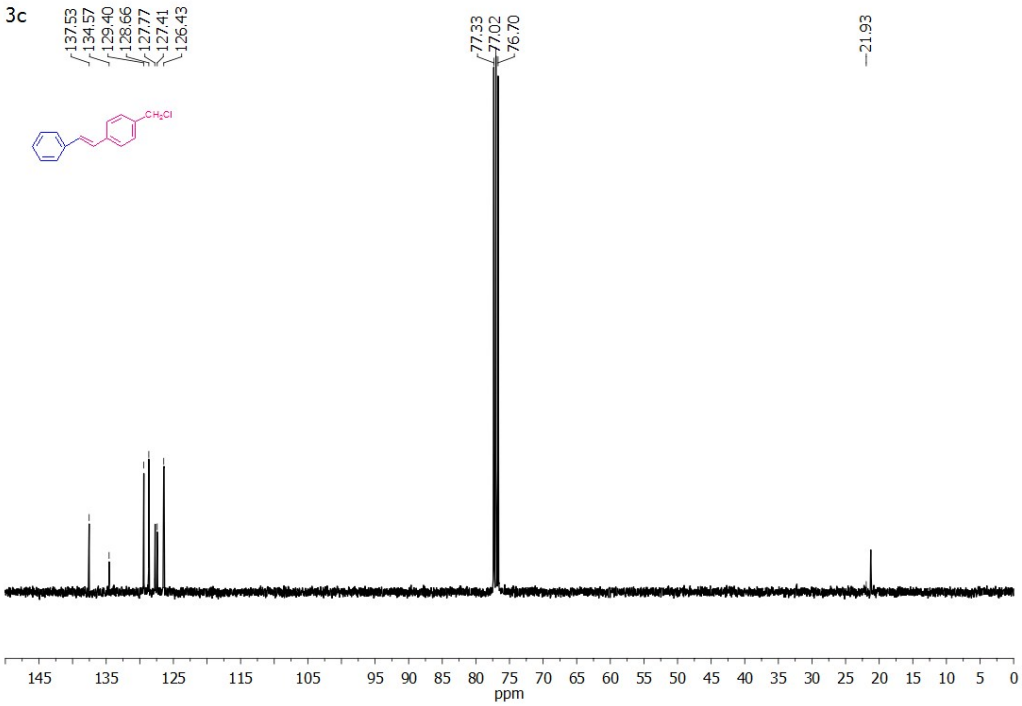


Fig. S32: ^{13}C NMR of 4-chloromethylene trans-stilbene (3c)

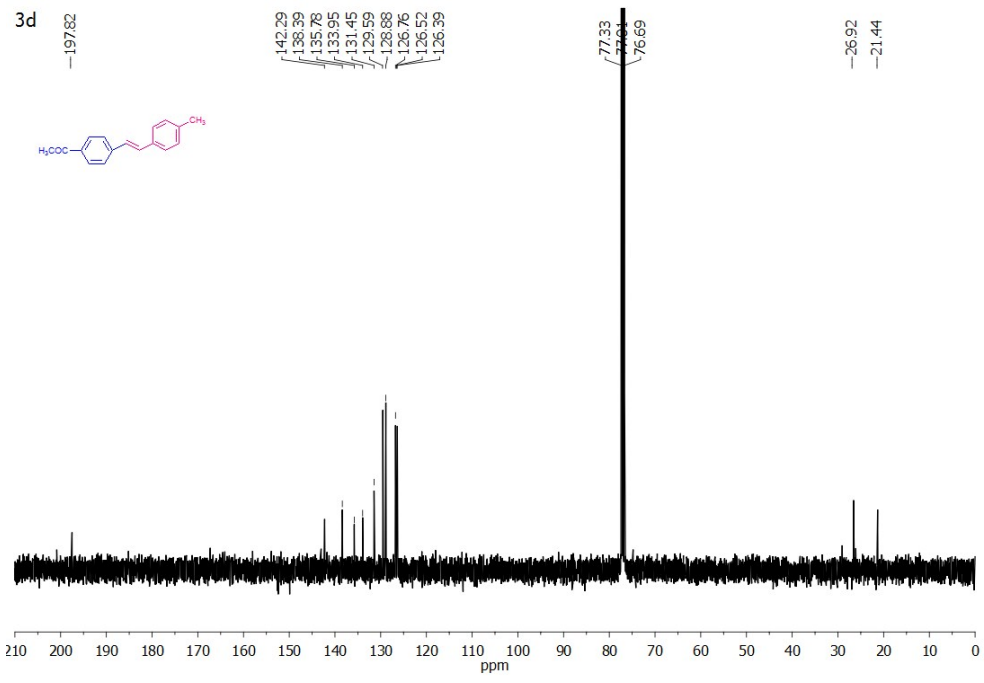


Fig. S33: ^{13}C NMR of 4-acetyl-4-methyl trans-stilbene (3d)

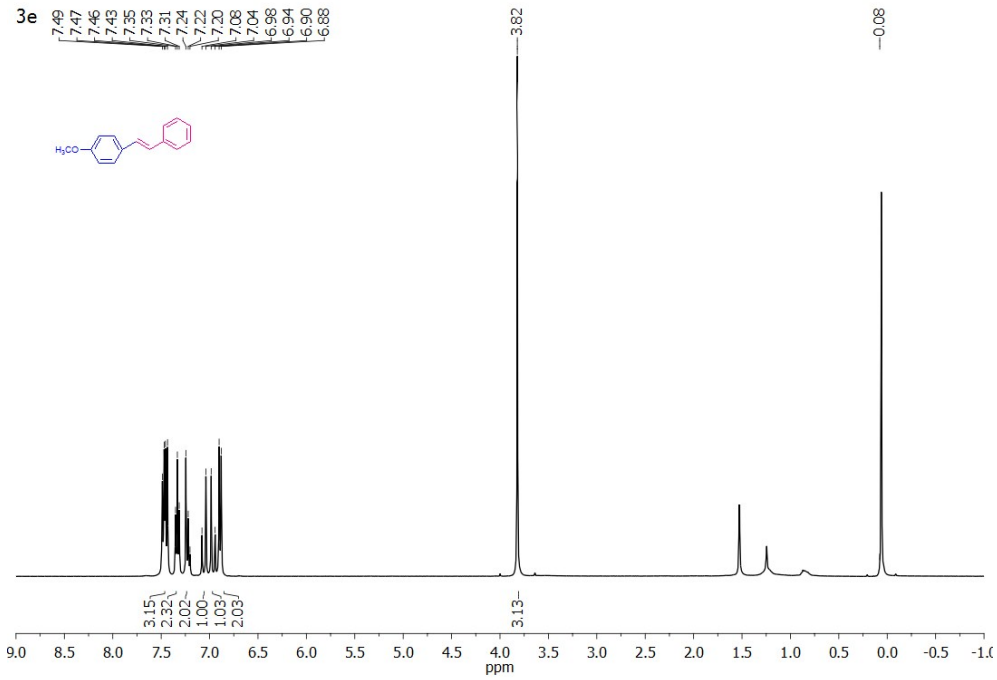


Fig. S34: ^{1}H NMR of 4-methoxy trans-stilbene (3e)

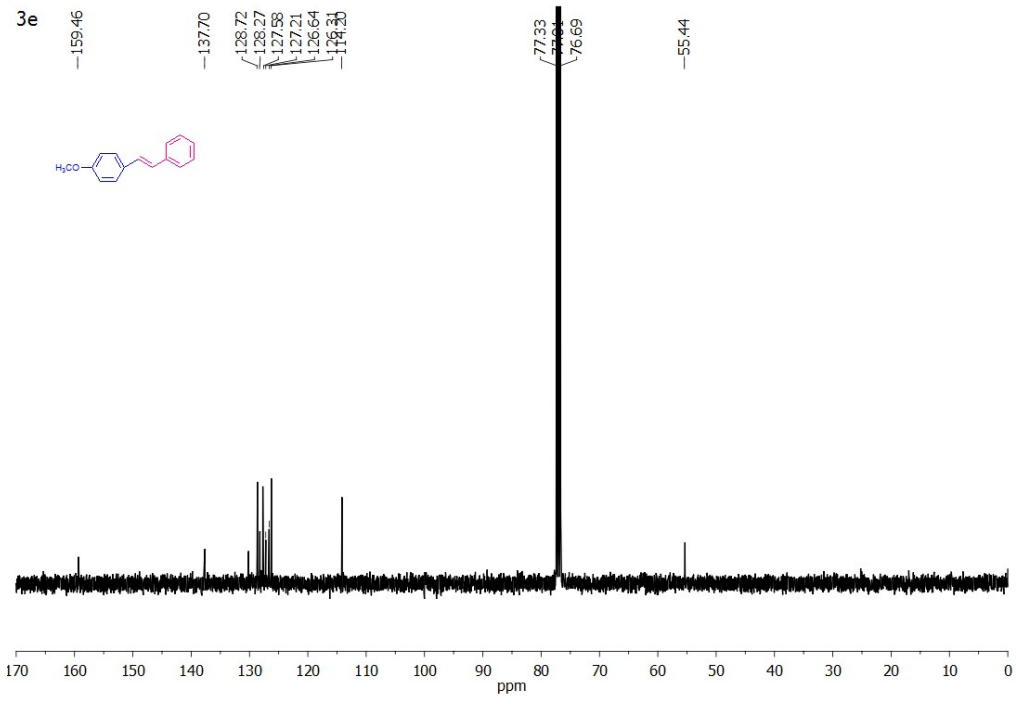


Fig. S35: ^{13}C NMR of 4-methoxy trans-stilbene (3e)

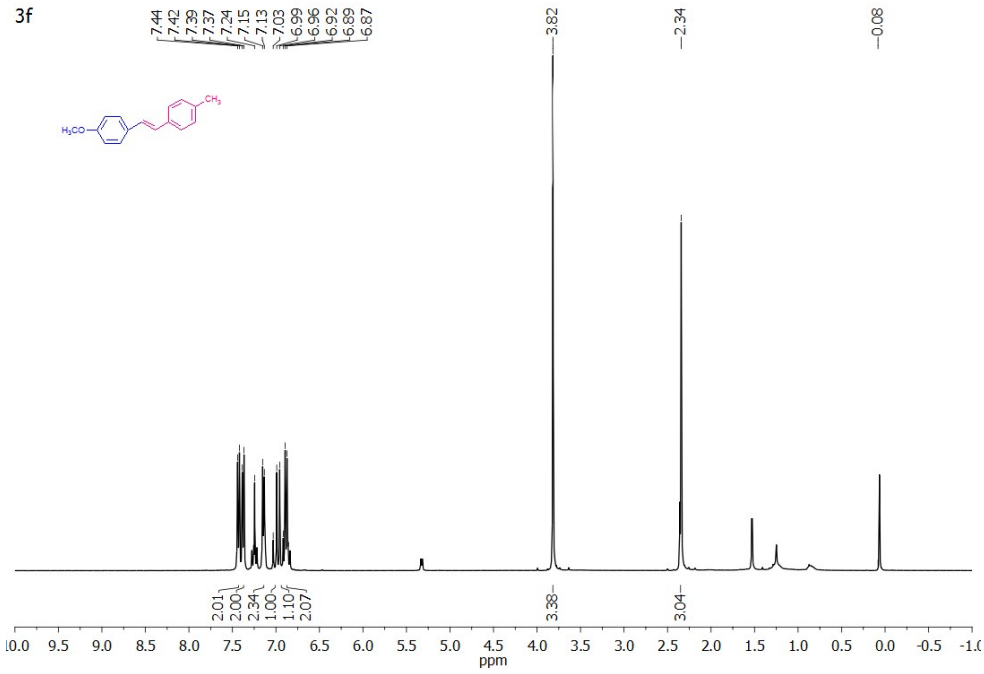


Fig. S36: ^{1}H NMR of 4-methoxy-4-methyltrans-stilbene (3f)

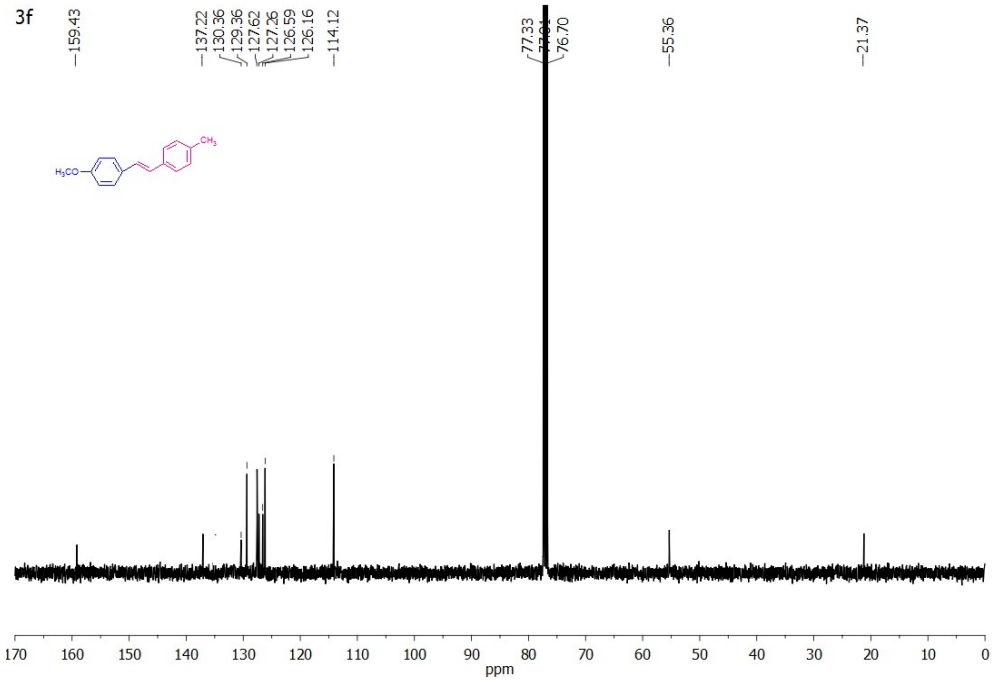


Fig. S37: ^{13}C NMR of 4-methoxy-4-methyltrans-stilbene (3f)

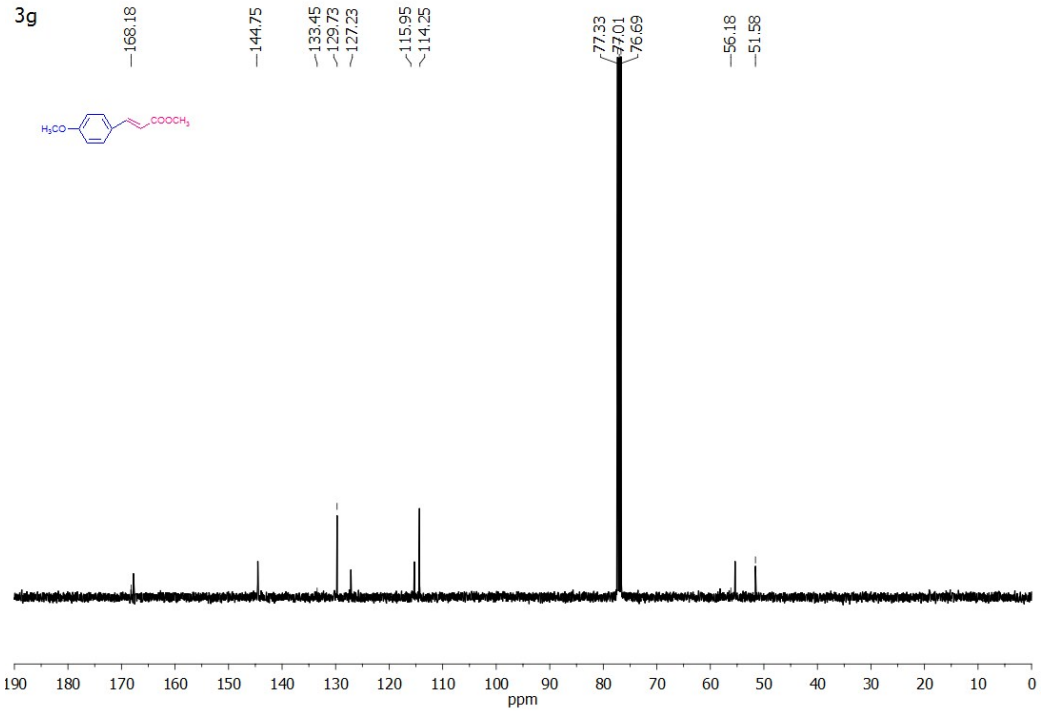


Fig. S38: ^{13}C NMR of (E)-methyl 3-(4-methoxyphenyl) acrylate (3g)

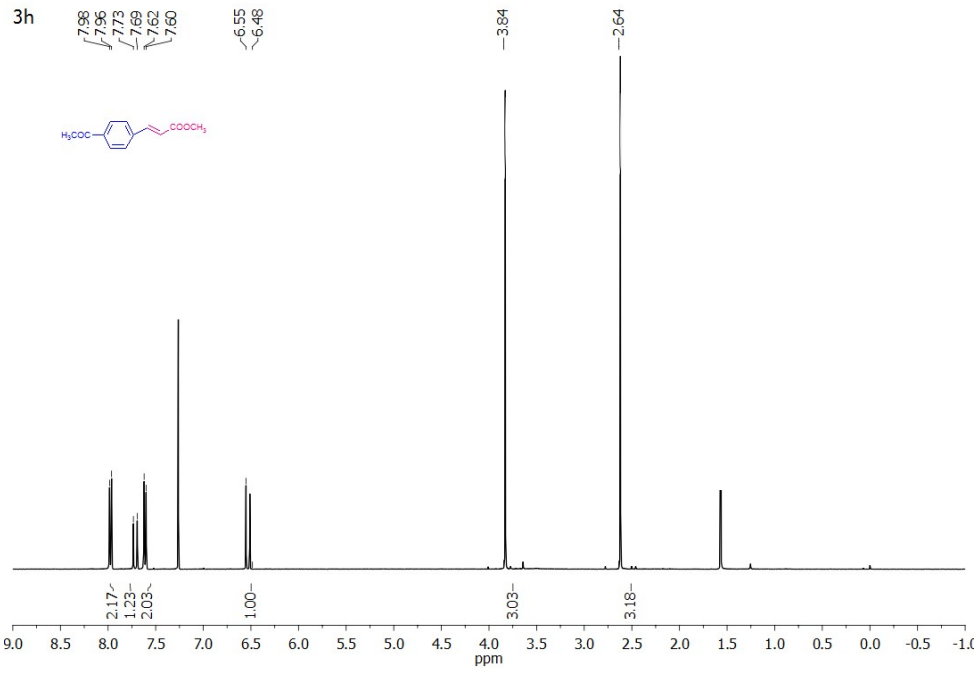


Fig. S39: ^{1}H NMR of (E)-methyl 3-(4-acetylphenyl) acrylate (3h)

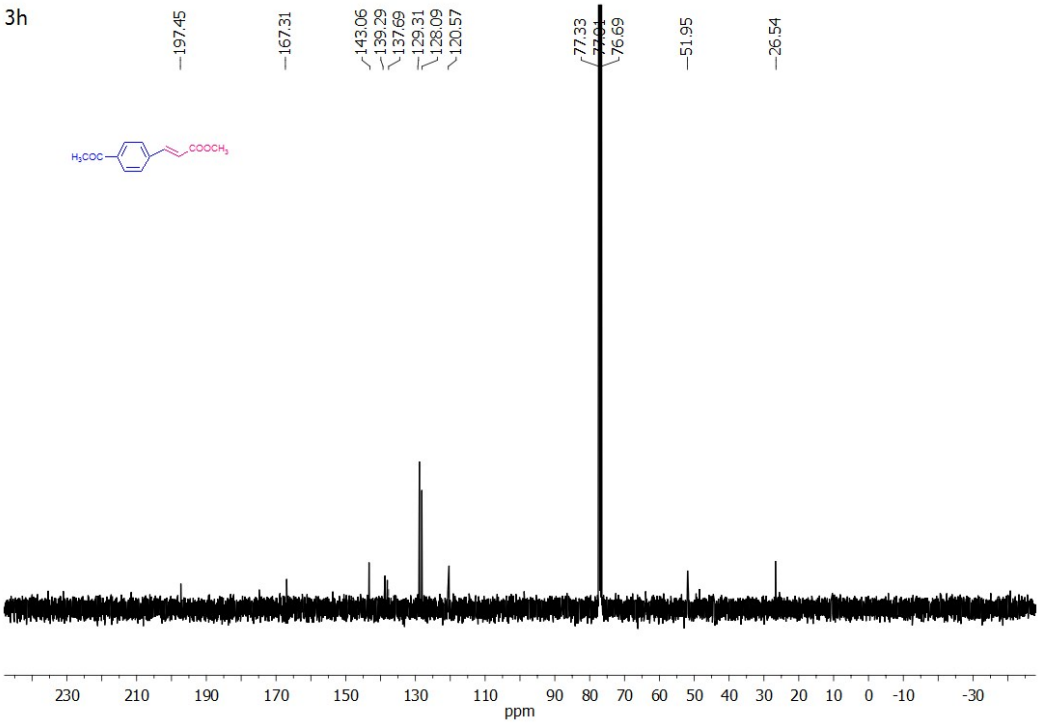


Fig. S40: ^{13}C NMR of (E)-methyl 3-(4-acetylphenyl) acrylate (3h)

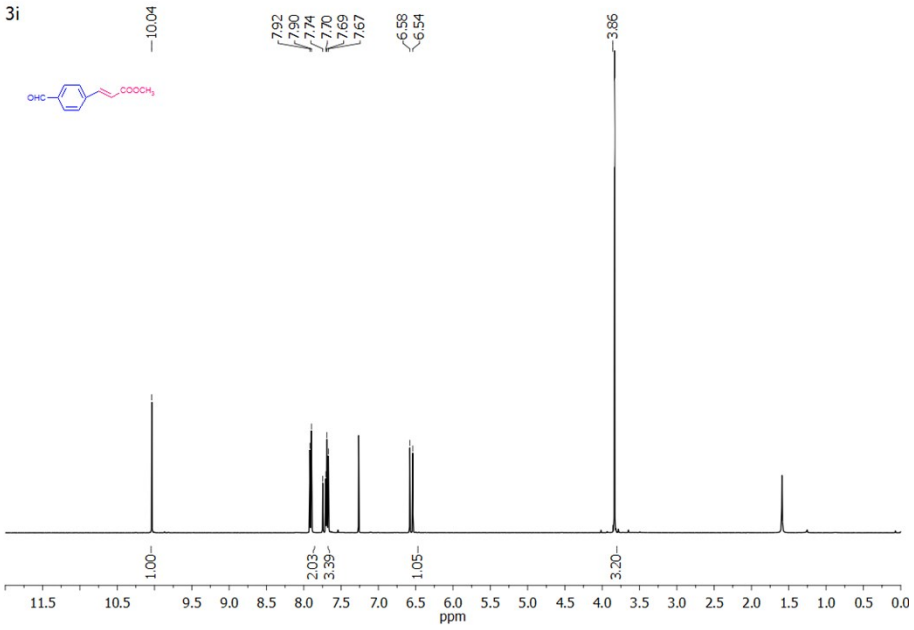


Fig. S41: ^{1}H NMR of (E)-methyl 3-(4-formylphenyl) acrylate (3i)

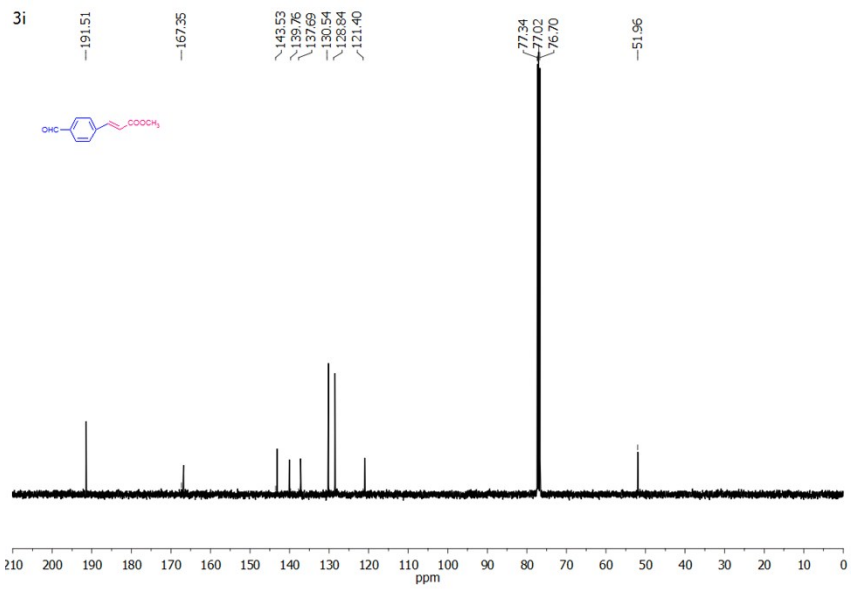


Fig. S42: ^{13}C NMR of (E)-methyl 3-(4-formylphenyl) acrylate (3i)

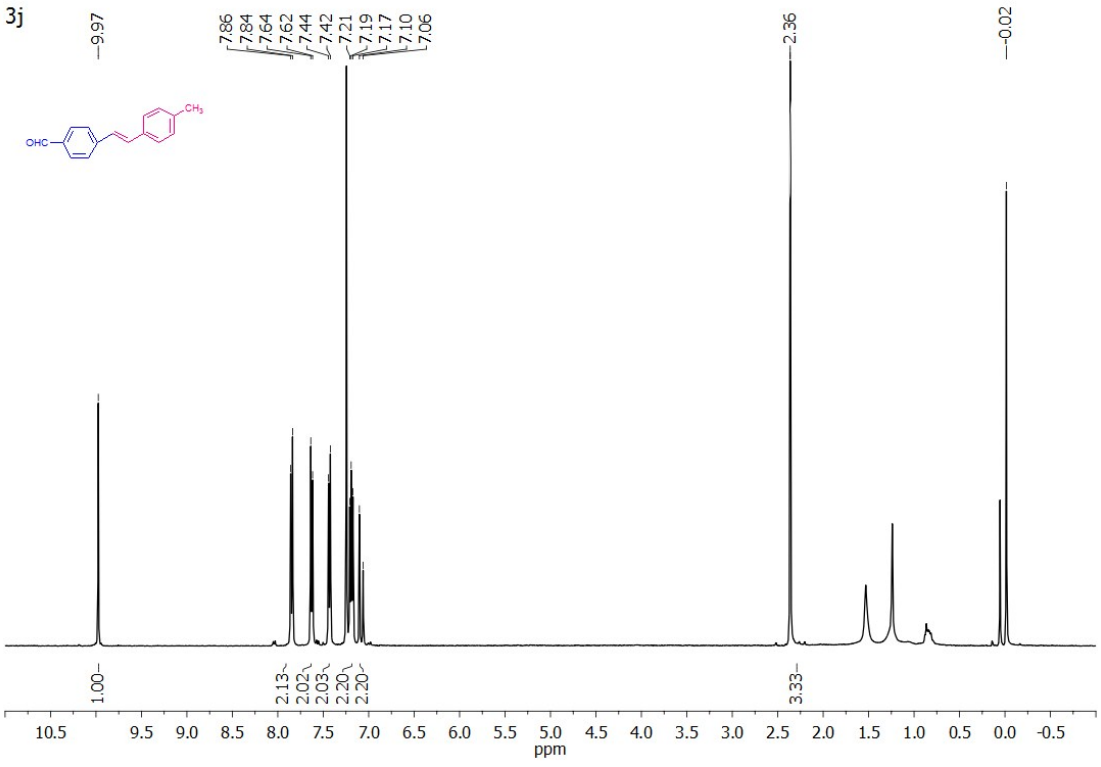


Fig. S43: ^{1}H NMR of 4-formyl-4-methyl trans-stilbene (3j)

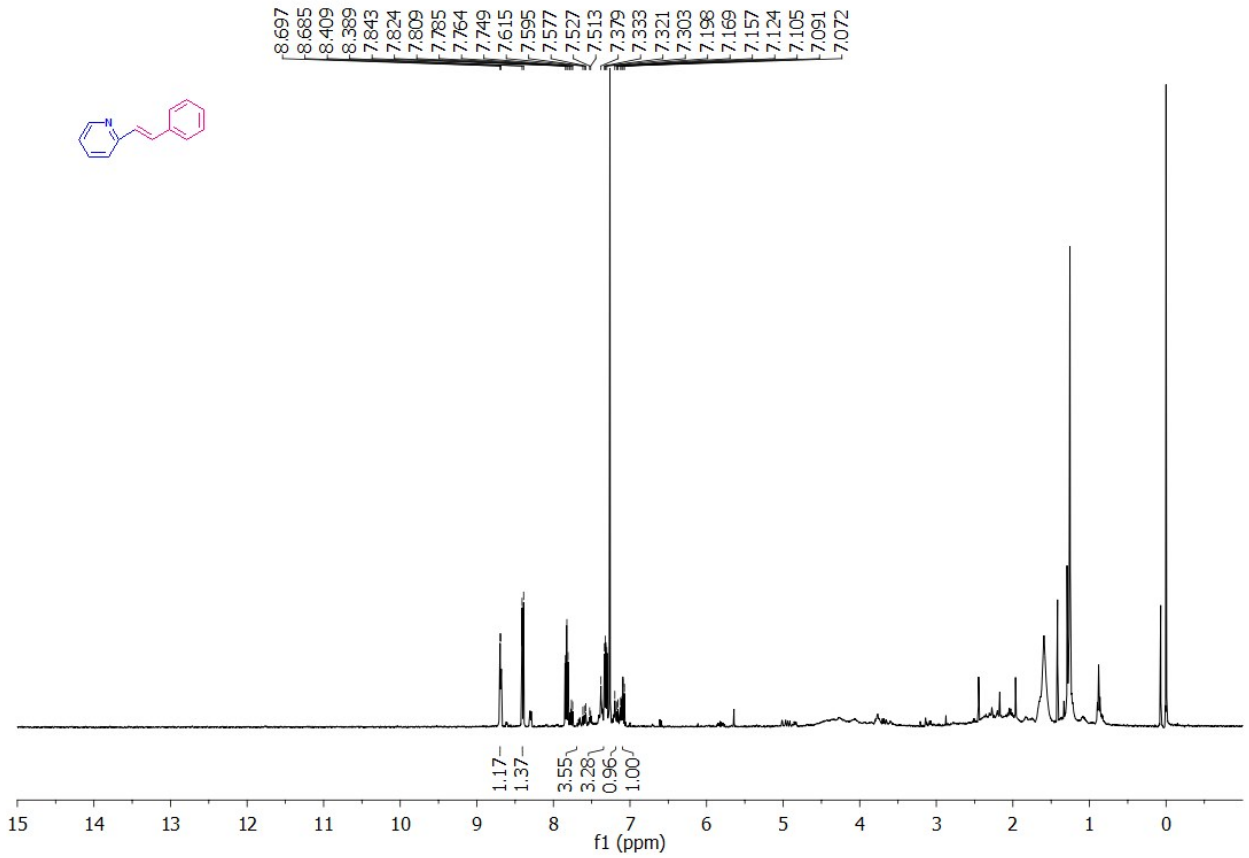


Fig. S44: ^{1}H NMR of 2-styryl pyridine (3k)