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

Furaldehyde based magnetic supported palladium nanoparticles as an efficient heterogenous catalyst for Mizoroki-Heck cross-coupling reaction

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1. Experimentals

General

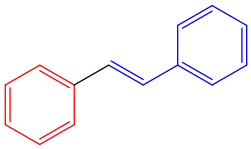
Chemicals and reagents were purchased from Sigma-Aldrich from a local vendor and used without further purifications. All solvents such as ethylacetate, hexane, *N,N′*-Dimethylformamide, were also purchased from local vendor and were distilled before use. The progress of the reactions was monitored using TLC on silica gel 60 F254 TLC plates from Merck. Column chromatography was performed for purification of crude on silica gel (100-200 mesh). Melting points were recorded by an open glass capillary sealed at one end tube. 1H NMR (400 MHz) and 13 C NMR (101 MHz) spectra on Bruker NMR spectrometer using TMS as an internal standard.

Typical procedure for Mizoroki-Heck cross coupling reaction (Compounds 3a -3n)

In a hot air dried 15 mL sealed tube, arylhalide (1.0 mmol), terminal alkene (1.2 mmol) were dissolved in 3 mL DMF and the resulting solution was purged with N_2 gas for about 3 mins. Then potassium triphosphate (3.0 mmol) and the nanocatalyst (0.02 mmol) were added and immediately the sealed tube was closed under N_2 atmosphere and continuously stirred at 110 °C until the reaction is complete. Then, the reaction mixture was diluted with ethylacetate and the catalyst was recovered using an external magnet. The organic-layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure to afford crude. The crude was further chromatographed on silica-gel bed using hexane:ethylacetate mixture (10:1) to get pure desired product.

2. Spectral data of compounds

Compound 3a



(E)-1,2-diphenylethene : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a off-white solid (0.352 g, 97%)

Melting point: 120-124°C

^{1}H NMR (400 MHz, DMSO) δ 7.67 – 7.56 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.27 (s, 1H).

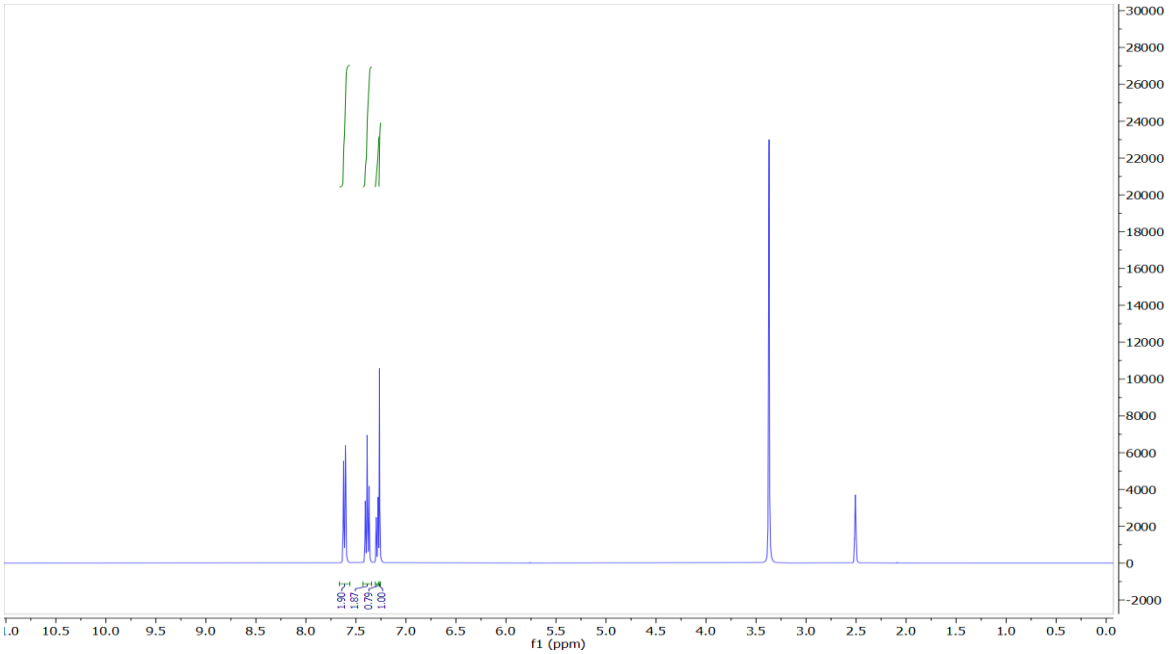
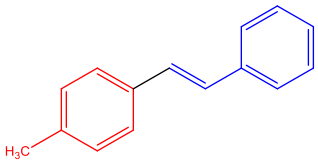


Fig. S1 : ^{1}H NMR spectrum of (E)-1,2-diphenylethene

Compound 3b



(E)-1-methyl-4-styrylbenzene : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a white solid (0.362 g, 93%)

Melting point: 104-106 °C

^{1}H NMR (400 MHz, DMSO) δ 7.61 – 7.56 (m, 2H), 7.55 – 7.45 (m, 2H), 7.37 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.21 (d, *J* = 2.3 Hz, 3H), 7.19 (s, 1H), 2.32 (s, 3H).

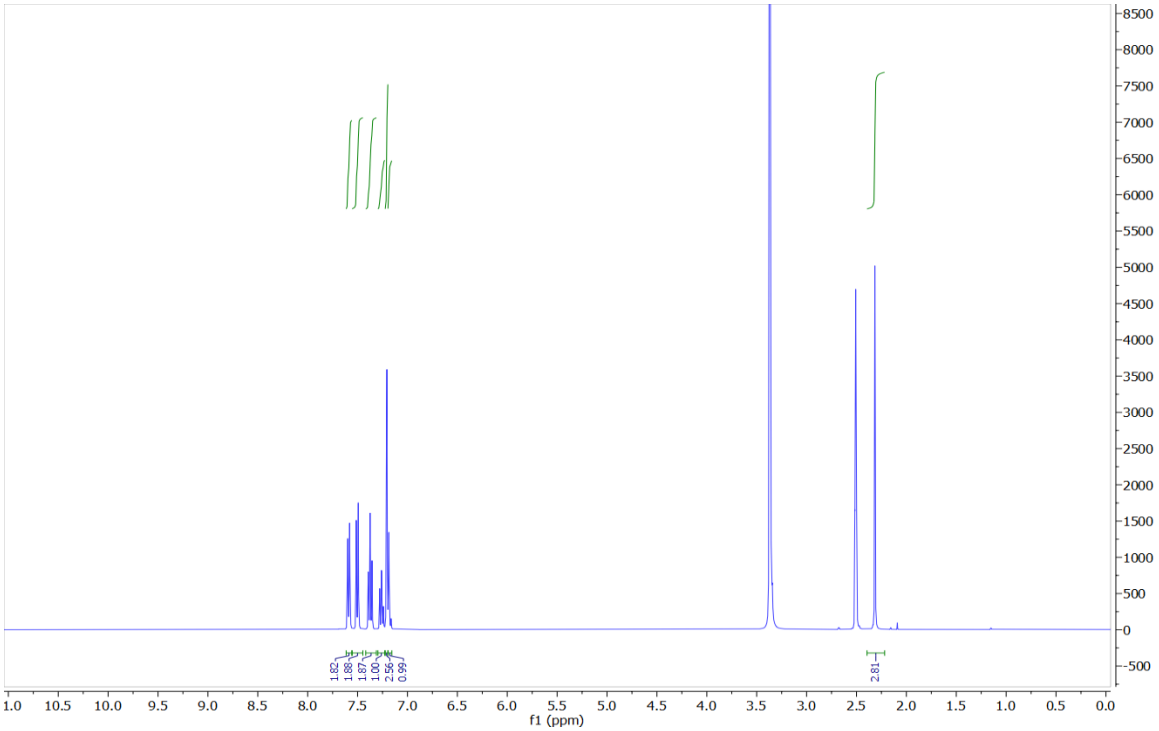
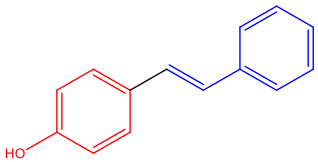


Fig. S2 : ^{1}H NMR spectrum of (E)-1-methyl-4-styrylbenzene

Compound 3c



(E)-4-styrylphenol : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a off-white solid (0.374 g, 95%)

Melting point: 95-98 °C

^{1}H NMR (400 MHz, DMSO) δ 9.60 (s, 1H), 7.58 – 7.51 (m, 2H), 7.47 – 7.39 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.18 (m, 1H), 7.15 (d, *J* = 16.4 Hz, 1H), 7.01 (d, *J* = 16.4 Hz, 1H), 6.82 – 6.73 (m, 2H).

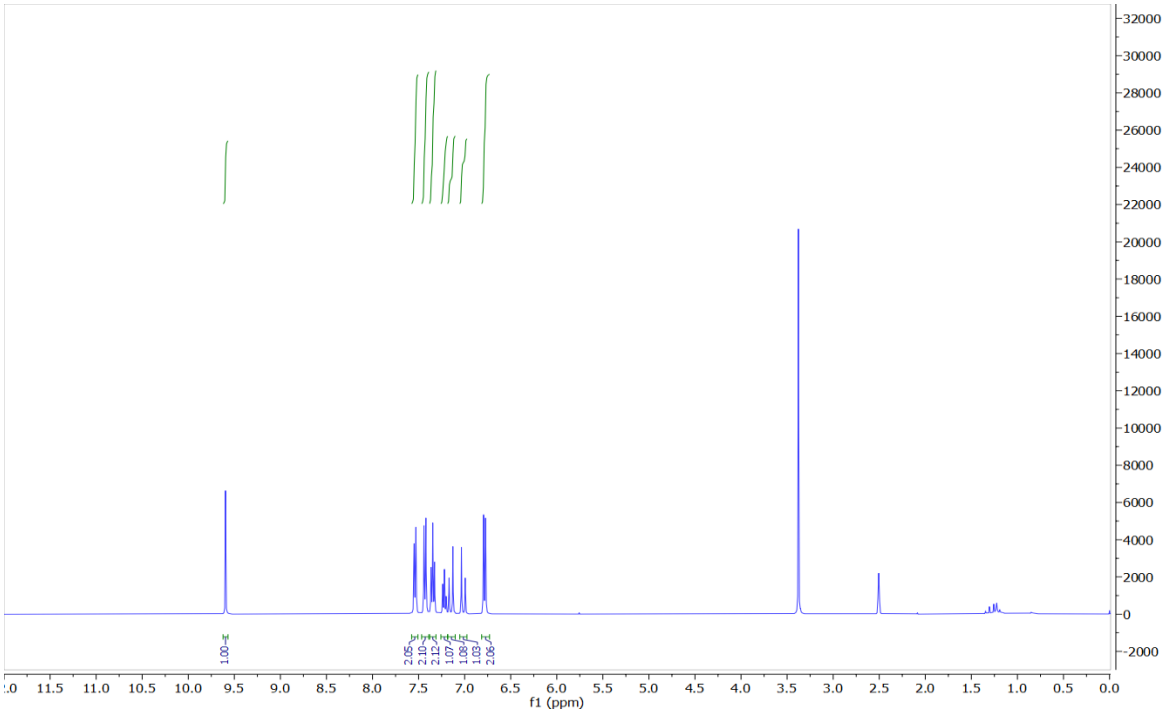


Fig. S3 : ^{1}H NMR spectrum of (E)-4-styrylphenol

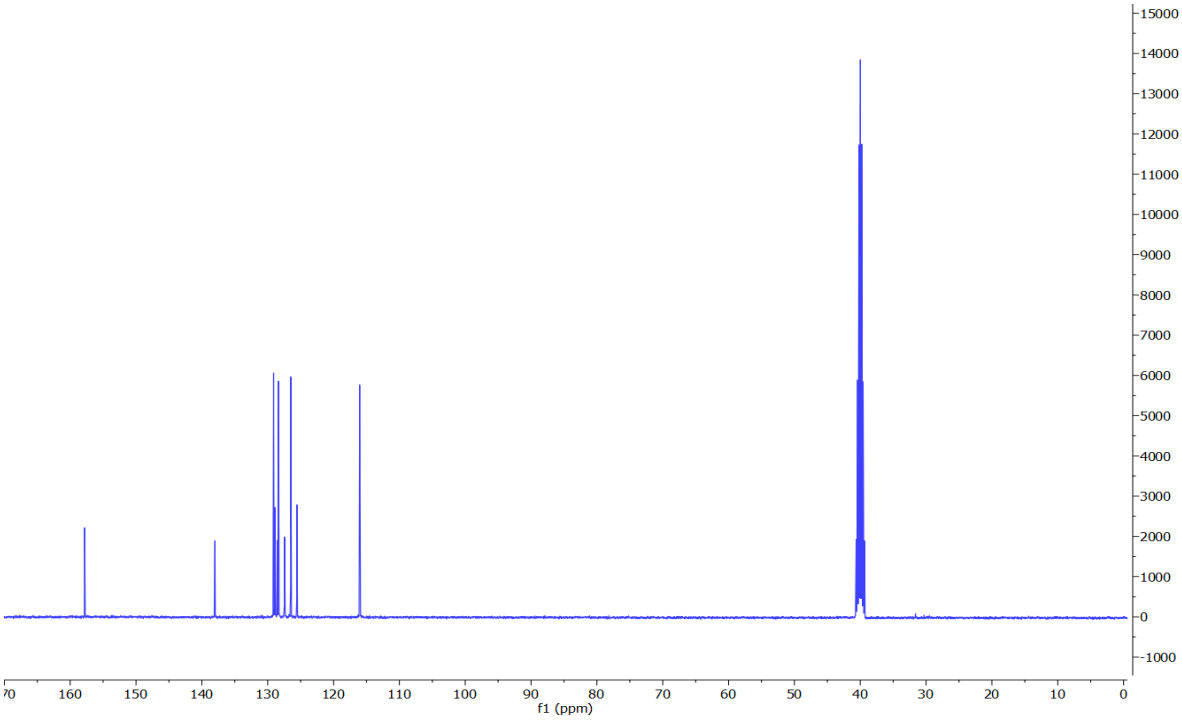
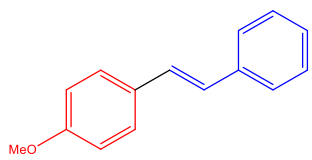


Fig. S4 : ^{13}C NMR spectrum of (E)-4-styrylphenol

Compound 3d



(E)-1-methoxy-4-styrylbenzene : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a white solid (0.391 g, 93%)

Melting point: 133-137 °C

^{1}H NMR (400 MHz, DMSO) δ 7.56 (td, *J* = 7.1, 1.8 Hz, 4H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.16 (m, 2H), 7.09 (d, *J* = 16.4 Hz, 1H), 6.99 – 6.91 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 159.46, 137.85, 130.13, 129.13, 128.53, 128.27, 127.65, 126.63, 126.58, 114.65, 55.62, 40.68.

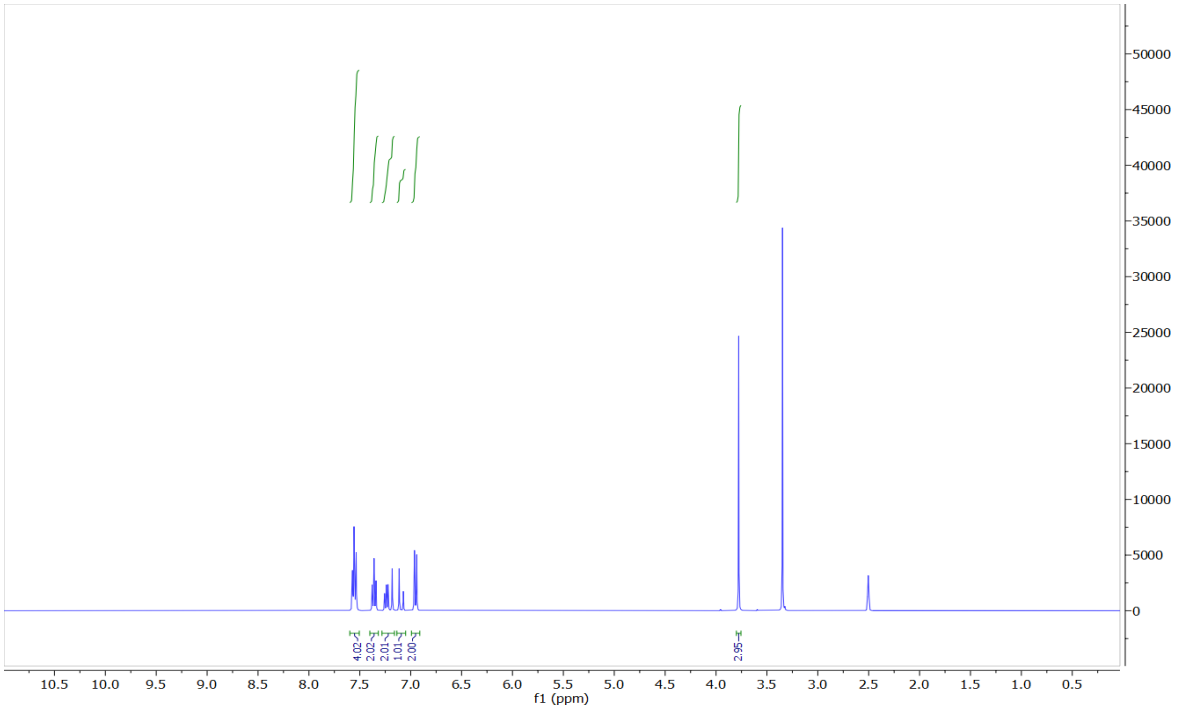


Fig. S5 : ^{1}H NMR spectrum of (E)-1-methoxy-4-styrylbenzene

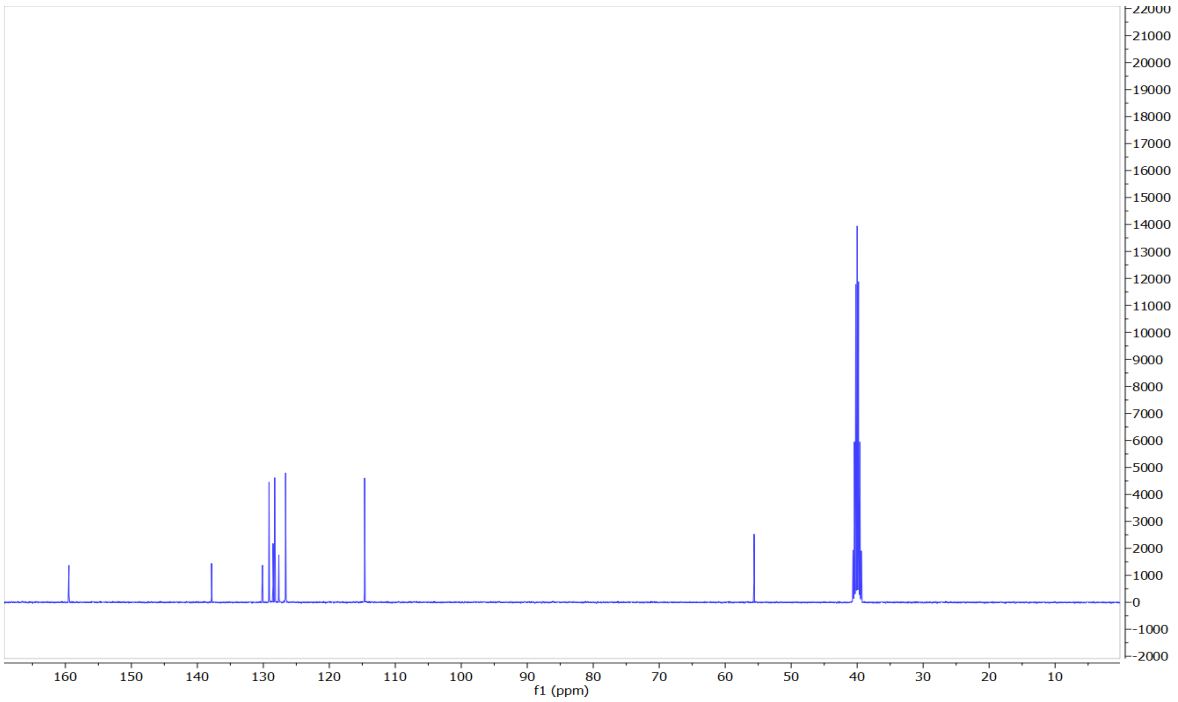
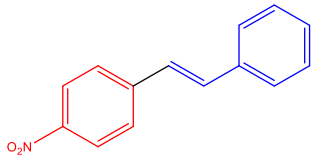


Fig. S6 : ^{13}C NMR spectrum of (E)-1-methoxy-4-styrylbenzene

Compound 3e



(E)-1-nitro-4-styrylbenzene : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a pale-yellow solid (0.373 g, 82%)

Melting point: 155-158 °C

^{1}H NMR (400 MHz, DMSO) δ 8.26 – 8.22 (m, 2H), 7.90 – 7.85 (m, 2H), 7.72 – 7.64 (m, 2H), 7.55 (d, *J* = 16.5 Hz, 1H), 7.44 (d, *J* = 6.3 Hz, 2H), 7.41 (d, *J* = 2.8 Hz, 1H), 7.38 – 7.31 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 146.67, 144.49, 136.75, 133.72, 129.32, 129.18, 127.78, 127.60, 126.85, 124.50.

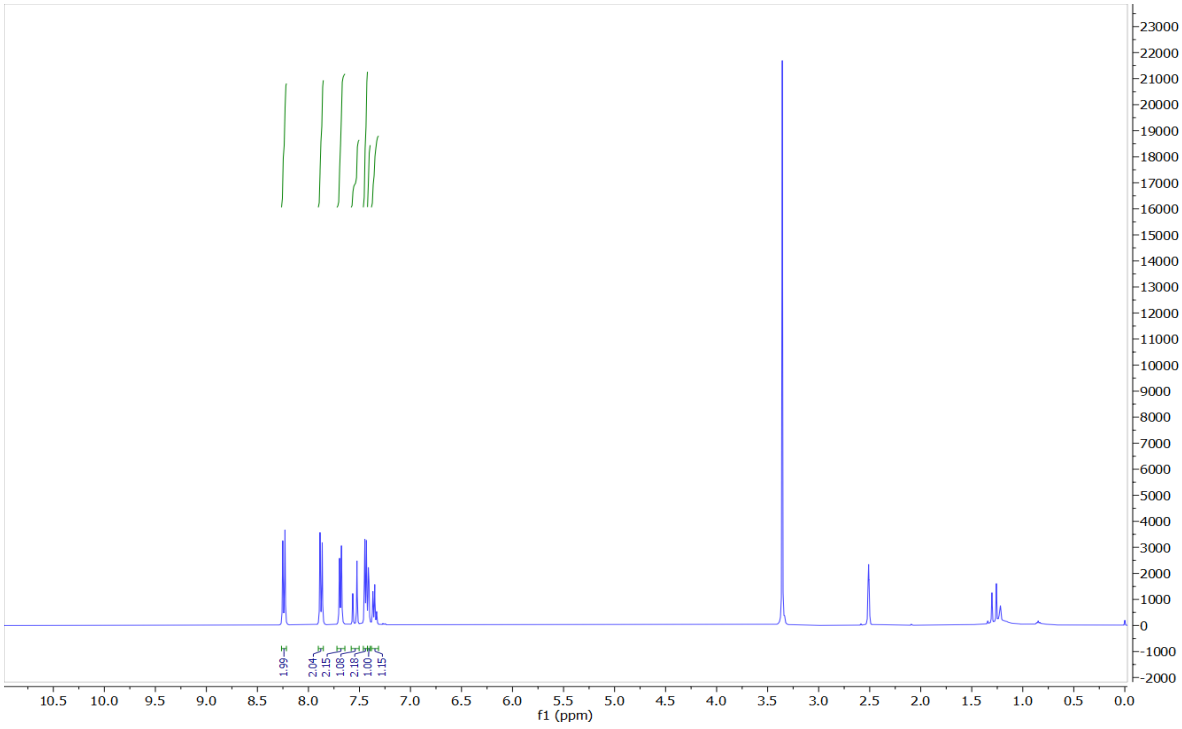


Fig. S7 : ^{1}H NMR spectrum of (E)-1-nitro-4-styrylbenzene

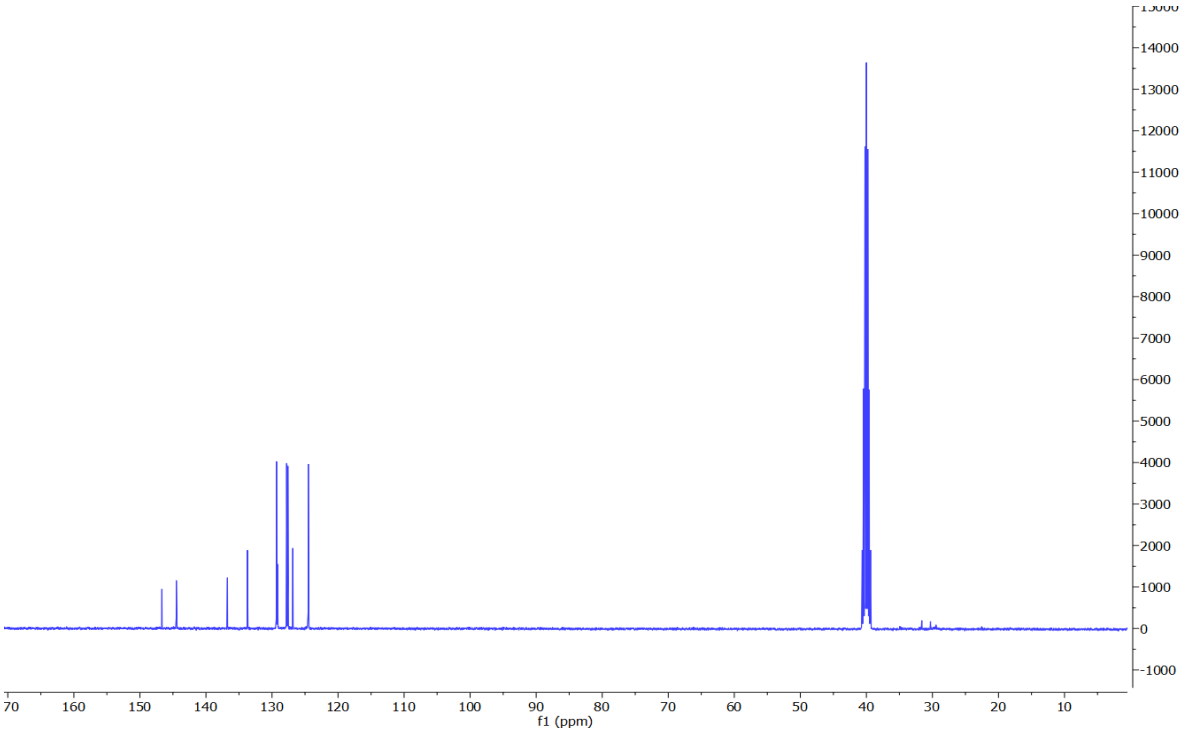
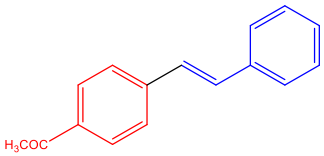


Fig. S8 : ^{13}C NMR spectrum of (E)-1-nitro-4-styrylbenzene

Compound 3f



(E)-1-acetyl-4-styrylbenzene : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a pale yellow solid (0.379 g, 85%)

Melting point: 145-148 °C

^{1}H NMR (400 MHz, DMSO) δ 8.01 – 7.92 (m, 2H), 7.76 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 1.9 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.48 – 7.40 (m, 3H), 7.40 – 7.26 (m, 3H), 2.58 (s, 3H).

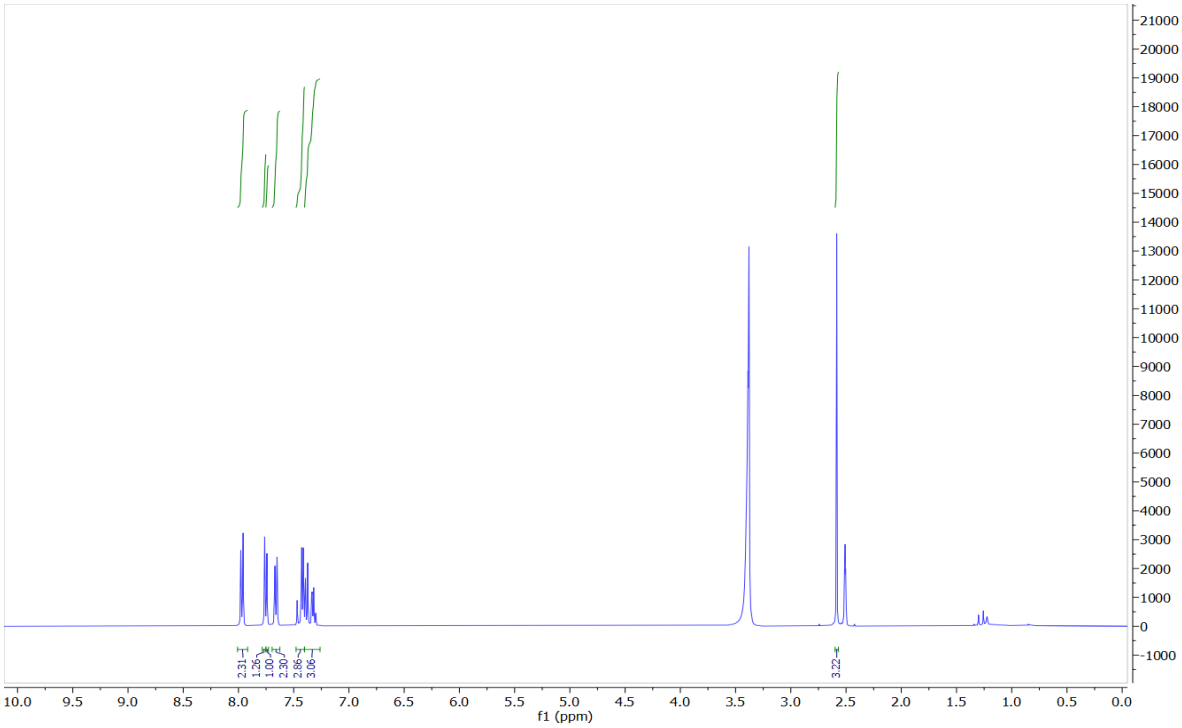
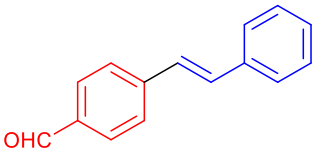


Fig. S9 : ^{1}H NMR spectrum of (E)-1-acetyl-4-styrylbenzene

Compound 3g



(E)-4-styrylbenzaldehyde: Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a white solid (0.350 g, 84%)

^{1}H NMR (400 MHz, DMSO) δ 9.99 (s, 1H), 7.96 – 7.89 (m, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.63 (m, 2H), 7.54 – 7.28 (m, 5H).

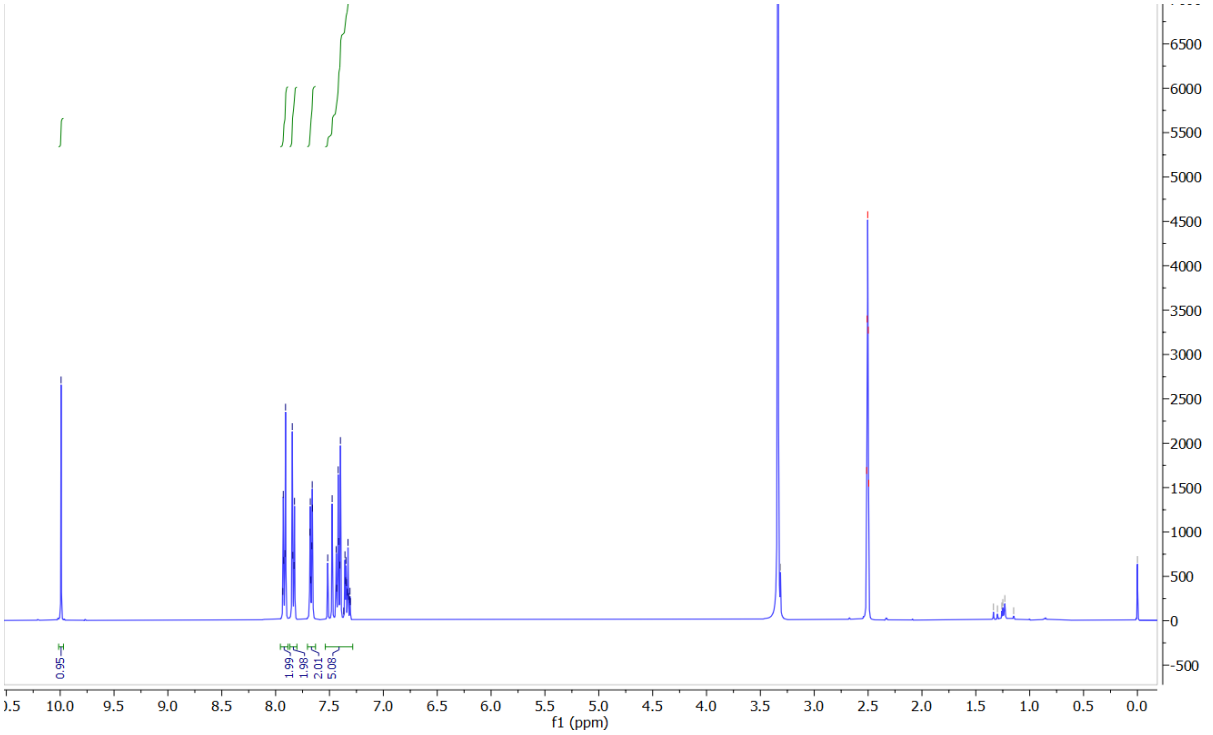
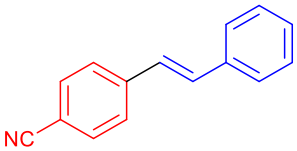


Fig. S10: ^{1}H NMR spectrum of (E)-4-styrylbenzaldehyde

Compound 3h



(E)-4-styrylbenzonitrile: Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a white solid (0.355 g, 86%)

^{1}H NMR (400 MHz, DMSO) δ 7.87 – 7.77 (m, 4H), 7.69 – 7.62 (m, 2H), 7.48 (d, *J* = 16.5 Hz, 1H), 7.42 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.39 – 7.28 (m, 2H).

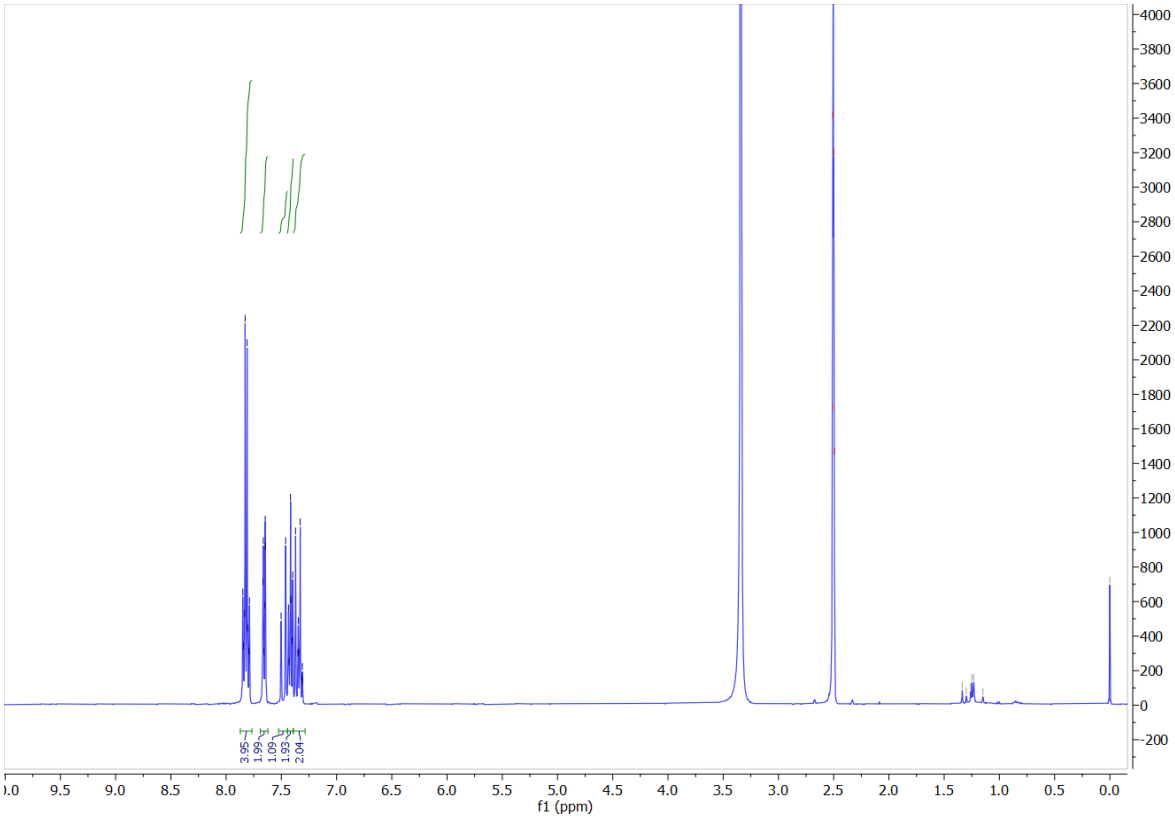
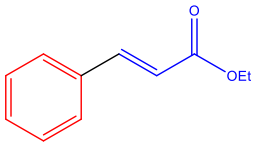


Fig. S11: ^{1}H NMR spectrum of (E)-4-styrylbenzonitrile

Compound 3i



Ethyl cinnamate: Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a colourless oil (0.343 g, 97%)

^{1}H NMR (400 MHz, DMSO) δ 7.76 – 7.65 (m, 3H), 7.47 – 7.40 (m, 3H), 6.65 (d, *J* = 16.1 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

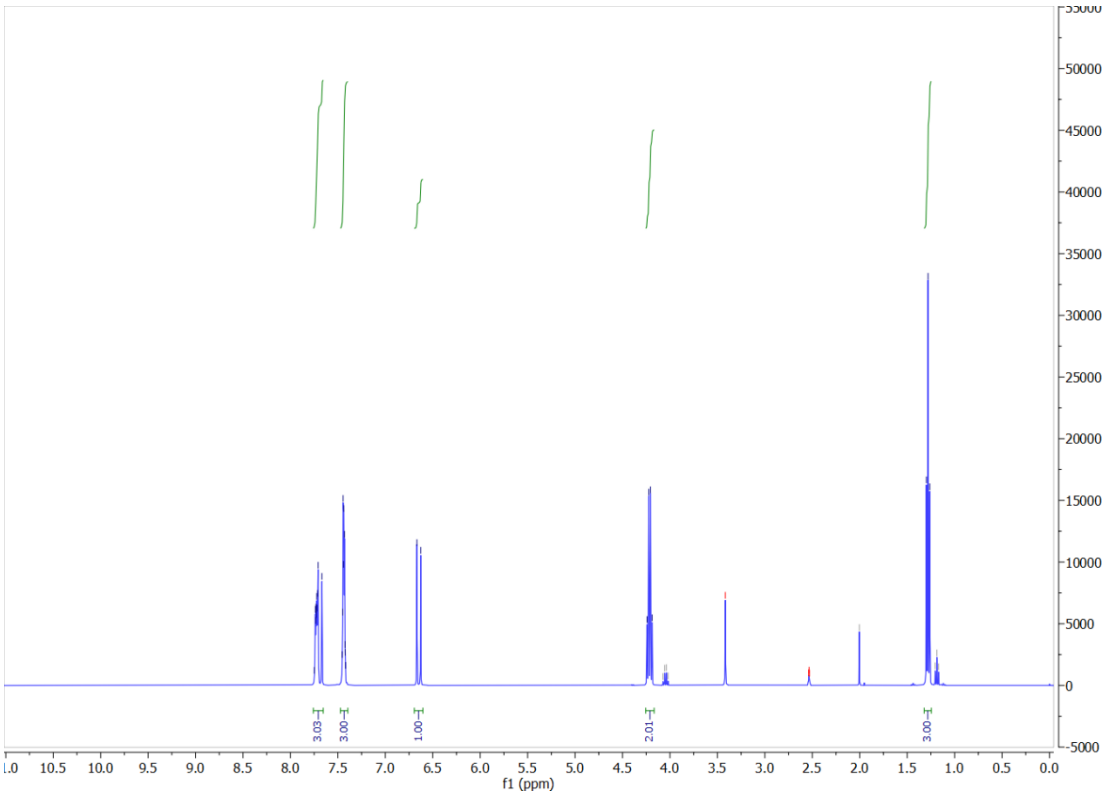
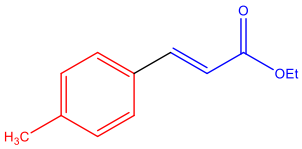


Fig. S12 : ^{1}H NMR spectrum of ethyl cinnamate

Compound 3j



ethyl (E)-3-(p-tolyl)acrylate: Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a colourless liquid (0.320 g, 84%)

^{1}H NMR (400 MHz, DMSO) δ 7.67 – 7.56 (m, 3H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.57 (d, *J* = 16.1 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.26 – 1.22 (m, 4H).

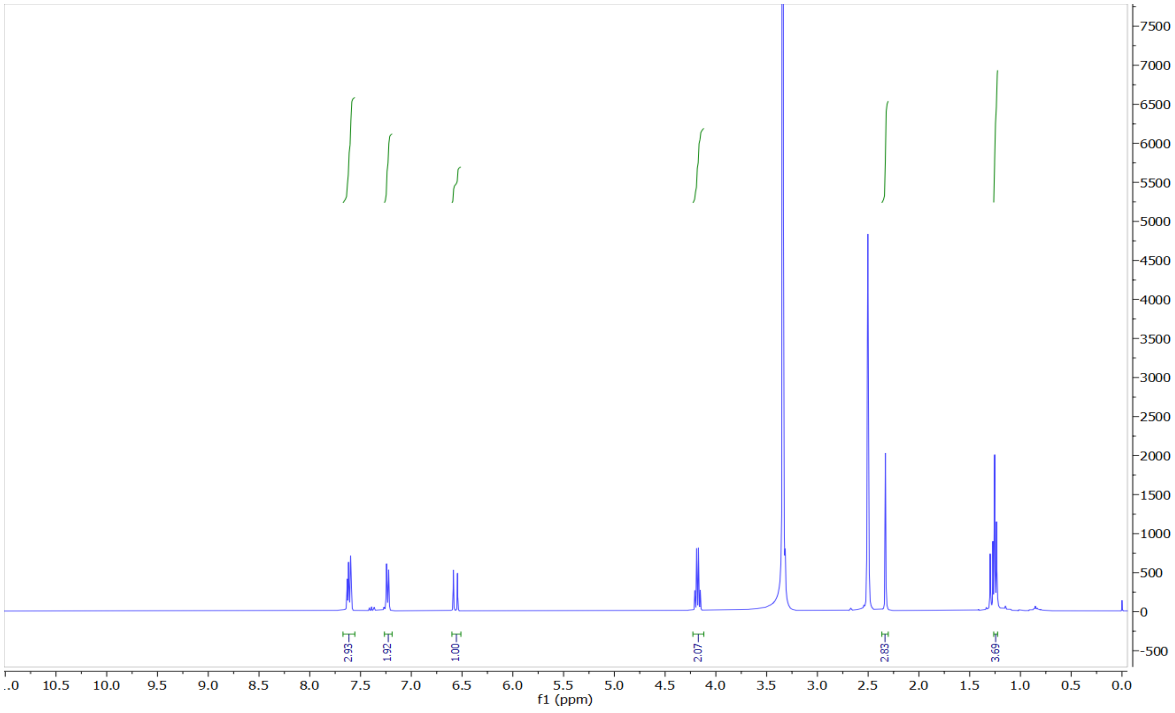
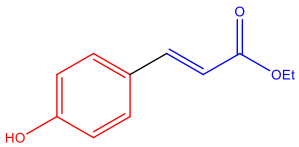


Fig. S13 : ^{1}H NMR spectrum of ethyl (E)-3-(p-tolyl)acrylate

Compound 3k



ethyl (E)-3-(4-hydroxyphenyl)acrylate : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a pale yellow solid (0.352 g, 91%)

Melting point: 84-87 °C

^{1}H NMR (400 MHz, DMSO) δ 10.02 (s, 1H), 7.64 – 7.45 (m, 3H), 6.87 – 6.70 (m, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

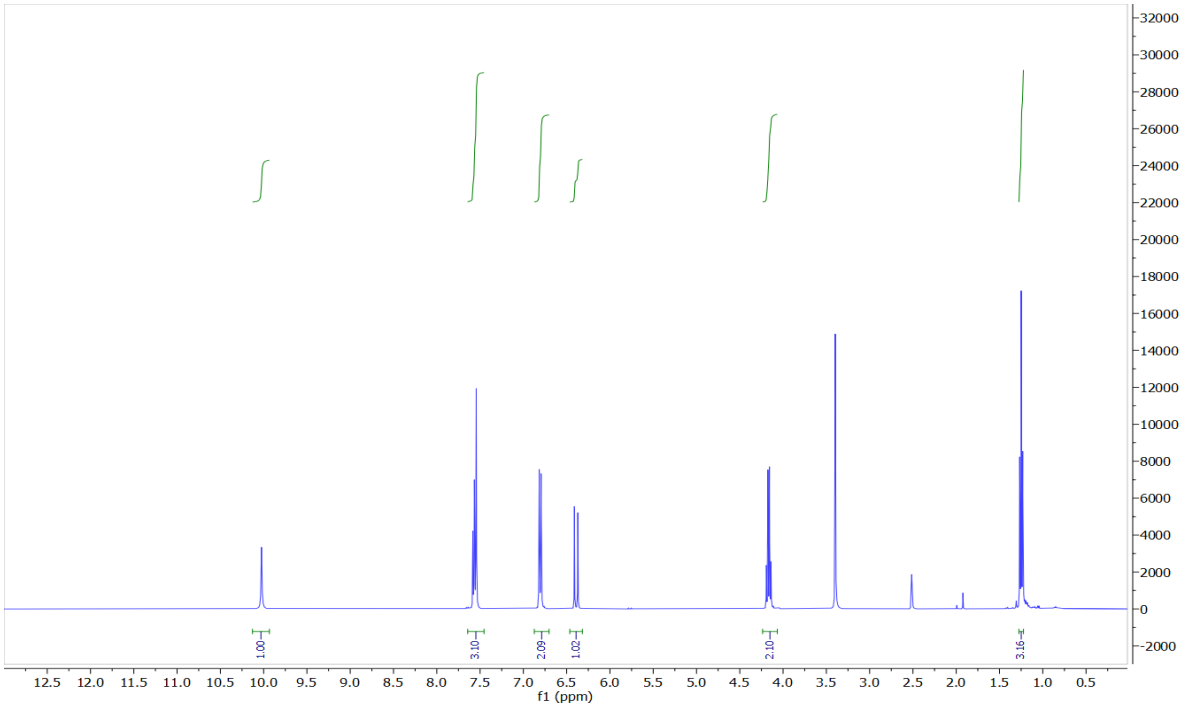
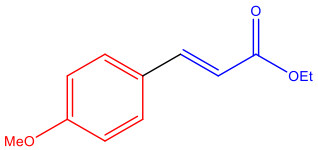


Fig. S14 : ^{1}H NMR spectrum of ethyl (E)-3-(4-hydroxyphenyl)acrylate

Compound 3l



ethyl (E)-3-(4-methoxyphenyl)acrylate : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a colourless liquid (0.331 g, 80%)

^{1}H NMR (400 MHz, DMSO) δ 7.72 – 7.64 (m, 2H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.10 – 6.87 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

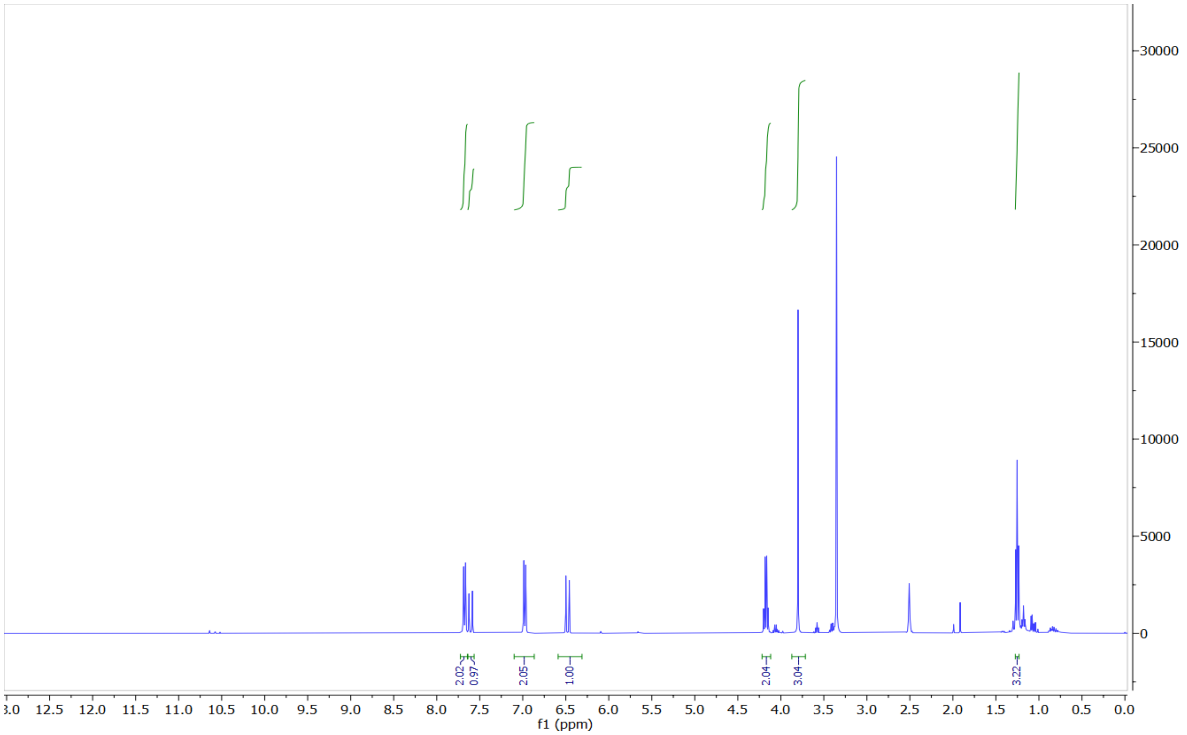
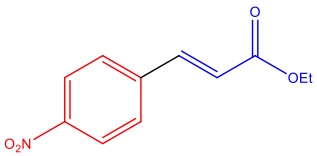


Fig. S15 : ^{1}H NMR spectrum of ethyl (E)-3-(4-methoxyphenyl)acrylate

Compound 3m



ethyl (E)-3-(4-nitrophenyl)acrylate : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a off-white solid (0.335 g, 75%)

Melting point: 122-125 °C

^{1}H NMR (400 MHz, DMSO) δ 8.30 – 8.15 (m, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 16.1 Hz, 1H), 6.84 (dd, *J* = 16.1, 1.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 166.15, 148.54, 142.27, 140.95, 129.92, 129.17, 124.70, 124.39, 122.95, 60.89, 14.61.

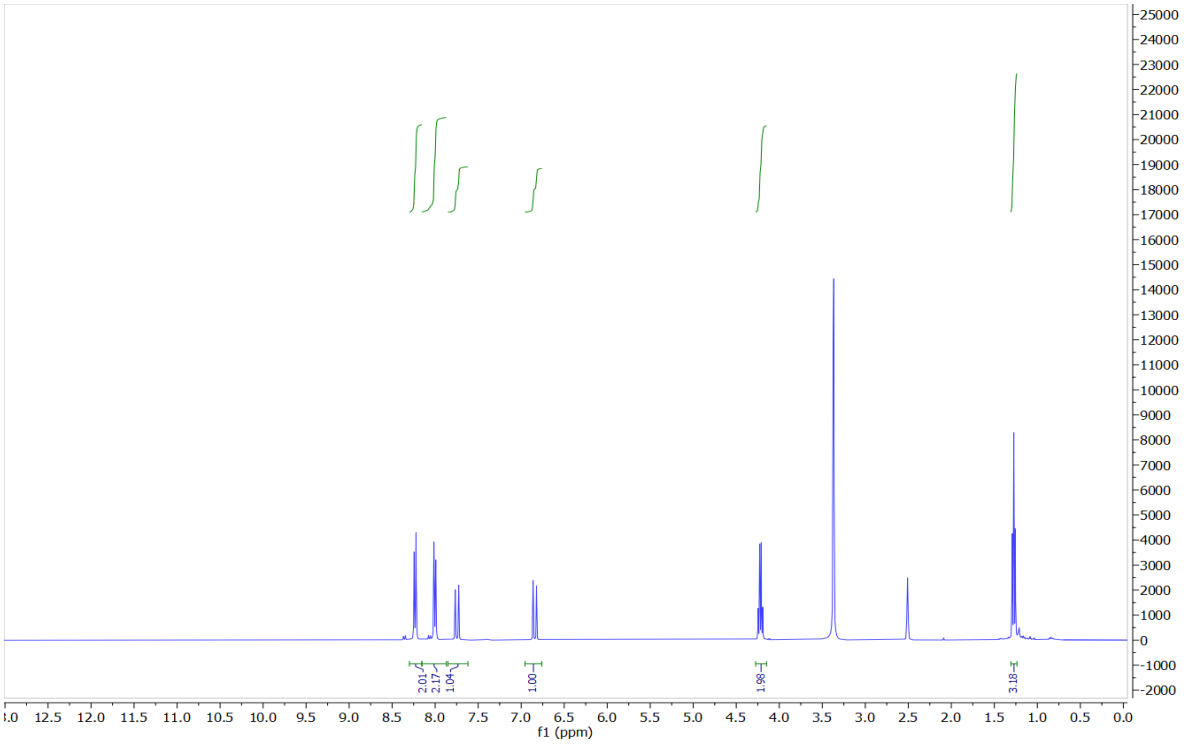


Fig. S16 : ^{1}H NMR spectrum of ethyl (E)-3-(4-nitrophenyl)acrylate

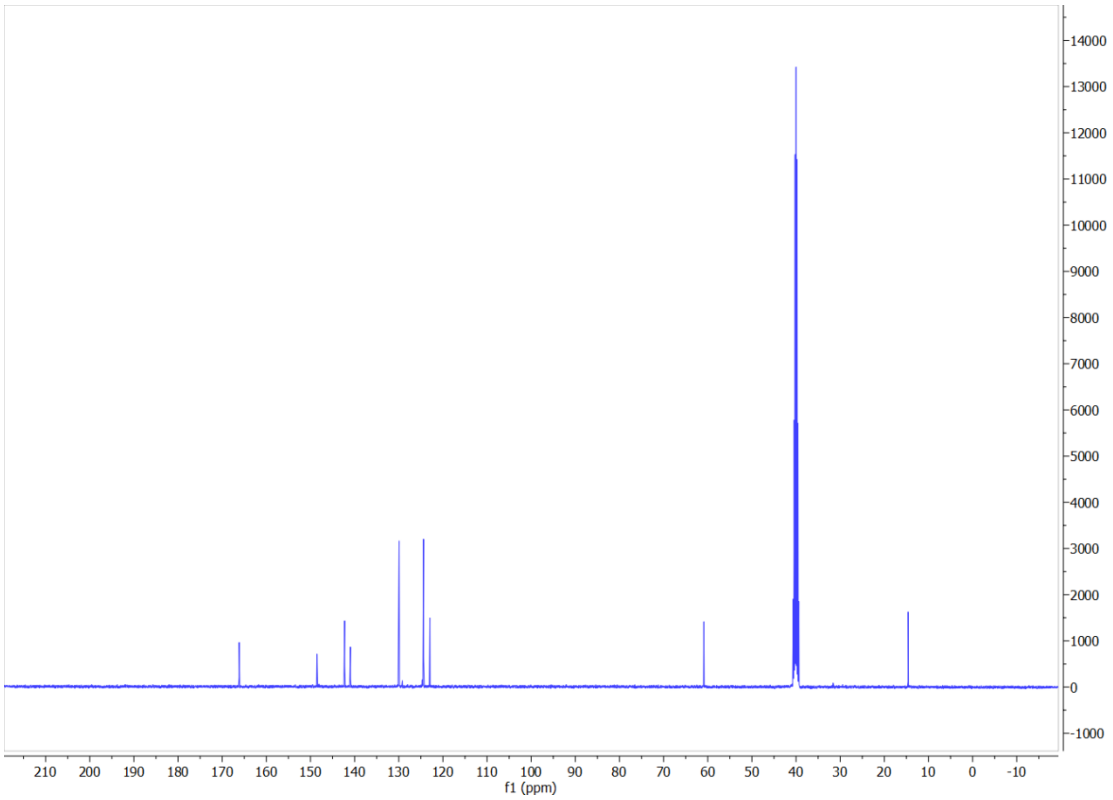
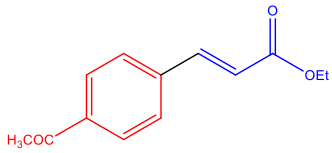


Fig. S17 : ^{13}C NMR spectrum of ethyl (E)-3-(4-nitrophenyl)acrylate

Compound 3n



ethyl (E)-3-(4-acetylphenyl)acrylate : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a pale yellow solid (0.338 g, 77%)

Melting point: 141-144 °C

^{1}H NMR (400 MHz, DMSO) δ 8.05 – 7.91 (m, 2H), 7.91 – 7.85 (m, 2H), 7.71 (d, *J* = 16.1 Hz, 1H), 6.78 (d, *J* = 16.1 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 197.89, 166.38, 143.45, 138.78, 138.17, 129.11, 128.99, 121.12, 60.71, 27.27, 14.62.

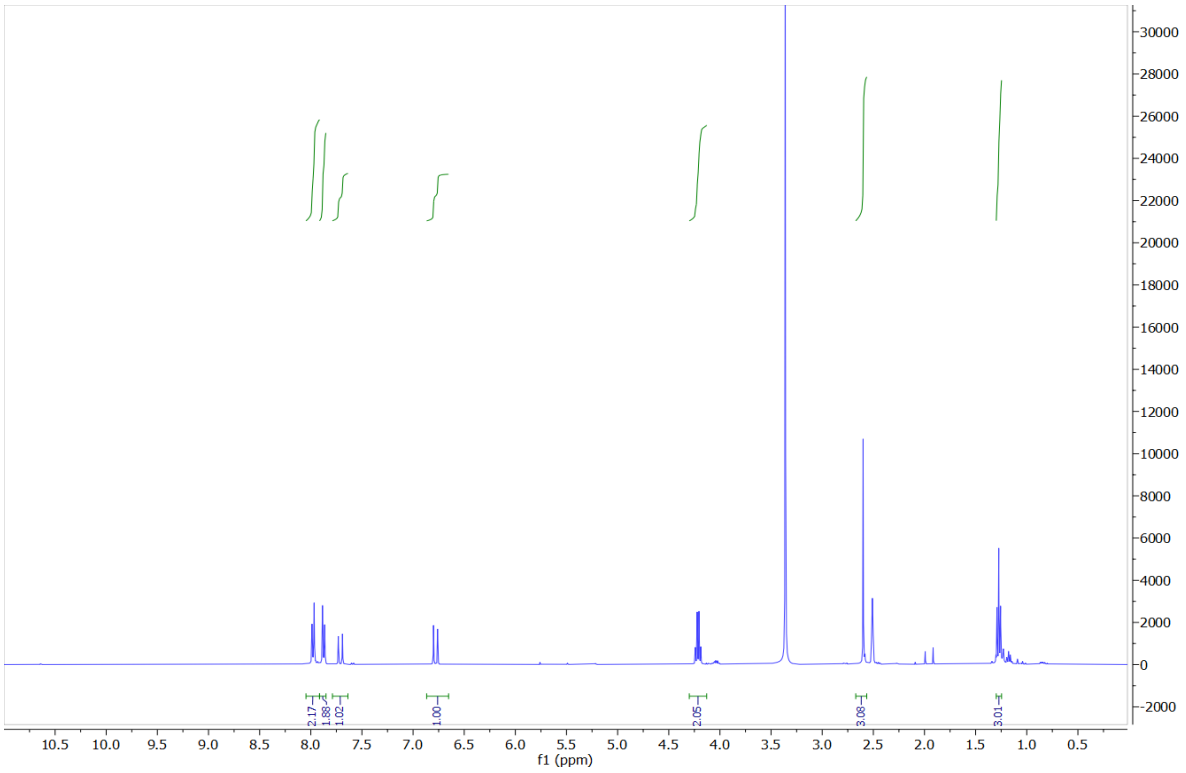


Fig. S18 : ^{1}H NMR spectrum of ethyl (E)-3-(4-acetylphenyl)acrylate

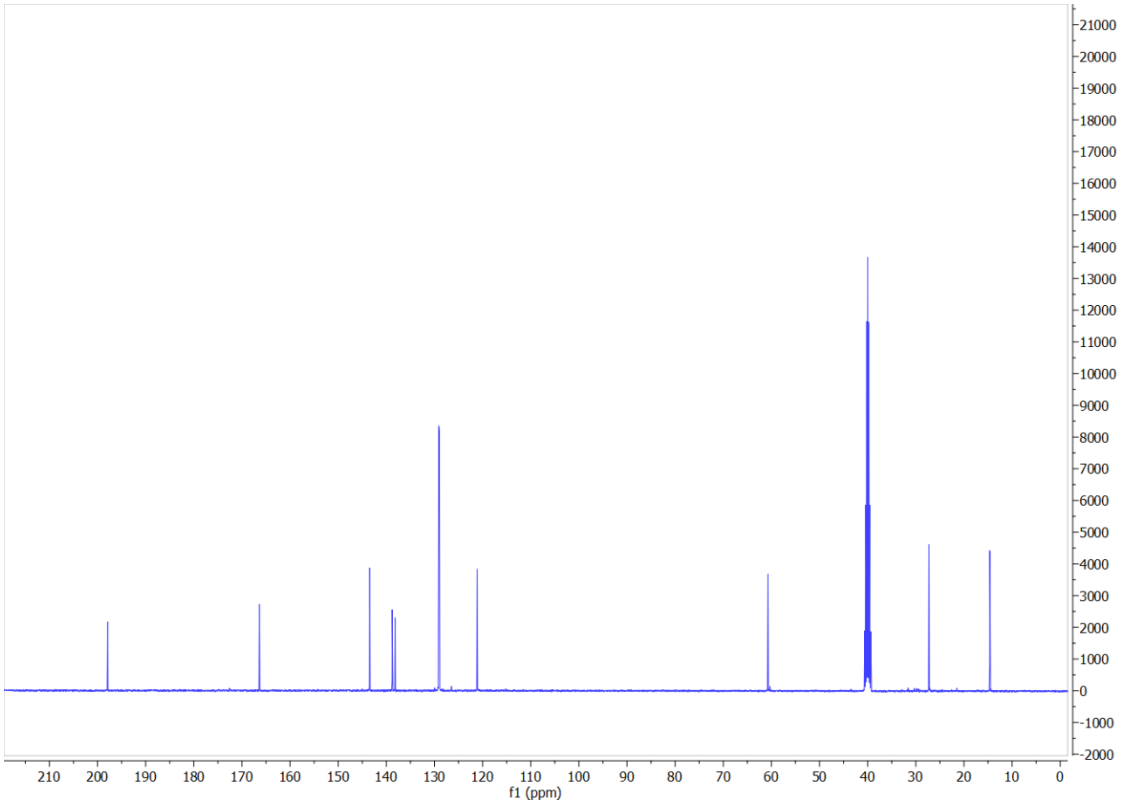
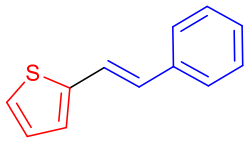


Fig. S19 : ^{13}C NMR spectrum of ethyl (E)-3-(4-acetylphenyl)acrylate

Compound 3o



(E)-2-styrylthiophene: Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a off-white solid (0.310 g, 83%)

^{1}H NMR (400 MHz, DMSO) δ 7.61 – 7.52 (m, 2H), 7.50 – 7.41 (m, 2H), 7.36 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.30 – 7.20 (m, 2H), 7.07 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.95 (d, *J* = 16.3 Hz, 1H).

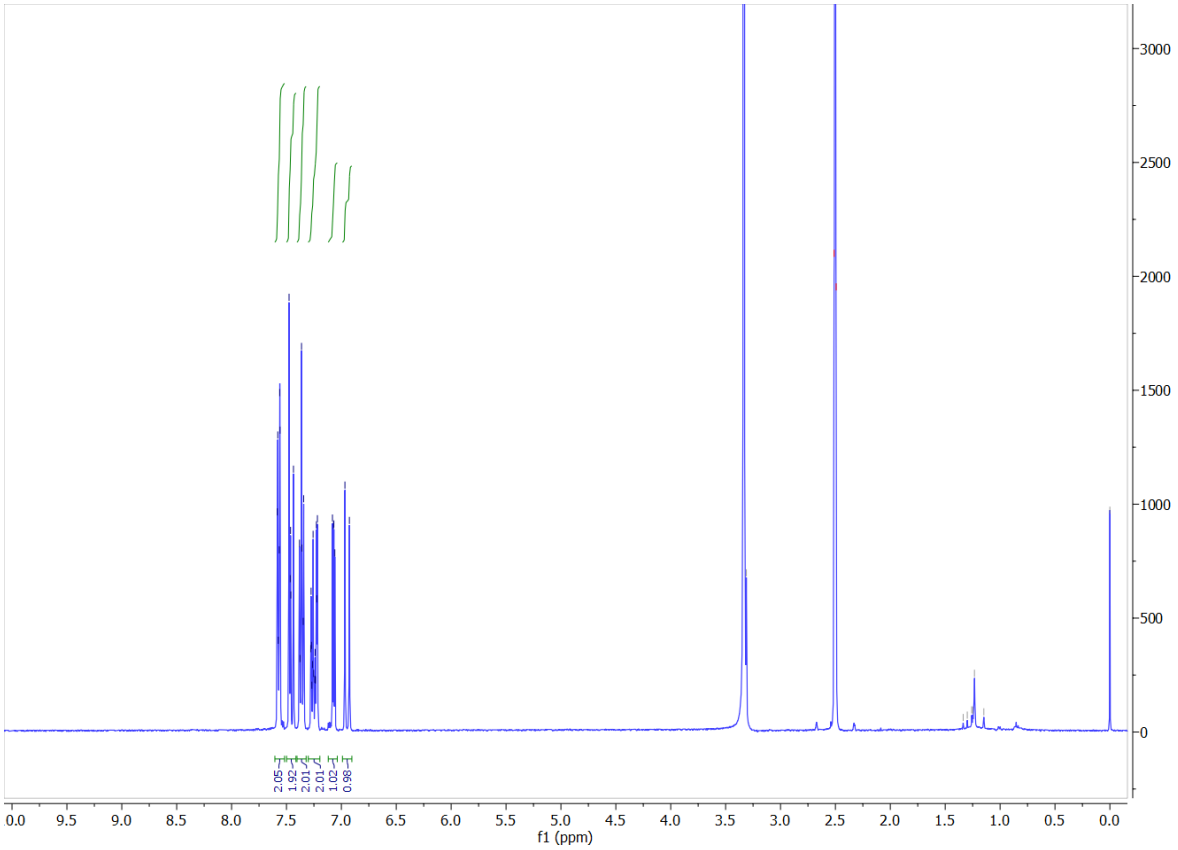
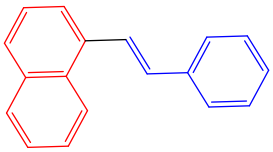


Fig. S20 : ^{1}H NMR spectrum of (E)-2-styrylthiophene

Compound 3p



(E)-1-styrylnaphthalene : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a pale yellow solid (0.392 g, 85%)

Melting point: 110-114 °C

^{1}H NMR (400 MHz, DMSO) δ 8.42 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.08 (d, *J* = 16.1 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.64 – 7.51 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.26 (m, 2H).

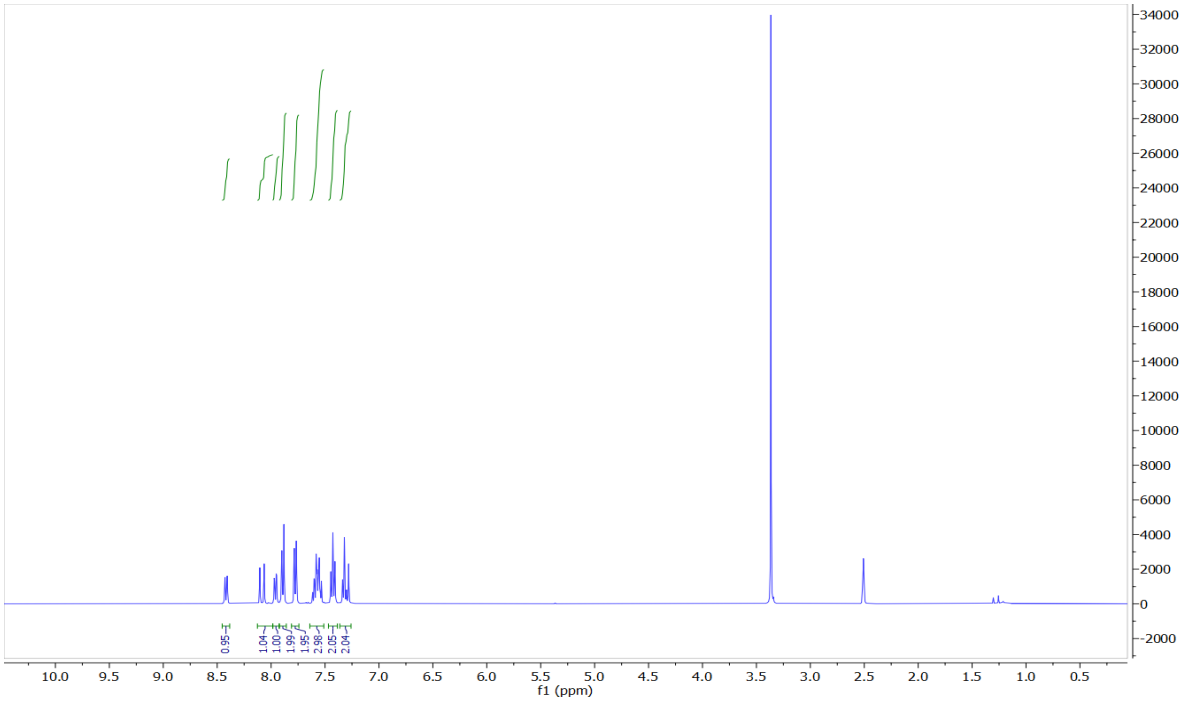
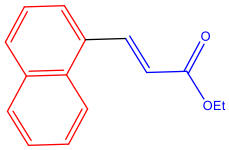


Fig. S21 : ^{1}H NMR spectrum of (E)-1-styrylnaphthalene

Compound 3q



ethyl (E)-3-(naphthalen-1-yl)acrylate : Synthesized on 2.0 mmol scale following the typical Mizoroki-Heck reaction procedure to obtain the product as a colourless liquid (0.363 g, 80%)

^{1}H NMR (400 MHz, DMSO) δ 8.46 (d, *J* = 15.7 Hz, 1H), 8.24 – 8.18 (m, 1H), 8.06 – 7.95 (m, 3H), 7.70 – 7.52 (m, 3H), 6.70 (d, *J* = 15.7 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 166.53, 141.08, 133.76, 131.24, 131.20, 131.08, 129.21, 127.68, 126.80, 126.18, 125.85, 123.41, 121.23, 60.68, 40.46, 31.60, 30.29, 29.46, 14.69.

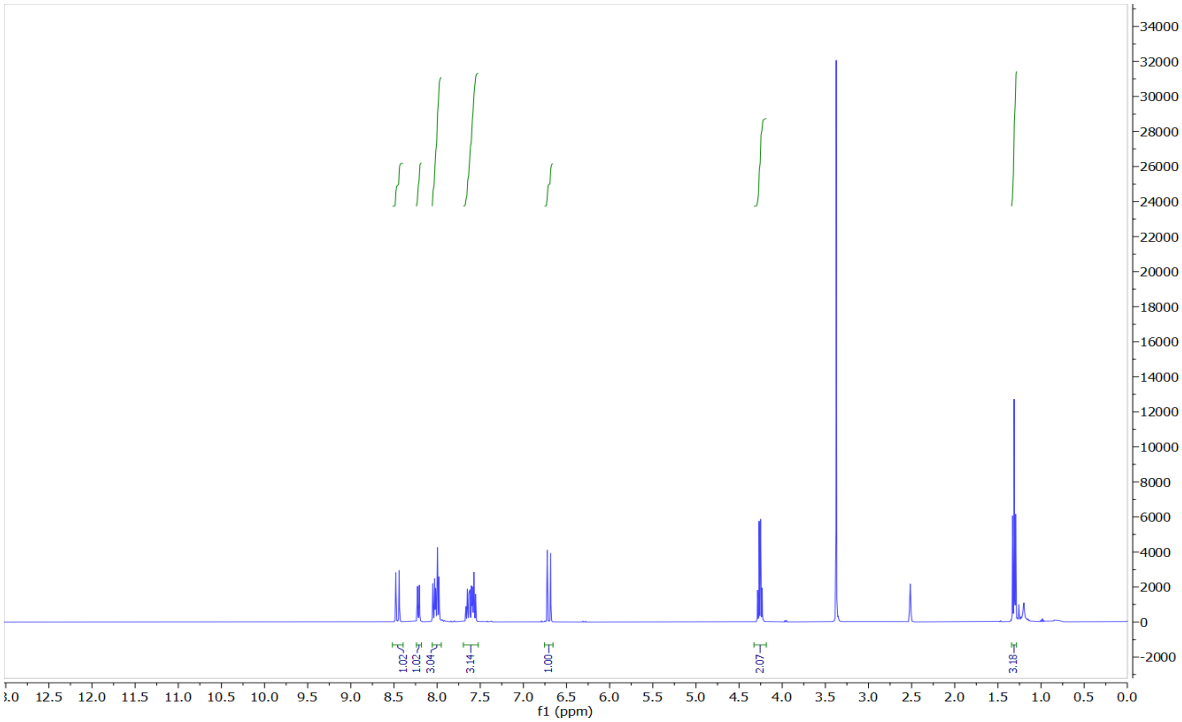


Fig. S22 : ^{1}H NMR spectrum of ethyl (E)-3-(naphthalen-1-yl)acrylate

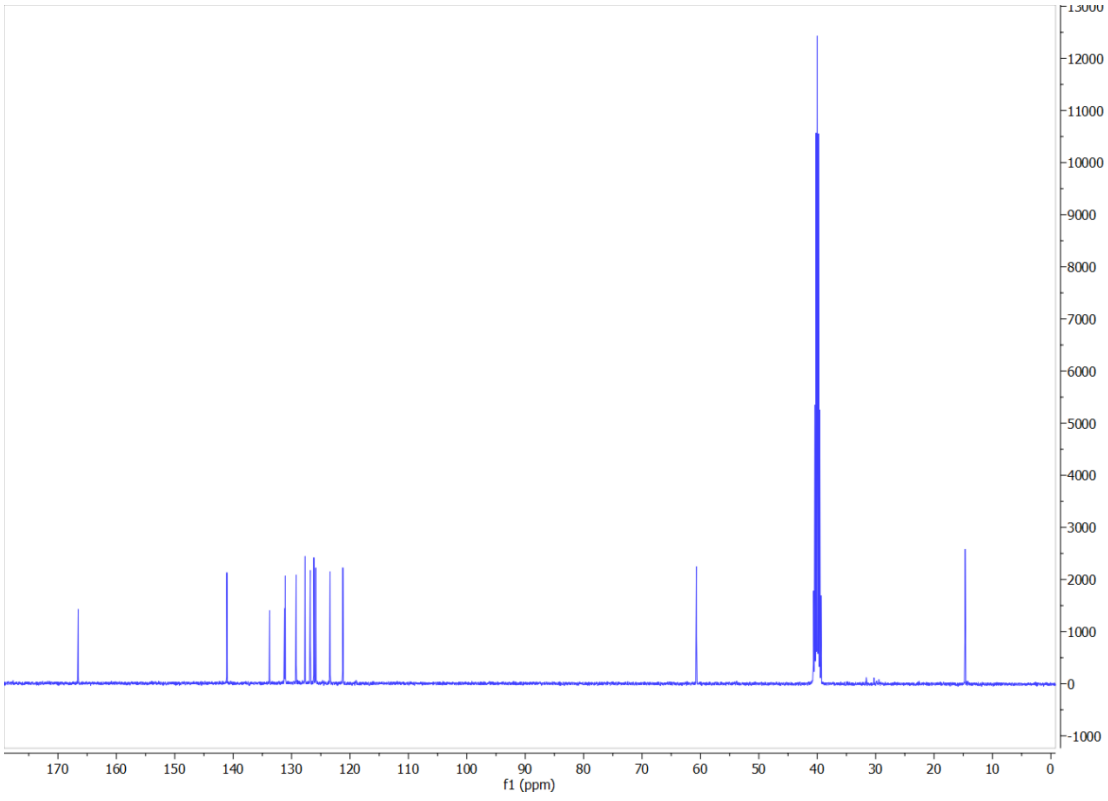


Fig. S23 : ^{13}C NMR spectrum of ethyl (E)-3-(naphthalen-1-yl)acrylate