Electronic Supplementary Information (ESI)

# Bis(*N*-substituted oxamate)palladate(II) complexes as effective catalysts for the sustainable Heck carbon-carbon coupling reactions in *n*-$Bu_4$NBr as solvent

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## General Procedure for the Synthesis of the Proligands

The ethyl ester derivative of the aniline derivate was prepared by following a previously reported procedure.[1] The corresponding aniline derivative (83 mmol) was dissolved in THF (250 ml) under dinitrogen in a two round flask equipped with a dropping funnel, then treated with ethyl chlorooxoacetate (9.3 mL, 83 mmol) in presence of triethylamine (12 mL, 83 mmol) at room temperature, under continuous stirring for 30 min. The resulting solution was filtered off and the solvent removed under vacuum to afford oily crude, which rapidly turns to solid. The obtained white solid was suspended in water and filtered off, washed with a small amount of diethyl ether and dried under vacuum.

**EtH-4-Fpma**: Yield: 85%; IR (KBr/cm$^{-1}$): 3322 (N–H), 3116, 2987, 2944, 2905 (C–H), 1732, 1687 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 1.41-1.46 (t, $J$ = 7.1Hz, 3H, $CH_3$), 4.39 – 4.46 (q, $J$ = 7.1Hz, 2H, $CH_2$), 7.05 – 7.11 (m, $J$ = 8.8 H, $J$ = 2.8 Hz, 2H, $H_{aryl}$), 7.60 – 7.64 (m, $J$ = 8.8 H, $J$ = 2.8 Hz, 2H, $H_{aryl}$), 8.86 (s, 1H, NH) ; $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 14.4, 64.26, 116.3, 116.6, 121.9, 122, 161.3, 192.2. Anal. calcd (found): C 56.87 (57.19); H 4.77 (5.58); N 6.63 (6.46).

**EtH-4-Clpma**: Yield: 90%; IR (KBr/cm$^{-1}$): 3334 (N–H), 3122, 2984, 2908, (C–H), 1729, 1698 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 1.29 – 1.34 (t, $J$ = 7.1Hz, 3H, $CH_3$), 4.27 – 4.35 (q, $J$ = 7.1Hz, 2H, $CH_2$), 7.41 – 7.44 (d, $J$ = 8.5 H, $J$ = 2.8 Hz 2H, $H_{aryl}$), 7.77 – 7.80 (d, $J$ = 8.5 H, $J$ = 2.8 Hz, 2H, $H_{aryl}$), 10.93 (s, 1H, NH); $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 14.2, 62.9, 122.4, 128.1, 129.1, 136.8, 155.9, 160.8. Anal. calcd (found): C 52.76 (51.26); H 4.43 (5,45); N 6.15 (5.62).

**EtH-4-Brpma**: Yield: 95%; IR (KBr/cm$^{-1}$): 3334 (N–H), 3129, 2981, 2905, (C–H), 1729, 1705 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 1.29 – 1.34 (t, $J$ = 7.1Hz, 3H, $CH_3$), 4.27 – 4.34 (q, $J$ = 7.1Hz, 2H, $CH_2$), 7.54 – 7.57 (m, $J$ = 8.5 H, $J$ = 2.8 Hz, 2H, $H_{aryl}$), 7.71 – 7.74 (m, $J$ = 8.5 H, $J$ = 2.8 Hz, 2H, $H_{aryl}$), 10.92 (s, 1H, NH); $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 14.2, 62.9, 116, 122.7, 132, 137, 155.9, 160.8. Anal.calcd (found): C 44.14 (47.74); H 3.70 (4.99); N 5.15 (5.42).

**EtH-4-MeOpma**: Yield: 94%; IR (KBr/cm$^{-1}$): 3352 (N–H), 3117, 2977, 2901, 2848 (C–H), 1724, 1697 (C=O); 1H NMR ($CDCl_3$) $\delta$ (ppm): 1.40 – 1.45 (t, $J$ = 7.1Hz, 3H, $CH_3$), 3.81 (s, 3H, $OCH_3$), 4.37 – 4.45 (q, $J$ = 7.1Hz, 2H, $CH_2$), 6.89 – 6.92 (m, $J$ = 8.5 H, $J$ = 2.8 Hz, 2H, $H_{aryl}$), 7.54 – 7.59 (m, $J$ = 8.5 H, $J$ = 2.8 Hz, 2H, $H_{aryl}$), 8.82 (s, 1H, NH); $^{13}$C NMR (CDCl3) $\delta$ (ppm): 14.4, 55.9, 64, 114.8, 121.8, 129.9, 154, 157.6, 161.6; Anal. calcd (found): C 59.19 (59.83), H 5.87 (6.81), N 6.27 (6.13).

**EtH-4-Isopma**: Yield: 82%; IR (KBr/cm$^{-1}$): 3303 (N–H), 3050, 2960, 2870 (C–H), 1739, 1691 (C=O); 1H NMR ($CDCl_3$) $\delta$ (ppm): 1.23 – 1.25 (d, $J$ = 6.9 Hz, 6H, $CH_3$), 1.41 – 1.45 (t, $J$ = 7.1Hz, 3H, $CH_3$), 2.86 – 2.95 (m, $J$ = 6.9 Hz, 1H, CH), 4.38 – 4.45 (q, 2H, $CH_2$), 7.22 – 7.26 (m, $J$ = 8.5 H, $J$ = 2.0 Hz, 2H, $H_{aryl}$), 7.53 – 7.58 (m, $J$ = 8.5 H, $J$ = 2.8 Hz, 2H, $H_{aryl}$), 8.83 (s, 1H, NH); $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 14.4, 24.3, 34.1, 64.1, 120.3, 127.5, 134.4, 146.7, 154.2, 161.5; Anal. calcd (found): C 66.36 (66.43), H 7.28 (7.73), N 5.95 (7.73).

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1 E. Pardo, R. Ruiz-García, J. Cano, X. Ottenwaelder, R. Lescouëzec, Y. Journaux, F. Lloret, and M. Julve, *Dalton. Trans.,* 2008, 2780.

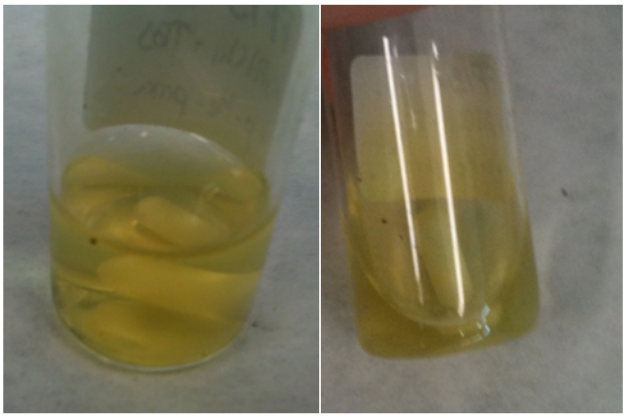
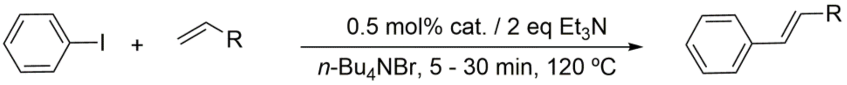
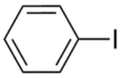
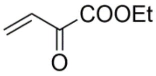
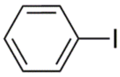
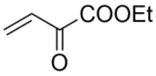
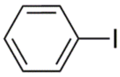
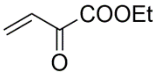
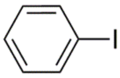
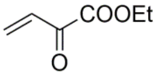
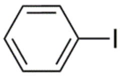
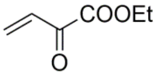
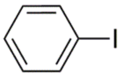
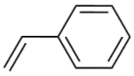
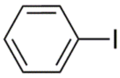
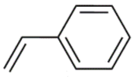
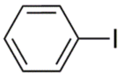
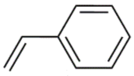
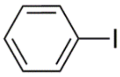
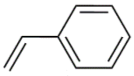
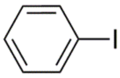
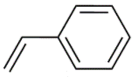


**Fig. S1** Stability of the palladium(II) oxamate-containing precatalyst after 90 days in water under ambient conditions.

## Catalytic Results of the Heck-Vinylation of Aryl Halides.

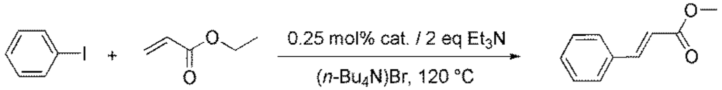
**Table S1.** Scope of Heck coupling reaction of iodobenzene with olefins



| Entry[a] | Aryl halide | Olefin | Catalyst | Time (min) | Yield | TON | TOF ($h^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 |  |  | **1** | 5 | 99 | 198 | 2376 |
| 2 |  |  | **2** | 5 | 99 | 198 | 2376 |
| 3 |  |  | **3** | 5 | 99 | 198 | 2376 |
| 4 |  |  | **4** | 5 | 99 | 198 | 2376 |
| 5 |  |  | **5** | 5 | 99 | 198 | 2376 |
| 6 |  |  | **1** | 30 | 99 | 198 | 396 |
| 7 |  |  | **2** | 30 | 99 | 198 | 396 |
| 8 |  |  | **3** | 30 | 99 | 198 | 396 |
| 9 |  |  | **4** | 30 | 99 | 198 | 396 |
| 10 |  |  | **5** | 30 | 99 | 198 | 396 |

[a] Reaction conditions: 0.5 mmol iodobenzene, 0.75 mmol olefin, 0.5 mol% cat.,1 mmol $Et_3N$, 5-30 min, 120 °C in *n*-$Bu_4NBr$. [b]Determined by GC-MS analysis using perfluorotributylamine (PFTBA) as internal standard.

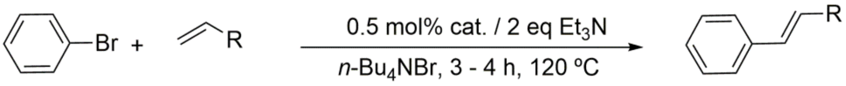
**Table S2**. Heck-vinylation of iodobenzene with ethyl acrylate in *n*-$Bu_4NBr$

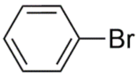
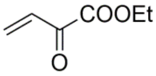
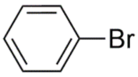
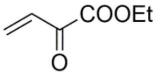
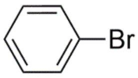
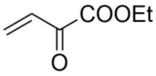
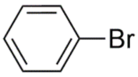
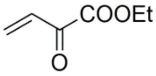
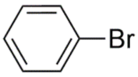
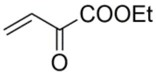
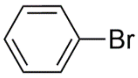
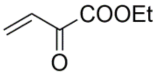
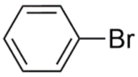
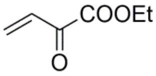
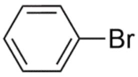
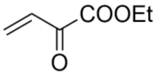
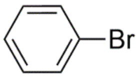
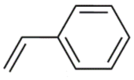
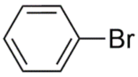
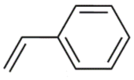
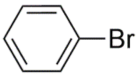
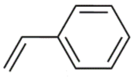
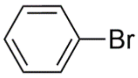
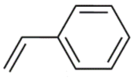
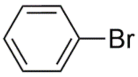
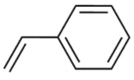


| Entry[a] | Catalyst | *Run* – Yield (%)[b] | | | | | | | | *Run* – TON / TOF ($h^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* |
| 1 | **1** | 97 | 94 | 99 | 99 | 97 | 98 | 99 | 99 | 388/4662 | 377/4525 | 400/4800 | 400/4800 | 388/4662 | 393/4719 | 400/4800 | 394/4732 |
| 2 | **2** | 63 | 79 | 94 | 93 | 94 | 96 | 97 | 97 | 253/3036 | 316/3789 | 374/4491 | 374/4487 | 378/4533 | 386/4732 | 388/4758 | 386/4735 |
| 3 | **3** | 69 | 12 | 53 | 77 | 81 | 86 | 88 | 83 | 277/3323 | 48/576 | 213/2561 | 307/2685 | 322/3869 | 345/4136 | 354/4242 | 333/3990 |
| 4 | **4** | 67 | 85 | 94 | 99 | 96 | 99 | 97 | 98 | 266/3193 | 339/4068 | 376/4516 | 400/4800 | 383/4598 | 400/4800 | 387/4645 | 391/4690 |
| 5 | **5** | 85 | 99 | 99 | 99 | 99 | 80 | 84 | 84 | 342/4100 | 400/4800 | 400/4800 | 400/4800 | 400/4800 | 319/3828 | 336/4035 | 338/4053 |

[a] Reaction conditions: 0.5 mmol iodobenzene, 0.75 mmol ethyl acrylate, 0.25 mol% cat., 1 mmol of $Et_3N$, 5 min, 120 °C in *n*-$Bu_4NBr$. [b]Determined by GC-MS analysis using perfluorotributylamine (PFTBA) as internal standard.

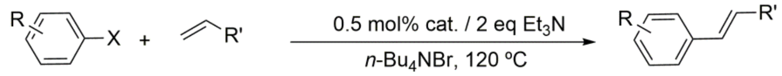
**Table S3.** Scope of Heck coupling of bromobenzene with olefins in *n*-$Bu_4NBr$



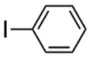
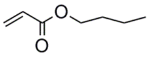
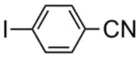
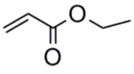
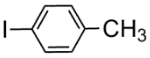
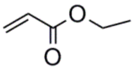
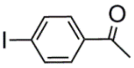
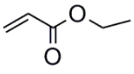
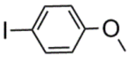
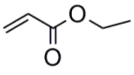
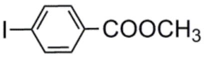
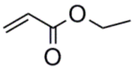
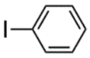
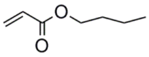
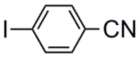
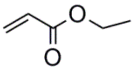
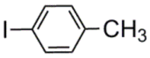
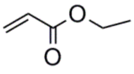
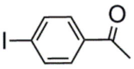
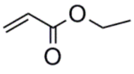
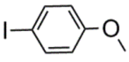
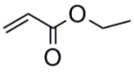
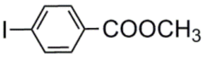
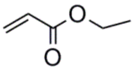
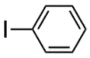
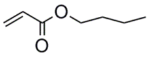
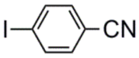
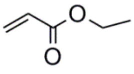
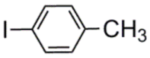
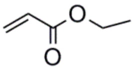
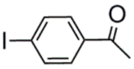
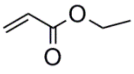
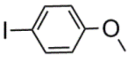
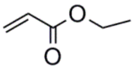
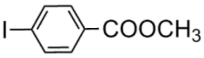
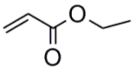
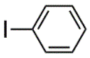
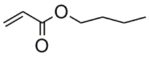
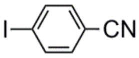
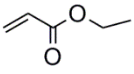
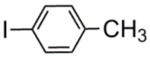
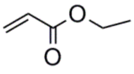
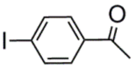
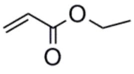
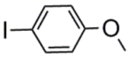
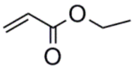
| Entry | Aryl halide | Olefin | Catalyst | Time (h) | Yield | TON | TOF ($h^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 |  |  | **1** | 3 | 99 | 198 | 66 |
| 2 |  |  | **2** | 3 | 90 | 180 | 60 |
| 3 |  |  | **3** | 3 | 91 | 182 | 61 |
| 4 |  |  | **4** | 3 | 82 | 163 | 54 |
| 5 |  |  | **5** | 3 | 89 | 177 | 59 |
| 6 |  |  | **[$PdCl_2$]** | 3 | 0 | 0 | 0 |
| 7 |  |  | **[$Pd_3(OAc)_6$]** | 3 | 0 | 0 | 0 |
| 8 |  |  | **[$Pd(dba)_2$]** | 3 | 74 | 148 | 37 |
| 9 |  |  | **1** | 4 | 92 | 184 | 46 |
| 10 |  |  | **2** | 4 | 76 | 152 | 38 |
| 11 |  |  | **3** | 4 | 77 | 155 | 39 |
| 12 |  |  | **4** | 4 | 92 | 184 | 46 |
| 13 |  |  | **5** | 4 | 90 | 179 | 45 |

[a] Reaction conditions: 0.5 mmol bromobenzene, 0.75 mmol olefin, 0.5 mol% cat.,1 mmol $Et_3N$, 3-4 h, 120 °C in *n*-$Bu_4NBr$. [b]Determined by GC-MS analysis using perfluorotributylamine (PFTBA) as internal standard

**Table S4**. Heck coupling of aryl halide with olefins in *n*-Bu$_4$NBr



X = I, Br, Cl

| Entry[a] | Catalyst | Aryl halide | Olefin | Time (min) | Runs – Yield[b] (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | 1 | 2 | 3 |
| 1 | **1** |  |  | 5 | 0 | 14 | 65 |
| 2 | **1** |  |  | 5 | 71 | 86 | 89 |
| 3 | **1** |  |  | 5 | 0 | 70 | 90 |
| 4 | **1** |  |  | 5 | 0 | 81 | 93 |
| 5 | **1** |  |  | 5 | 0 | 92 | 93 |
| 6 | **1** |  |  | 15 | 89 | 85 | 85 |
| 7 | **2** |  |  | 5 | 19 | 86 | 88 |
| 8 | **2** |  |  | 5 | 99 | 53 | 87 |
| 9 | **2** |  |  | 5 | 41 | 47 | 85 |
| 10 | **2** |  |  | 5 | 47 | 89 | 93 |
| 11 | **2** |  |  | 5 | 17 | 43 | 92 |
| 10 | **2** |  |  | 15 | 99 | - | 98 |
| 13 | **3** |  |  | 5 | 26 | 90 | 97 |
| 14 | **3** |  |  | 5 | 99 | 99 | - |
| 15 | **3** |  |  | 5 | 96 | 2 | 58 |
| 16 | **3** |  |  | 5 | 53 | 96 | 98 |
| 17 | **3** |  |  | 5 | 37 | 93 | 99 |
| 18 | **3** |  |  | 15 | 83 | 95 | 94 |
| 19 | **4** |  |  | 5 | 47 | 75 | 90 |
| 20 | **4** |  |  | 5 | 51 | 87 | 83 |
| 21 | **4** |  |  | 5 | 74 | 99 | 94 |
| 22 | **4** |  |  | 5 | 99 | 96 | 89 |
| 23 | **4** |  |  | 5 | 41 | 94 | 99 |

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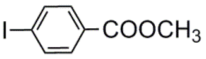
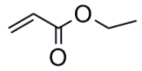
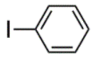
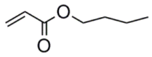
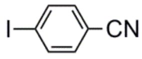
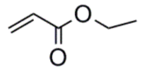
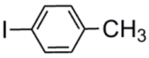
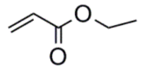
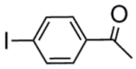
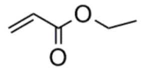
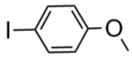
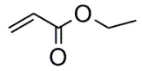
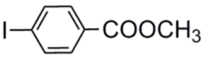
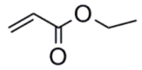
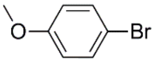
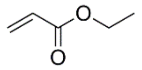
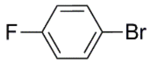
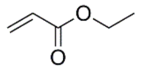
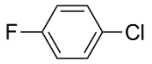
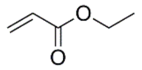
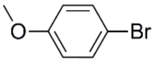
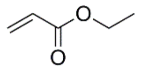
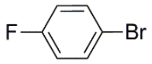
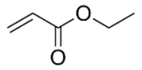
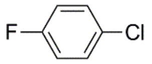
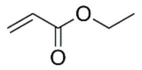
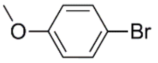
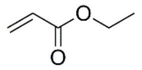
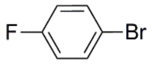
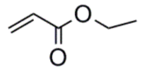
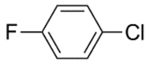
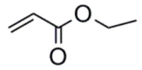
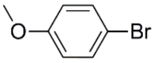
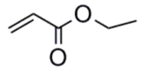
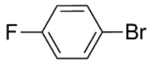
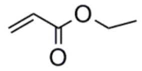
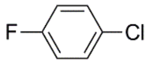
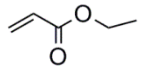
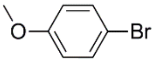
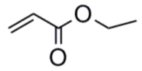
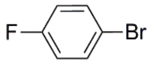
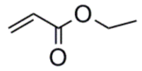
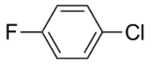
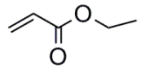
| 24 | **4** |  |  | 15 | 99 | 99 | 99 |
| 25 | **5** |  |  | 5 | 80 | 87 | 92 |
| 26 | **5** |  |  | 5 | - | 86 | 88 |
| 27 | **5** |  |  | 5 | 37 | 90 | 99 |
| 28 | **5** |  |  | 5 | 75 | 93 | 99 |
| 29 | **5** |  |  | 5 | 69 | 99 | 99 |
| 30 | **5** |  |  | 15 h | 99 | 99 | 99 |
| 31 | **1** |  |  | 1.5 h | 99 | *[c] | *[c] |
| 32 | **1** |  |  | 4 h | 92 | *[c] | *[c] |
| 33 | **1** |  |  | 72 h | *[c] | *[c] | *[c] |
| 34 | **2** |  |  | 1.5 h | 99 | *[c] | *[c] |
| 35 | **2** |  |  | 4 h | 94 | *[c] | *[c] |
| 36 | **2** |  |  | 72 h | 13 | *[c] | *[c] |
| 37 | **3** |  |  | 1.5 h | 99 | *[c] | *[c] |
| 38 | **3** |  |  | 4 h | 93 | *[c] | *[c] |
| 39 | **3** |  |  | 72 h | *[c] | *[c] | *[c] |
| 40 | **4** |  |  | 1.5 h | 99 | *[c] | *[c] |
| 41 | **4** |  |  | 4 h | 91 | *[c] | *[c] |
| 42 | **4** |  |  | 72 h | *[c] | *[c] | *[c] |
| 43 | **5** |  |  | 1.5 h | 99 | *[c] | *[c] |
| 44 | **5** |  |  | 4 h | 94 | *[c] | *[c] |
| 45 | **5** |  |  | 72 h | *[c] | *[c] | *[c] |

[a] Reaction conditions: 0.5 mmol aryl halide, 0.75 mmol olefins, 0.5 mol% cat., 1 mmol $Et_3N$, 120 °C in *n*-$Bu_4NBr$. [b] Determined by GC-MS analysis using perfluorotributylamine (PFTBA) as internal standard. [c] Not tested.

## NMR Spectra of the Catalytic Products.

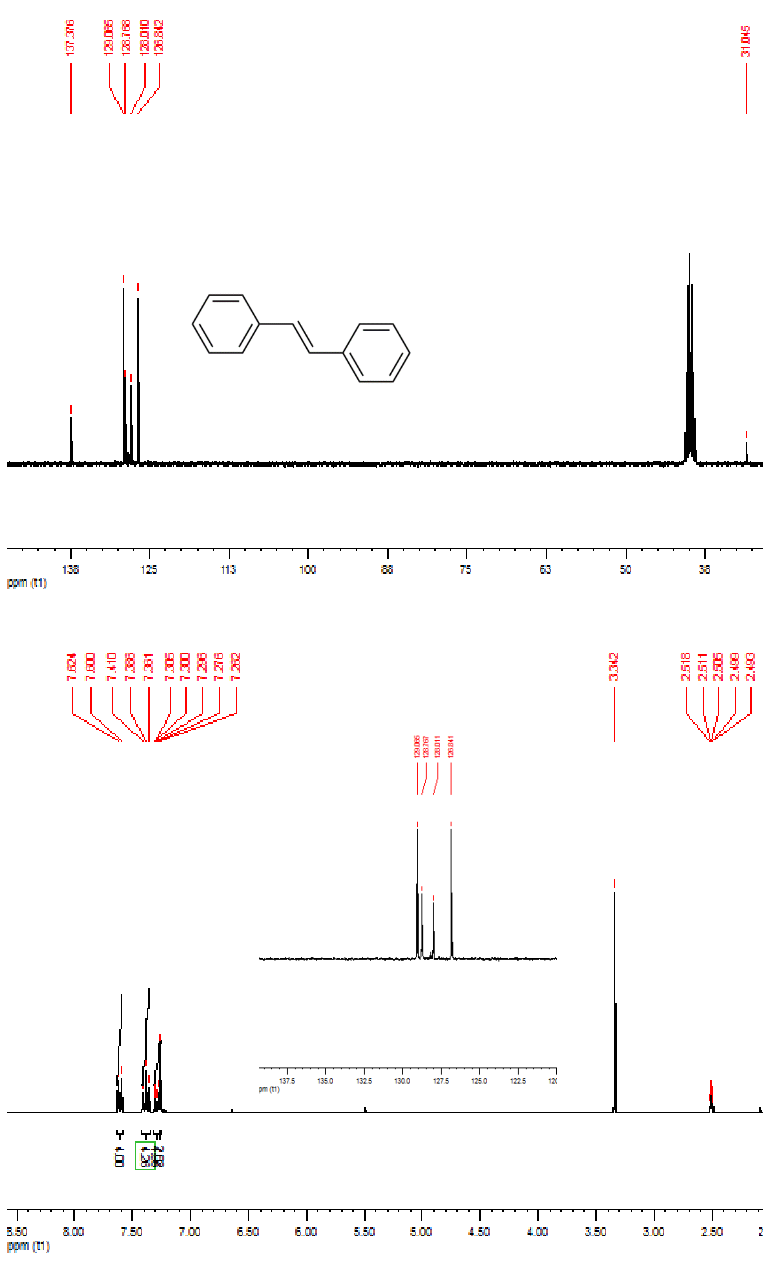


**Fig. S2** $^1$H-NMR, $^{13}$C-NMR and Dept-135-NMR (inset) spectra of (*E*)-1,2-diphenylethene.

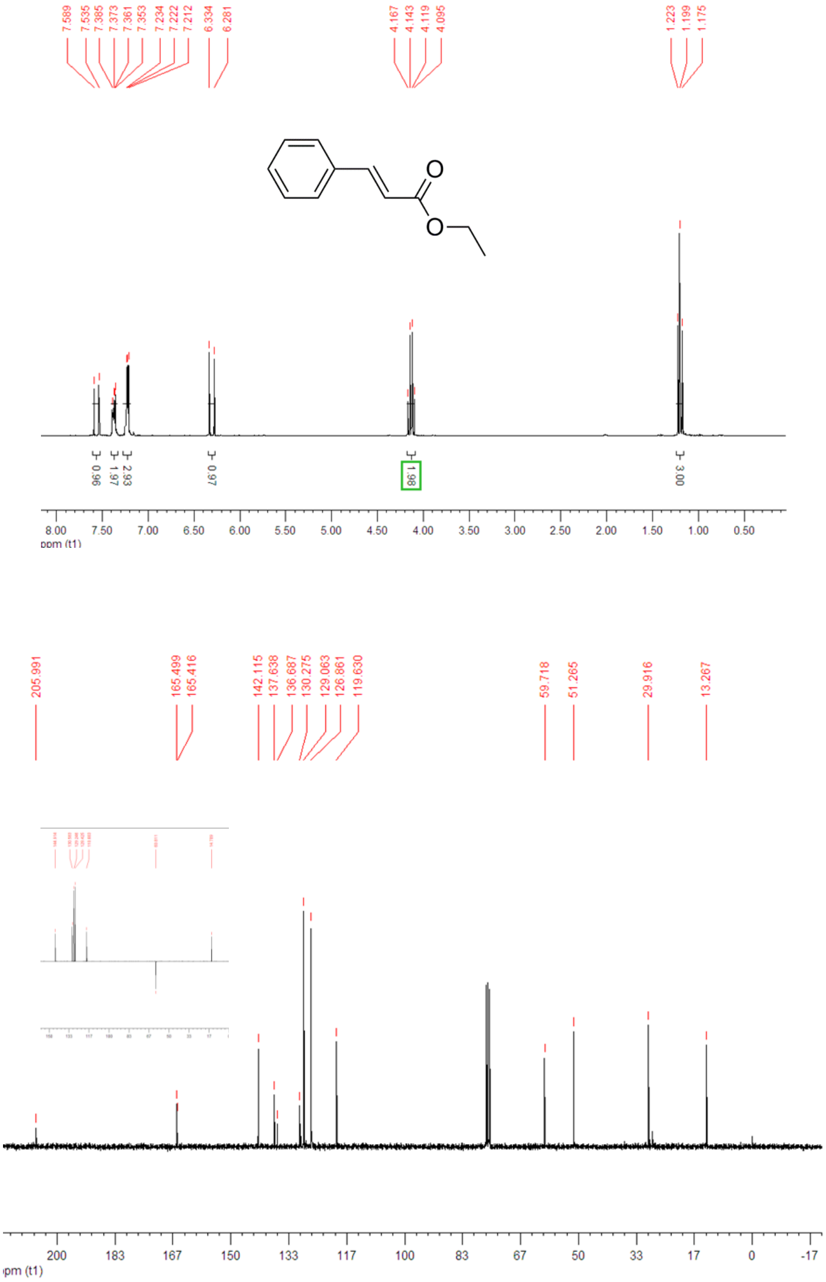


**Fig. S3** $^{1}$H-NMR, $^{13}$C-NMR and Dept-135-NMR (inset) spectra of ethyl (2*E*)-3-phenylprop-2-enoate.

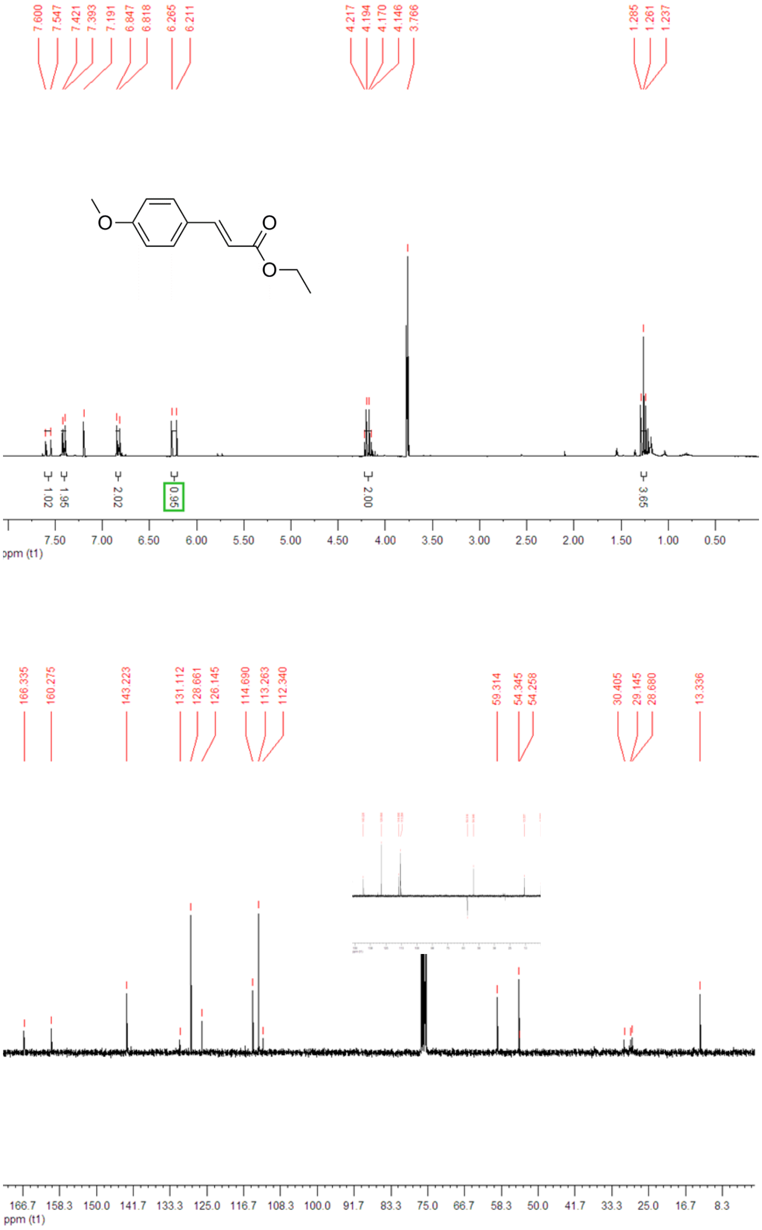


**Fig. S4** $^{1}$H-NMR, $^{13}$C-NMR and Dept-135-NMR spectra of ethyl (2*E*)-3-(4-methoxyphenyl)prop-2-enoate.

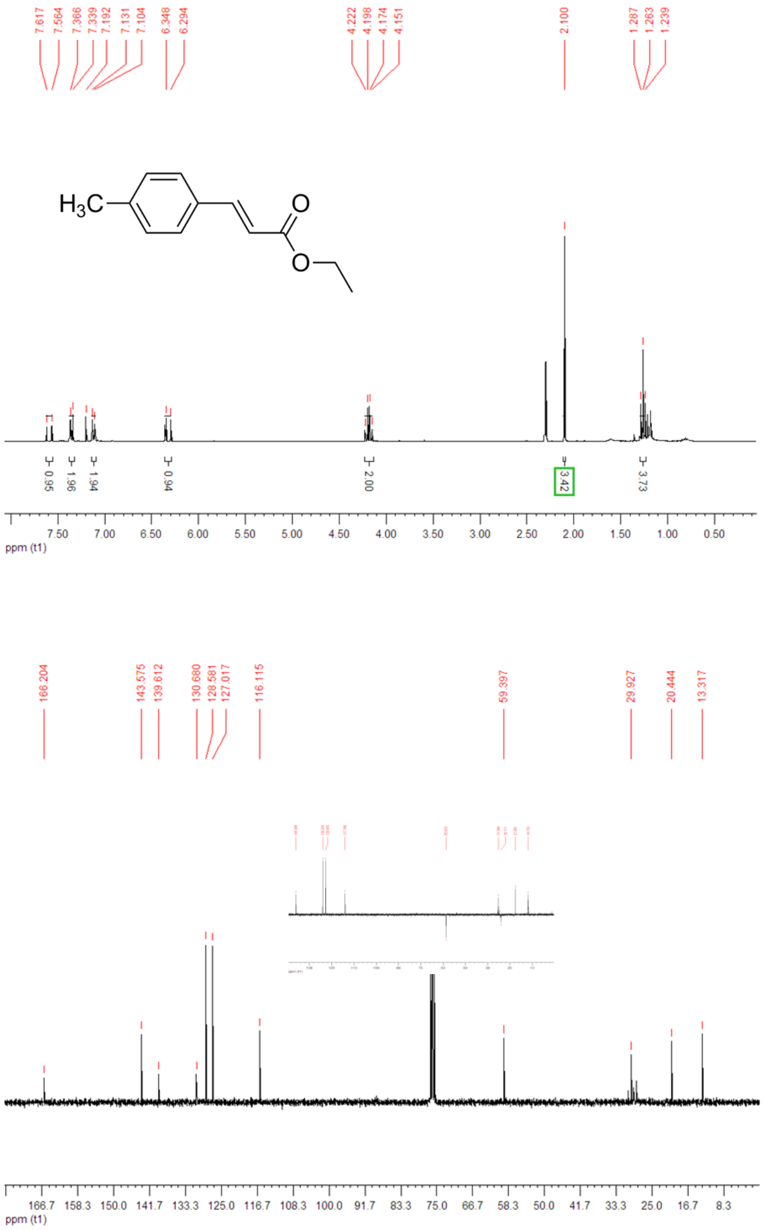


**Fig. S5** $^{1}$H-NMR, $^{13}$C-NMR and Dept-135-NMR (inset) spectra of ethyl (2*E*)-3-(4-methylphenyl)prop-2-enoate.

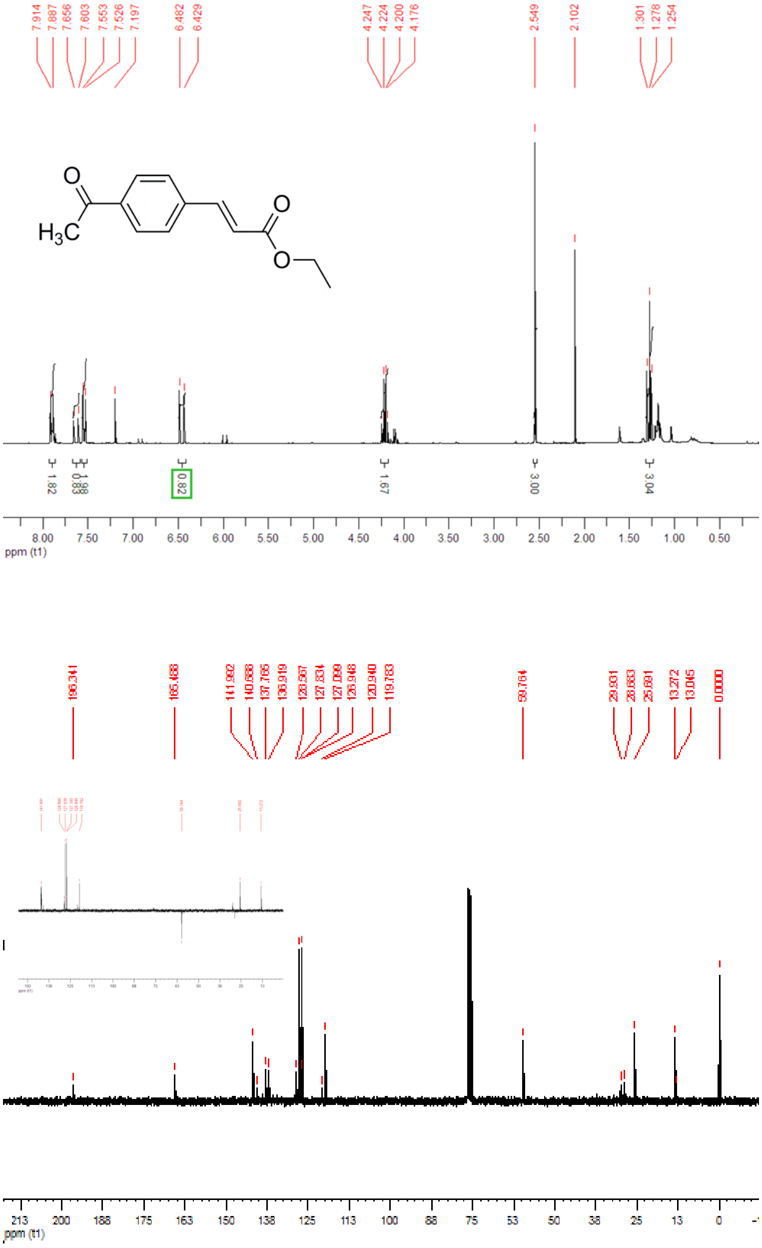


**Fig. S6** $^1$H-NMR; $^{13}$C-NMR and Dept-135-NMR (inset) spectra of ethyl (4-acetylphenyl)prop-2-enoate.

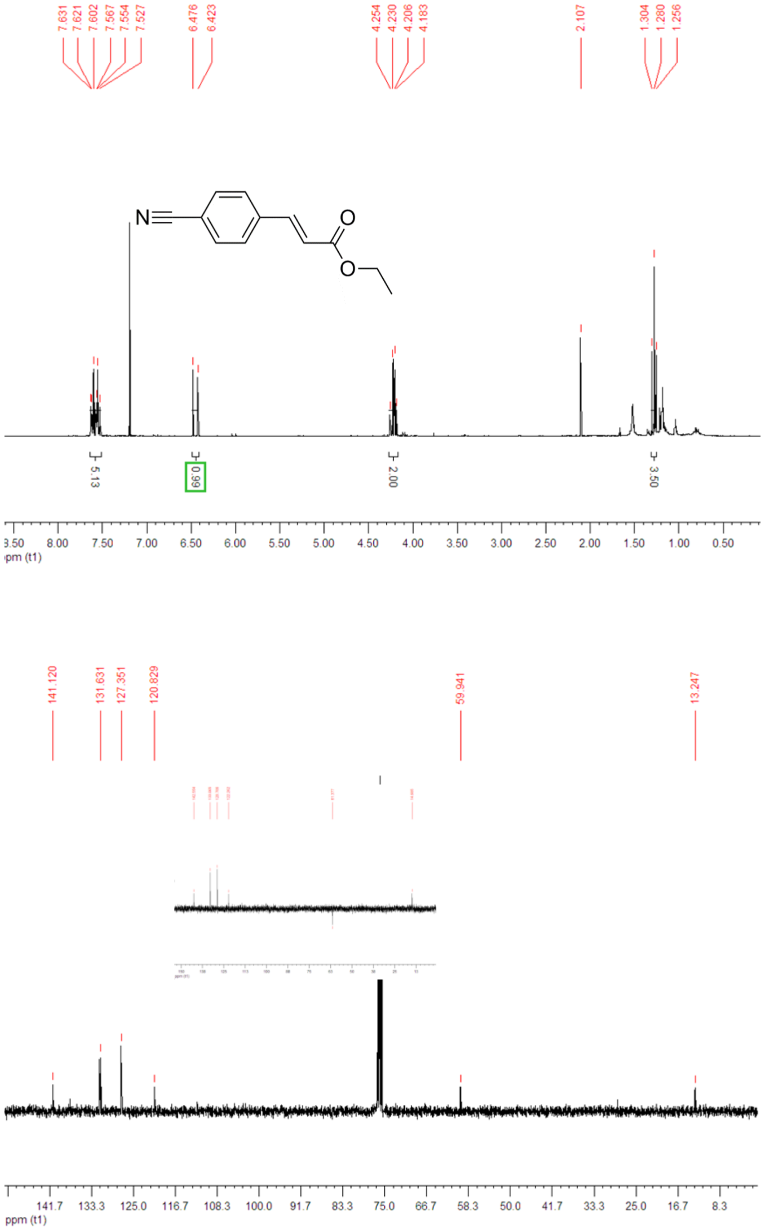


**Fig. S7** $^1$H-NMR; $^{13}$C-NMR and Dept-135-NMR (inset) spectra of ethyl (2*E*)-3-(4-cyanophenyl)prop-2-enoate.

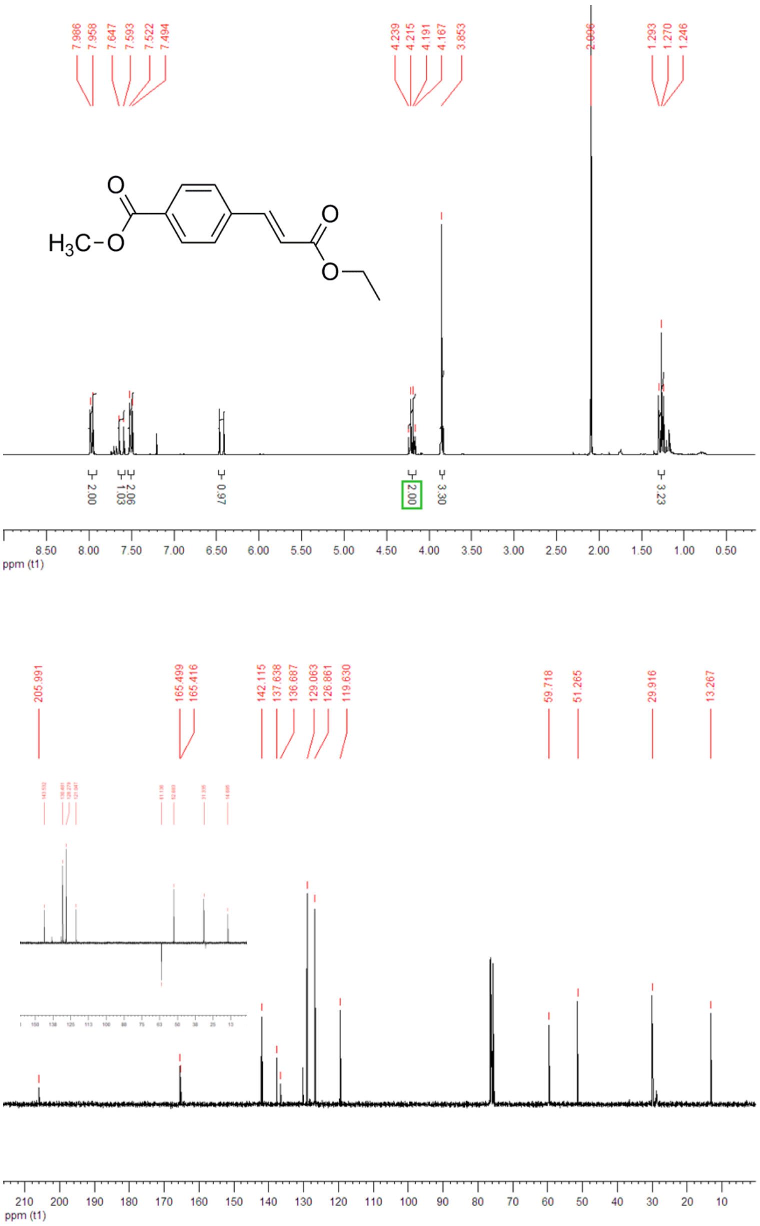


**Fig. S8** $^1$H-NMR, $^{13}$C-NMR and Dept-135-NMR (inset) spectra of methyl (2*E*)-4-(3-ethoxy-3-oxoprop-1-en-1-yl]benzoate.