N-Heterocyclic Carbene (NHC)-Ligated Cyclopalladated *N,N*-Dimethylbenzyl-amine: A Highly Active, Practical and Versatile Heck-Mizoroki Precatalyst

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SUPPORTING INFORMATION

General Experimental

All reagents, ligands, catalysts and solvents were purchased from commercial sources and used without further purification, unless otherwise indicated. Deuterated solvents were purchased from Sigma-Aldrich. TLC plates and reaction vials (screw-cap threaded, caps attached, 17 × 60 mm) were purchased from VWR. ^{1}H and ^{13}C NMR data were acquired at 25 °C on a Bruker AV 400 spectrometer. The elemental analyses were performed at the National University of Singapore. Prior to the analysis, the samples were dissolved in CH_2Cl_2 and filtered, the solvent was removed under reduced pressure, and the neat compounds were dried at 56 °C, 5 Torr over P_2O_5 for 18 h. Flash chromatography was performed in a CombiFlash Sq16 on normal-phase silica gel cartridges (12 g) with ethyl acetate gradients (solvent B) in hexane (solvent A). The stock solution of the catalyst was prepared by dissolving the required amount of IMes-Pd(dmba)Cl (**1**) (7.26 mg/mL for 0.5 mol% or 29.03 mg/mL for 2 mol%) in reagent-grade NMP, and degassing the solution with Ar over 10–20 min.

Synthetic Procedures

Large-scale synthesis of IMes-Pd(dmba)Cl (1). A 1-L, two-necked flask was charged with a large, egg-shaped magnetic stirrer bar, $PdCl_2$ (32.3 g, 182 mmol), CH_3CN (370 mL; HPLC grade) and *N*,*N*-dimethylbenzylamine (**4**) (29 mL, 25.8 g, 191 mmol). One of the necks was equipped with a reflux condenser and the other was closed with a glass stopper. The mixture was heated at reflux until a clear, dark orange solution was formed and $PdCl_2$ was dissolved completely (in ~ 25 min). Finely powdered K_2CO_3 (62.9 g, 455 mmol) was added in one portion, and the mixture was stirred until the solution changed color to bright canary yellow (in ~ 5 min). IMes·HCl (**3**) (65.1 g, 191 mmol) was added in one portion, and the reflux continued for another 30 min. After cooling, the mixture was diluted with CH_2Cl_2 and filtered, and the volatiles were removed in vacuum. IMes-Pd(dmba)Cl (**1**) (95.2 g, 90 % yield, white crystalline solid) was crystallized from CH_3CN (30 mL), filtered and dried in high vacuum; mp: 225–230 °C (with decomposition). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10 (s, 2H), 6.99 (s, 2H), 6.83–6.76 (m, 4H), 6.70 (td, *J* = 7.6, 1.2 Hz, 1H), 6.58 (d, *J* = 7.2, 1.2 Hz, 1H), 3.53 (s, 2H), 2.45 (s, 6H), 2.44 (s, 6H), 2.29 (s, 6H), 2.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.6, 149.3, 147.6, 138.3, 138.3, 137.4, 136.2, 133.9, 129.4, 128.7, 123.9, 123.2, 123.0, 121.2, 72.2, 50.0, 21.1, 20.2, 19.8. Anal. calcd for $C_{30}H_{36}ClN_3Pd$ (580.50): C, 62.07; H, 6.25; N, 7.24. Found: C, 62.02; H, 6.37; N, 7.40.

General procedure for Heck-Mizoroki reaction (A). In a vial with a magnetic stirrer bar, the arylbromide (1 mmol) and the olefin (1.5 mmol at 0.5 mol% or 1.2 mmol at 2 mol% **1**) were weighed in (if solids) or added via syringe (if liquids), followed by K_2CO_3 (276 mg, 2.0 mmol). Stock solution of IMes-Pd(dmba)Cl (**1**; 400 μL) was added and the atmosphere above the reaction mixture was purged with Ar over 30 sec. The vial was closed with a screw cap, and heated at 140 °C with vigorous stirring over 18 h. Two reactions were done side by side. After cooling, the combined reaction mixtures were filtered (CH_2Cl_2, total 20 mL). The crude product was loaded directly over a short pad of silica gel, and purified by flash chromatography. For experiments conducted in air, the same procedure was followed, except that the purging of precatalyst stock solution and reaction vial with Ar was omitted.

General procedure for Heck-Mizoroki reaction (B). In a vial with a magnetic stirrer bar, the arylbromide (1 mmol) and the olefin (1.5 mmol at 0.5 mol% or 1.2 mmol at 2 mol% **1**) were weighed in (if solids) or added via syringe (if liquids). *i*Pr_2NEt (350 μL, 258 mg, 2.0 mmol) and stock solution of IMes-Pd(dmba)Cl (**1**; 400 μL) were added, and the atmosphere above the reaction mixture was purged with Ar over 30 sec. The vial was closed with a screw cap, and heated at 120 °C with vigorous stirring over 18 h. Two reactions were done side by side. After cooling, the combined reaction mixtures were filtered (CH_2Cl_2, 20 mL). The crude product was loaded directly over a short pad of silica gel and purified by flash chromatography. For reactions under air, identical procedure was followed, except that purging of the catalyst stock solution and reaction vial with Ar was omitted.

(*E*)-*Tert*-butyl 3(4-methoxyphenyl)acrylate (7).[1] Following procedure A (2 mol% **1**), **7** (234 mg, 100%) was obtained as a colorless oil from *p*-bromoanisole (**5**) (125 μL, 187 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 0 to 10 %, 10 min).

(*E*)-*Tert*-butyl 3-*p*-tolylacrylate (8).[2] Following procedure A (0.5 mol% **1**), **8** (218 mg, 95%) was obtained from *p*-bromotoluene (171 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a pale yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10%, 15 min).

(*E*)-*Tert*-butyl 3-*m*-tolylacrylate (9).[2] Following procedure A (0.5 mol% **1**), **9** (216 mg, 91%) was obtained from 3-bromotoluene (120 μL, 169 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a pale yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10%, 15 min).

(*E*)-*Tert*-butyl 3-*o*-tolylacrylate (10).[3] Following procedure A (0.5 mol% **1**), **10** (182 mg, 84%) was obtained from 2-bromotoluene (120 μL, 171 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a pale yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10%, 15 min).

(*E*,*E*)-Di-*tert*-butyl benzene-1,4-dipropenoate (11).[4] Following procedure A (0.5 mol% **1**), **11** (133 mg, 81%) was obtained from 1,4-dibromobenzene (118 mg, 0.5 mmol) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10%, 15 min).

(*E*)-*Tert*-butyl 3-(2-naphthyl)acrylate (12).[5] Following procedure A (0.5 mol% **1**), **12** (254 mg, 96%) was obtained from 2-bromonaphthalene (207 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a colorless solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10%, 15 min).

(*E*)-*Tert*-butyl 3-(4-(trifluoromethyl)phenyl)acrylate (13).[6] Following procedure A (0.5 mol% **1**), **13** (240 mg, 88%) was obtained from 1-bromo-4-(trifluoromethyl)benzene (140 μL, 228 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a white crystalline solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10%, 10 min).

(*E*)-*Tert*-butyl 3-(3,5-difluorophenyl)acrylate (14). Following procedure A (0.5 mol% **1**), **14** (197 mg, 82%) was obtained from 1-bromo-3,5-difluorobenzene (115 μL, 193 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as white needles after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10%, 15 min); mp 65.3-67.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 15.9 Hz, 1H), 7.03–7.00 (m, 2H), 6.81 (tt, J = 8.7, 2.3 Hz, 1H), 6.34 (d, J = 15.9 Hz, 1H), 1.54 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.5, 163.1 (dd, $^{1}J_{C\text{-}F}$ = 241 Hz, $^{3}J_{C\text{-}F}$ = 6 Hz,), 140.9 (t, $^{4}J_{C\text{-}F}$ = 3 Hz), 137.9 (t, $^{3}J_{C\text{-}F}$ = 10 Hz), 122.9, 110.5 (dd, $^{2}J_{C\text{-}F}$ = 20 Hz, $^{4}J_{C\text{-}F}$ = 8 Hz,), 105.1 (t, $^{2}J_{C\text{-}F}$ = 26 Hz), 81.1, 28.1. Anal. calcd for $C_{13}H_{14}F_2O_2$ (240.25): C, 64.99; H, 5.87. Found: C, 65.47; H, 6.08.

(*E*)-*Tert*-butyl 3-(4-nitrophenyl)acrylate (15).[7] Following procedure A (0.5 mol% **1**), **15** (149 mg, 60%) was obtained from 1-bromo-4-nitrobenzene (202 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 20%, 15 min).

(*E*)-*Tert*-butyl 3-(4-formylphenyl)acrylate (16).[6] Following procedure A (0.5 mol% **1**), **16** (84.6 mg, 36 %) was obtained from 4-bromobenzaldehyde (185 mg) and *tert*-

butyl acrylate (**6**) (220 μL, 193 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 20%, 15 min).

Methyl 3-(*E*)-2-((*tert*-butoxycarbonyl)vinyl)benzoate (17). Following procedure A (0.5 mol% **1**), **17** (262 mg, 87%) was obtained from methyl 3-bromobenzoate (215 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 15%, 15 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13 (s, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 16.0 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 1.50 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 165.9, 142.2, 134.9, 132.1, 130.7, 128.9, 128.8, 121.4, 80.6, 52.2, 28.1. Anal. calcd for $C_{15}H_{18}O_4$ (262.30): C, 68.86; H, 6.92. Found: C, 68.54; H, 6.93.

(*E*)-*Tert*-butyl 3-(4-(*N*,*N*-dimethylamino)phenyl)acrylate (18).[8] Following procedure A (0.5 mol% **1**), **18** (225 mg, 91%) was obtained from 4-bromo-*N*,*N*-dimethylaniline (200 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a pale yellow solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 15%, 15 min).

(*E*)-*Tert*-butyl 3-(4-(benzyloxy)phenyl)acrylate (19).[9] Following procedure A (0.5 mol% **1**), **19** (291 mg, 94%) was obtained from 4-benzyloxy-1-bromobenzene (263 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 15%, 15 min).

(*E*)-*Tert*-butyl 3-(2-thienyl)acrylate (20).[10] Following procedure A (0.5 mol% **1**), **20** (179 mg, 87%) was obtained from 2-bromothiophene (96 μL, 162 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 15%, 15 min).

(*E*)-*Tert*-butyl 3-(3-pyridyl)acrylate (21).[11] Following procedure A (0.5 mol% **1**), **21** (225 mg, 91%) was obtained from 3-bromopyridine (98 μL, 158 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a pale yellow solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 15%, 15 min).

(*E*)-*Tert*-butyl 3-(2,4,6-triisopropylphenyl)acrylate (22). Following procedure A (2 mol% **1**), **22** (239 mg, 72 %) was obtained from 1-bromo-2,4,6-triisopropylbenzene (253 μL, 283 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient: 0%, 10 min, followed by 0 to 10%, 10 min); mp 93–95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, *J* = 16.3 Hz, 1H), 7.04 (s, 2H),

5.87 (d, *J* = 16.3 Hz, 1H), 3.14 (heptet, *J* = 6.9 Hz, 2H), 2.91 (heptet, *J* = 6.9 Hz, 1H), 1.57 (s, 9H), 1.28 (d, *J* = 6.9 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 148.7, 146.4, 143.3, 130.4, 126.1, 120.8, 80.6, 34.4, 34.3, 30.6, 28.3, 24.0. Anal. calcd for $C_{22}H_{34}O_2$ (330.50): C, 79.95; H, 10.37. Found: C, 79.42; H, 10.56.

(*E*)-*N*-isopropyl-3-mesitylacrylamide (23). Following procedure A (2 mol% **1**), **23** (163 mg, 70 %) was obtained from 2-bromomesitylene (155 μL, 199 mg) and *N*-isopropylacrylamide (136 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in dichloromethane: 10 to 40%, 20 min); mp 183–184 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 15.9 Hz, 1H), 6.89 (s, 2H), 5.94 (d, *J* = 15.9 Hz, 1H), 5.44 (broad d, 1H), 4.24 (heptet of doublets, *J* = 5.8, 1.3 Hz, 1H), 2.32 (s, 6H), 2.29 (s, 3H) 1.24 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.0, 139.3, 137.7, 136.6, 131.6, 129.0, 125.9, 41.6, 22.9, 21.1, 21.0. Anal. calcd for $C_{15}H_{21}NO$ (231.33): C, 77.88; H, 9.15; N, 6.05. Found: C, 77.92; H, 9.32; N, 5.88.

(*E*)-3-(4-(methylthio)phenyl)-1-(morpholine-1'-yl)-prop-2-en-1-one (24). Following procedure A (2 mol% **1**), 4-bromothioanisole (203 mg) and *N*-acryloyl morpholine (150 μL, 169 mg) were used. The reactions were cooled and combined after filtration (CH_2Cl_2, a total of 30 mL), washed with water (5 × 20 mL) and dried ($MgSO_4$); the volatiles were removed under reduced pressure. **24** (169 mg, 75 %) was obtained as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane-CH_2Cl_2 (volume ratio = 5:1) gradient: 0 to 25%, 25 min); mp 113–119 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 15.4 Hz, 1H), 7.44 (m, 2H), 7.22 (m, 2H), 6.80 (d, *J* = 15.4 Hz, 1H), 3.73 (m, 8H), 2.49 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7, 142.7, 141.1, 131.7, 128.2, 126.1, 115.4, 66.9, 15.3. Anal. calcd for $C_{14}H_{17}NO_2S$ (263.36): C, 63.85; H, 6.51; N, 5.32. Found: C, 64.03; H, 6.51; N, 5.20.

(*E*)-*Tert*-butyl 3-(4-hydroxy-3-((1'-phenyl-1'*H*-pyrazol-4'-yl)formyl)phenyl)-acrylate (25). Following procedure A (2 mol% **1**), **25** (301 mg, 77%) was obtained from (5-bromo-2-hydroxyphenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (343 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a pale yellow solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 10 to 20%, 10 min); mp 129–131 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.23 (s, 1H), 8.51 (s, 1H), 8.21 (s, 1H), 8.03 (d, *J* = 2.2 Hz, 1H), 7.78 (m, 2H), 7.73 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.55 (m, 3H), 7.43 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 1.57 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 191.8, 166.3, 164.1, 142.4, 142.1, 139.1, 134.6, 131.6, 130.6, 129.8, 128.1, 126.0, 123.1, 120.0, 119.9,

119.4, 118.9, 80.7, 28.2. Anal. calcd for $C_{23}H_{22}N_2O_2$ (390.43): C, 70.75; H, 5.68; N, 7.17. Found: C, 70.43; H, 5.80; N, 6.89.

(*E*)-*Tert*-butyl 3-(4-amino-3,5-dimethylphenyl)acrylate (26). Following procedure A (2 mol% **1**), **26** (218 mg, 88 %) was obtained from 4-bromo-3,5-dimethylaniline (200 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 10 to 20%, 20 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, *J* = 16.0 Hz, 1H), 7.15 (s, 2H), 6.19 (d, *J* = 16.0 Hz, 1H), 3.84 (broad s, 2H), 2.19 (s, 6H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 145.0, 144.3, 128.6, 124.3, 121.5, 115.3, 79.8, 28.3, 17.6. Anal. calcd for $C_{15}H_{21}NO_2$ (247.33): C, 72.84; H, 8.56; N, 5.66. Found: C, 72.52; H, 8.59; N, 5.52.

(*E*)-*Tert*-butyl 3-(3,4,5-trimethoxyphenyl)acrylate (27).[12] Following procedure A (2 mol% **1**), **27** (268 mg, 91%) was obtained from 5-bromo-1,2,3-trimethoxybenzene (247 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 15%, 15 min).

(*E*)-*Tert*-butyl 3-(2,3-dimethoxynaphthalen-4-yl)acrylate (28). Following procedure A (2 mol% **1**), **28** (218 mg, 88%) was obtained from 1-bromo-2,3-dimethoxynaphthalene (267 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 5 to 15%, 20 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (d, *J* = 16.2 Hz, 1H), 8.09 (m, 1H), 7.73 (m, 1H), 7.46–7.37 (m, 2H), 7.20 (s, 1H), 6.61 (d, *J* = 16.2 Hz, 1H), 4.00 (s, 3H), 3.86 (s, 3H), 1.58 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.6, 151.8, 148.5, 136.8, 131.3, 127.3, 127.1, 126.8, 125.6, 124.7, 124.3, 124.1, 108.6, 80.6, 60.8, 55.7, 27.4. Anal. calcd for $C_{19}H_{22}O_4$ (314.38): C, 72.59; H, 7.05. Found: C, 72.49; H, 7.30.

(*E*)-*Tert*-butyl 3-(2,4,6-trimethoxyphenyl)acrylate (29). Following procedure A (2 mol% **1**), **29** (121 mg, 41%) was obtained from 2-bromo-1,3,5-trimethoxybenzene (248 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 20%, 20 min); mp 140–145 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 16.2 Hz, 1H), 6.68 (d, *J* = 16.2 Hz, 1H), 6.12 (s, 3H), 3.87 (s, 6H), 3.85 (s, 3H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.4, 161.1, 134.4., 119.4, 106.0, 90.4, 79.5, 55.7, 55.4, 28.3. Anal. calcd for $C_{16}H_{22}O_5$ (294.34): C, 65.29; H, 7.53. Found: C, 65.65; H, 8.09. In addition, unreacted starting bromide (137 mg, 55%) was recovered before the elution of product **29**.

(*E*)-*Tert*-butyl 3-(2,4-dimethoxypyrimidin-5-yl)acrylate (30). Following procedure A (2 mol% **1**), **30** (224 mg, 84%) was obtained from 5-bromo-2,4-dimethoxypyrimidine (219 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 20 to 40%, 20 min); mp 129–132 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (s, 1H), 7.20 (d, *J* = 15.8 Hz, 1H), 6.90 (d, *J* = 15.8 Hz, 1H), 3.45 (s, 3H), 3.39 (s, 3H), 1.50 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.8, 161.4, 150.8, 144.2, 135.0, 121.2, 109.1, 80.4, 37.5, 28.1. Anal. calcd for $C_{13}H_{18}N_2O_4$ (266.29): C, 58.63; H, 6.81; N, 10.52. Found: C, 58.71; H, 6.92; N, 10.41.

(*E*)-*Tert*-butyl 3-(isoquinolin-4-yl)acrylate (31). Following procedure A (2 mol% **1**), **31** (213 mg, 83%) was obtained from 4-bromoisoquinoline (267 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a yellow solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 10 to 30%, 20 min); mp 51–56 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.24 (s, 1H), 8.74 (d, *J* = 0.4 Hz, 1H), 8.27 (dd, *J* = 15.8, 0.7 Hz, 1H), 8.15 (dd, *J* = 8.5, 0.7 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.79 (td, *J* = 8.4, 1.3 Hz, 1H), 7.67 (td, *J* = 8.1, 1.1 Hz, 1H), 6.53 (dd, *J* = 16.6, 0.8 Hz, 1H), 1.58 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 165.7, 153.8, 141.5, 137.6, 133.7, 131.2, 128.3, 128.1, 127.6, 125.9, 124.3, 122.7, 81.1, 28.2. Anal. calcd for $C_{16}H_{17}NO_2$ (255.31): C, 75.27; H, 6.71; N, 5.49. Found: C, 75.24; H, 6.94; N, 5.34.

(*E*)-*Tert*-butyl 3-(1-methyl-1*H*-imidazol-5-yl)acrylate (32). Following procedure A (2 mol% **1**), 5-bromo-*N*-methylimidazole (161 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) were used. The reactions were cooled and combined after filtration (CH_2Cl_2, a total of 30 mL), washed with water (5 × 20 mL) and dried ($MgSO_4$); the volatiles were removed under reduced pressure. The product **32** (106 mg, 51%) was obtained as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 30 to 70%, 20 min); mp 75–77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (s, 1H), 7.44 (dd, *J* = 16.0, 0.4 Hz, 1H), 7.43 (s, 1H), 6.22 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 1.84 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.3, 140.7, 131.9, 128.8, 128.5, 118.3, 80.8, 32.3, 28.2. HR-MS (FAB) calcd for $C_{11}H_{16}N_2O_2$ ($[M+H]^+$): 209.1285. Found: 209.1279 (δ -2.80 ppm).

(*E*)-*Tert*-butyl 3-(1,3,5-trimethyl-1*H*-pyrazol-4-yl)acrylate (33). Following procedure A (4 mol% **1**; 0.8 mL of stock solution), 4-bromo-1,3,5-trimethyl-1*H*-pyrazole (189 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) were used. The reactions were cooled and combined after filtration (CH_2Cl_2, a total of 30 mL), washed with water (5 × 20 mL) and dried ($MgSO_4$); the volatiles were removed under reduced pressure. The product **33** (77 mg, 32 %) was obtained as a white solid after column chromatography on silica gel (ethyl acetate

gradient in hexane: 20 to 40 %, 20 min); mp 110–114 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, *J* = 16.1 Hz, 1H), 5.97 (d, *J* = 16.1 Hz, 1H), 3.73 (s, 3H), 2.33 (d, *J* = 8.6 Hz, 6H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 167.5, 147.4, 140.1, 135.0, 115.6, 113.2, 80.0, 36.0, 28.3, 13.9, 10.2. Anal. calcd for $C_{13}H_{20}N_2O_2$ (236.31): C, 66.07; H, 8.53; N, 11.85. Found: C, 65.71; H, 8.18; N, 11.61. In addition, unreacted starting bromide (93 mg, 49 %) was recovered before the elution of product **33**.

(*E*)-*Tert*-butyl 3-(benzo[*b*]thiophen-3-yl)acrylate (34). Following procedure A (2 mol % **1**), **34** (154 mg, 59 %) was obtained from 3-bromothianaphthene (130 μL, 213 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 0 to 10 %, 10 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.88 (dd, *J* = 16.0, 0.7 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.47 (m, 1H), 7.41 (m, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 1.57 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 140.5, 137.2, 135.3, 131.8, 127.5, 125.0, 124.9, 123.0, 122.1, 120.7, 80.7, 28.3. Anal. calcd for $C_{15}H_{16}O_2S$ (260.35): C, 69.20; H, 6.19. Found: C, 69.46; H, 6.53.

(1'*R*,2'*R*,3'*R*,5'*S*)-4-iodo-*N*-(2',6',6'-bicyclo[3.1.1]hept-3'-yl)phenylsulfonamide (35a). Pyridine (600 μL, 593 mg, 7.5 mmol) and (-)-isopinocampheylamine (920 μL, 842 mg, 5.5 mmol) were added to a solution of *p*-iodophenylsulfonyl chloride (1.51 g, 5 mmol) in dry CH_2Cl_2 (10 mL) in succession under Ar. The solution was stirred overnight, transferred into a separatory funnel (CH_2Cl_2), and washed with water (10 mL), 10% aqueous H_2SO_4 (10 mL), saturated aqueous $NaHCO_3$ solution (10 mL), brine (10 mL), and dried ($MgSO_4$). The volatiles were removed under reduced pressure. Sulfonamide **35a** was obtained as a white solid (1.18 g, 56%) after flash chromatography (Combiflash 40 g silica gel cartridge, ethyl acetate gradient in hexane: 0 to 60 %, 30 min); mp 150–151 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, *J* = 13.0 Hz, 2H), 7.63 (d, *J* = 13.0 Hz, 2H), 4.71 (d, *J* = 9.0 Hz, 1H), 3.55 (m, 1H), 2.37 (m, 1H), 2.27 (m, 1H), 1.86 (broad m, 1H), 1.79 (broad m, 1H), 1.79 (t, *J* = 6.3 Hz, 1H), 1.52 (ddd, *J* = 14.1, 6.1, 2.4 Hz, 1H), 1.18 (s, 3H), 0.96 (d, *J* = 7.0, 3H), 0.92 (s, 3H), 0.78 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.3, 138.3, 128.5, 99.7, 53.0, 47.5, 46.4, 41.5, 38.3, 38.3, 35.2, 27.8, 23.4, 20.0. Anal. calcd for $C_{16}H_{22}INO_2S$ (419.32): C, 45.83; H, 5.29; N, 3.34. Found: C, 46.16; H, 5.26; N, 3.30.

(1'R,2'R,3'R,5'S)-(*E*)-*Tert*-butyl 3-(4-(*N*-(2',6',6'-bicyclo[3.1.1]hept-3'-yl)sulfonamido)phenyl)acrylate (35). Following the general procedure (2 mol% of **1**), **35** (319 mg, 76 %) was obtained from **35a** (419 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a pale

yellow solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 5 to 30 %, 20 min); mp 145–148 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 16.4 Hz, 1H), 6.47 (d, *J* = 16.4 Hz, 1H), 4.87 (broad m, 1H), 3.55 (qt, *J* = 8.4 Hz, 1H), 2.43 (m, 1H), 2.31 (m, 1H), 1.83–1.77 (m, 3H), 1.58–1.51 (m, 1H), 1.54 (s, 9H), 1.17 (s, 3H), 0.92 (d, *J* = 7.6 Hz, 3H), 0.91 (s, 3H), 0.79 (d, *J* = 9.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 142.2, 141.4, 138.6, 128.3, 127.6, 123.3, 81.1, 52.9, 47.5, 41.5, 38.3, 35.2, 28.1, 27.8, 23.4, 19.9. HR-MS (FAB) calcd for $C_{23}H_{34}NO_4S$ ($[M+H]^+$): 420.2203. Found: 420.2195 (δ -1.89 ppm).

3-(4-Chlorophenyl)acrylonitrile (36).[13] Following procedure A (0.5 mol% **1**, 100°C), **36** (143 mg, 88 %) was obtained from 1-chloro-4-iodobenzene (239 mg) and *tert*-butyl acrylate (**6**) (220 μL, 193 mg) as a colorless oil (*E*:*Z* = 6:1 determined by ^{1}H NMR spectroscopy) after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 10 to 30 %, 15 min).

(*E*)-3-(4-chlorophenyl)-*N*,*N*-diisopropylacrylamide (37).[14] Following procedure A (2 mol% **1**), **37** (252 mg, 95 %) was obtained from *p*-chloroiodobenzene (238 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 10 to 30 %, 20 min).

(*E*)-*Tert*-butyl 3-(4-methoxy-2-nitrophenyl)acrylate (38). Following procedure A (2 mol% **1**), **38** (189 mg, 68 %) was obtained from 4-iodo-3-nitroanisole (279 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a yellow oil after column chromatography on silica gel (ethyl acetate gradient: 0 to 20 %, 20 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 15.8 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 2.6 Hz, 1H), 7.50 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 3.91 (s, 3H), 1.54 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 28.2, 56.0, 81.0, 109.3, 120.0, 122.8, 123.5, 129.9, 138.2, 149.3, 160.7, 165.4. Anal. calcd for $C_{14}H_{19}NO_5$ (279.29): C, 60.21; H, 6.14; N, 5.02. Found: C, 60.55; H, 6.22; N, 5.00.

(*E*)-*N*-isopropyl-3-(2,6-dimethoxyphenyl)acrylamide (39). Following procedure A (2 mol% **1**), 2,6-dimethoxyiodobenzene (264 mg) and *N*-isopropylacrylamide (136 mg) were used. The reactions were cooled and combined after filtration (CH_2Cl_2, a total of 30 mL), washed with water (5 × 20 mL) and dried ($MgSO_4$); the volatiles were removed under reduced pressure. Amide **39** (309 mg, 88 %) was obtained as a white solid after trituration with hexane/diethyl ether mixture (volume ratio = 1:1), and dried in high vacuum; mp 171–172 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, *J* = 15.9 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 15.9 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 5.25 (broad s, 1H), 4.23 (heptet, *J* = 6.6

Hz, 1.3 Hz, 1H), 3.87 (s, 6H), 2.29 (s, 3H) 1.21 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 159.7, 131.2, 130.3, 123.8, 112.6, 103.7, 55.7, 41.4, 22.9. Anal. calcd for $C_{14}H_{19}NO_3$ (249.31): C, 67.45; H, 7.68; N, 5.62. Found: C, 67.08; H, 7.48; N, 5.62.

(*E*)-*Tert*-butyl 3-(3-amino-4-methoxyphenyl)acrylate (40). Following procedure A (2 mol% **1**), 4-iodo-2-amino-anisole (249 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) were used. The reactions were cooled and combined after filtration (CH_2Cl_2, a total of 30 mL), washed with water (5 × 20 mL) and dried ($MgSO_4$); the volatiles were removed under reduced pressure. Product **40** (249 mg, 79 %) was obtained as a pale yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 10 to 30 %, 20 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 15.9 Hz, 1H), 6.96 (m, 2H), 6.75 (m, 1H), 6.19 (d, *J* = 15.9 Hz, 1H), 3.87 (s, 3H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.9, 149.1, 143.9, 136.4, 127.7, 120.0, 117.4, 113.2, 110.1, 80.1, 55.5, 28.2. Anal. calcd for $C_{14}H_{19}NO_3$ (249.31): C, 67.45; H, 7.68; N, 5.62. Found: C, 67.57; H, 7.67; N, 5.49.

(*E*)-*N*,*N*-diisopropyl-3-(5-methylthiophen-2-yl)acrylamide (41). Following procedure A (2 mol% **1**), **39** (197 mg, 78 %) was obtained from 2-iodo-5-methylthiophene (224 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a white crystalline solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 20 to 40 %, 20 min); mp 73–79 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, *J* = 15.0 Hz, 1H), 6.96 (s, 1H), 6.65 (s, 1H), 6.50 (d, *J* = 15.0 Hz, 1H), 4.03 (broad s, 1H), 3.88 (broad s, 1H), 2.47 (s, 3H), 1.32 (broad d, 12H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 165.9, 141.8, 138.8, 134.3, 130.2, 126.2, 118.0, 47.7 (broad), 45.8 (broad), 21.7 (broad), 20.7 (broad), 15.7. Anal. calcd for $C_{14}H_{21}NOS$ (251.39): C, 66.89; H, 8.42; N, 5.57. Found: C, 66.95; H, 8.41; N, 5.54.

(*E*)-*Tert*-butyl 3-(2-aminopyrimidin-5-yl)acrylate (42). Following procedure A (2 mol% **1**), **42** (173 mg, 63 %) was obtained from 2-amino-5-iodopyrimidine (221 mg) and *tert*-butyl acrylate (**6**) (175 μL, 154 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 10 to 30 %, 20 min); mp 209–212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.46 (s, 2H), 7.40 (d, *J* = 16.0 Hz, 1H), 6.28 (d, *J* = 16.1 Hz, 1H), 5.47 (broad s, 2H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0, 163.1, 157.8, 137.2, 119.1, 118.2, 80.7, 28.2. Anal. calcd for $C_{11}H_{15}N_3O_2$ (221.26): C, 59.71; H, 6.83; N, 18.99. Found: C, 59.59; H, 6.83; N, 18.95.

1,2,3-Trimethoxy-5-styrylbenzene (43).[15] Following procedure A (2 mol% **1**), **43** (246 mg, 91 %) was obtained from 5-bromo-1,2,3-trimethoxybenzene (247 mg) and styrene

(175 μL, 154 mg) as a yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 0 to 15 %, 15 min).

2-(2,5-dimethylstyryl)benzonitrile (44). Following procedure B (2 mol% **1**), **44** (188 mg, 81%) was obtained from 2-bromobenzonitrile (182 mg) and 2,5-dimethylstyrene (175 μL, 159 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10 %, 10 min); mp 72–76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.55–7.50 (m, 2H), 7.37 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.13–7.07 (m, 2H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 141.0, 135.9, 135.0, 133.4, 133.2, 132.8, 131.4, 130.5, 129.5, 127.5, 126.4, 125.5, 125.0, 118.2, 111.1, 21.1, 19.5. Anal. calcd for $C_{17}H_{15}N$ (233.31): C, 87.52; H, 6.48; N, 6.00. Found: C, 87.38; H, 6.66; N, 5.91.

2-(4-Methoxystyryl)-5-methylthiophene (45).[16] Following procedure A (2 mol% **1**), **45** (181 mg, 79 %) was obtained from 2-iodo-5-methylthiophene (120 μL, 222 mg) and 1-methoxy-4-vinylbenzene (161 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 0 to 10 %, 10 min).

3-(4-Chlorostyryl)-4-hydroxybenzaldehyde (46). Following procedure A (2 mol% **1**), 3-bromo-4-hydroxybenzaldehyde (201 mg) and 1-chloro-4-vinylbenzene (144 μL, 166 mg) were used. The reactions were cooled and combined after filtration (CH_2Cl_2, a total of 30 mL), washed with 10% aqueous H_2SO_4 (5 × 20 mL), washed with water (3 × 20 mL) and dried ($MgSO_4$); the volatiles were removed under reduced pressure. Product **44** (190 mg, 74 %) was obtained as a yellow solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 20 to 40 %, 20 min); mp 121.0-125.5 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.30–10.75 (broad s, 1H), 9.84 (s, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 7.69 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.46–7.35 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.7, 161.1, 136.7, 132.4, 130.9, 129.7, 129.2, 129.1, 128.6, 128.6, 124.7, 123.7, 116.8. Anal. calcd for $C_{15}H_{11}ClO_2$ (258.04): C, 69.64; H, 4.29. Found: C, 69.27; H, 4.51.

(3-Trifluoromethylstyryl)ferrocene (47). Following procedure A (2 mol % **1**), **45** (339 mg, 95 %) was obtained from 4-bromobenzotrifluoride (165 μL, 270 mg) and vinylferrocene (201 mg) as deep orange crystals after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 0 to 10%, 15 min); mp 154–155 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (m, 4H), 7.00 (d, *J* = 16.4 Hz, 1H), 6.72 (d, *J* = 16.4 Hz, 1H), 4.50 (s, 2H), 4.34 (s, 2H), 4.16 (s, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 130.0,

128.3 (q, $^{2}J_{C\text{-}F}$ = 32 Hz), 125.7, 125.7, 125.6 (q, $^{1}J_{C\text{-}F}$ = 4 Hz), 125.0 (q, $^{3}J_{C\text{-}F}$ = 132 Hz), 69.5, 69.3, 67.2. Anal. calcd for $C_{19}H_{15}F_3Fe$ (356.16): C, 64.07; H, 4.24. Found: C, 64.56; H, 4.38.

4-(3-Methylstyryl)pyridine (48). Following procedure A (2 mol% **1**), **48** (181 mg, 92%) was obtained from 3-bromotoluene (120 μL, 169 mg) and 4-vinyl pyridine (120 μL, 127 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10%, 15 min); mp 74–76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.58 (d, *J* = 6.2 Hz, 2H), 7.36–7.34 (m, 4H), 7.31–7.25 (m, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 16.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2, 144.7, 138.5, 136.1, 133.3, 129.6, 128.8, 127.7, 125.7, 124.3, 120.8, 21.4. Anal. calcd for $C_{14}H_{13}N$ (195.26): C, 86.12; H, 6.71; N, 7.17. Found: C, 86.22; H, 6.77; N, 7.01.

3,5-Dimethylphenyl trifluoromethanesulfonate (49).[17] A 250-mL round-bottom flask was charged with a magnetic stirrer bar, *N*,*N*-dimethylaminopyridine (50 mg, 0.4 mmol) and 3,5-dimethylphenol (2.44 g, 20 mmol). The flask was then evacuated and flushed with Ar three times, and placed into an ice bath. Anhydrous CH_2Cl_2 (20 mL), followed by pyridine (10 mL, 791 mg, 124 mmol), were added in one portion via a syringe and the mixture was stirred for 15 min. Trifluoromethanesulfonyl anhydride (3.7 mL, 6.21 g, 22 mmol) was added drop-wise at 0 °C. Subsequently, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was quenched with water (20 mL) and stirred for 20 min. The organic layer was extracted with CH_2Cl_2 (3 × 15 mL), combined and washed with 10% aqueous H_2SO_4 (5 × 30 mL) and water (3 × 20 mL), and dried ($MgSO_4$); the volatiles were removed under reduced pressure to yield **49** (4.47 g, 88 %) as a colorless oil. Compound **49** was used without further purification.

General procedure for Heck-Mizoroki reaction of aryltriflates (C). A vial was charged with a magnetic stirrer bar, 3,5-dimethylphenyl trifluoromethanesulfonate (**49**) (190 μL, 254 mg, 1 mmol), the olefin (1.2 mmol), TBAB (322 mg, 1 mmol) and K_2CO_3 (276 mg, 2.0 mmol). Stock solution of **1** (2 mol%; 400 μL) was added, and the atmosphere above the reaction mixture was purged with Ar over 30 sec. The vial was closed with a screw cap and heated at 140 °C with vigorous stirring over 18 h. Two reactions were performed side by side. After cooling, the reactions were combined after filtration (CH_2Cl_2, a total of 30 mL), washed with water (5 × 20 mL) and dried ($MgSO_4$); the volatiles were removed under reduced pressure. The crude product was loaded directly over a short pad of silica gel, and purified by flash chromatography.

(*E*)-*Tert*-butyl 3-(3,5-dimethylphenyl)acrylate (50). Following procedure C (2 mol% **1**), **50** (364 mg, 79 %) was obtained from *tert*-butyl acrylate (**6**) (175 µL, 154 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 10 min, followed by 0 to 10 %, 15 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, *J* = 16.0 Hz, 1H), 7.14 (s, 2H), 7.02 (s, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 6H), 1.54 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 143.9, 138.3, 134.6, 131.8, 125.8, 119.7, 80.4, 28.2, 21.2. Anal. calcd for $C_{15}H_{20}O_2$ (232.32): C, 77.55; H, 8.68. Found: C, 77.07; H, 8.33.

***N*,*N*-diisopropyl 3-(3,5-dimethylphenyl)acrylamide (51).** Following procedure C, **51** (364 mg, 64 %) was obtained from *N*,*N*-diisopropylacrylamide (186 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0%, 5 min, followed by 0 to 20%, 15 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, *J* = 15.4 Hz, 1H), 7.11 (s, 2H), 6.97 (s, 1H), 6.81 (d, *J* = 15.4 Hz, 1H), 4.13 (broad s, 1H), 3.84 (broad s, 1H), 2.33 (s, 6H), 1.40–1.32 (broad m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 141.2, 138.2, 135.6, 131.1, 125.4, 120.2, 48.0 (broad), 45.9 (broad), 21.7 (broad), 21.3, 20.7 (broad). HR-MS (FAB) calcd for $C_{17}H_{26}NO$ ($[M+H]^+$): 260.2009. Found: 260.2008 (δ -0.33 ppm).

1-(3,5-Dimethylstyryl)-4-methoxybenzene (52). Following procedure C (2 mol% **1**), **52** (173 mg, 73 %) was obtained from 4-methoxystyrene (161 mg) as a white crystalline solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 0 to 15 %, 20 min); mp 56–58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (m, 2H), 7.14 (s, 2H), 7.06 (m, 1H), 6.97 (m, 1H), 6.92 (m, 2H), 3.85 (s, 3H), 2.35 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 138.1, 137.5, 130.3, 129.1, 127.8, 127.6, 126.8, 124.2, 114.1, 55.3, 21.3. Anal. calcd for $C_{17}H_{18}O$ (238.32): C, 85.67; H, 7.61. Found: C, 85.27; H, 7.70.

1-(4-Chlorostyryl)-3,5-dimethylbenzene (53). Following procedure C (2 mol% **1**), **53** (136 mg, 56 %) was obtained from 4-chlorostyrene (145 µL, 167 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 10 min, followed by 0 to 15 %, 20 min); mp 54–58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (m, 2H), 7.33 (m, 2H), 7.15 (s, 2H), 7.05 (s, 2H), 6.95 (s, 1H), 2.36 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.2, 136.9, 133.0, 129.7, 129.5, 128.8, 127.6, 127.6, 127.0, 124.5, 21.3. Anal. calcd for $C_{16}H_{15}Cl$ (242.09): C, 79.17; H, 6.23. Found: C, 79.59; H, 6.29.

General procedure for double Heck-Mizoroki arylation reaction (D). In a vial with a magnetic stirrer bar, the arylbromide (2.2 mmol) and *tert*-butyl acrylate (**6**) (145 µL, 128 mg, 1.0 mmol) were weighed in (if solids) or added via syringe (if liquids), followed by the addition of K_2CO_3 (276 mg, 2.0 mmol). Stock solution of IMes-Pd(dmba)Cl (**1**) (4 mol%;

800 μL) was added, and the atmosphere above the reaction mixture was purged with Ar over 30 sec. The vial was closed with a screw cap and heated at 140 °C with vigorous stirring over 18 h. Two reactions were performed side by side. After cooling, the combined reaction mixtures were filtered (CH_2Cl_2, a total of 20 mL), washed with H_2O (5 × 20 mL) and dried ($MgSO_4$); the volatiles were removed under reduced pressure. The crude product was loaded directly over a short pad of silica gel, and purified by flash chromatography.

***Tert*-butyl (*E*)-2-methoxycinnamate (54).**[6] Following procedure D (4 mol% **1**), **54** (236 mg, 100 %) was obtained from 2-bromoanisole (275 μL, 412 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min).

***Tert*-butyl 3,3-bis(3-methoxyphenyl)acrylate (55).** Following procedure D (4 mol % **1**), **55** (313 mg, 92%) was obtained from 3-bromoanisole (275 μL, 412 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.21 (m, 2H), 6.93–6.75 (m, 6H), 6.28 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 1.55 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 165.8, 159.2, 153.8, 140.7, 129.3, 129.0, 121.7, 120.8, 120.1, 114.6, 114.5, 113.8, 113.6, 80.4, 55.3, 55.2, 27.8. Anal. calcd for $C_{21}H_{24}O_4$ (340.41): C, 74.09; H, 7.11. Found: C, 74.12; H, 7.12.

***Tert*-butyl 3,3-bis(4-methoxyphenyl)acrylate (56).**[18] Following procedure D (4 mol% **1**), **56** (310 mg, 91 %) was obtained from 4-bromoanisole (275 μL, 412 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min).

***Tert*-butyl (*E*)-2-methylcinnamate (10).**[3] Following procedure D (4 mol% **1**), **10** (186 mg, 86 %) was obtained from 2-bromotoluene (265 μL, 376 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min).

***Tert*-butyl 3,3-di-(3-tolyl)acrylate (57).** Following procedure D (4 mol% **1**), **57** (249 mg, 81%) was obtained from 3-bromotoluene (270 μL, 380 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min). ^{1}H NMR ($CDCl_3$, 400 7. MHz): δ 7.29–7.25 (broad m, 1H), 7.22–7.15 (m, 3H), 7.15 (broad s, 3H), 7.07–7.05 (broad m, 1H), 7.01–6.99 (broad m, 2H), 6.24 (s, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.0, 154.7, 141.1, 139.5, 137.9, 137.3, 137.3, 129.9, 129.8, 128.6, 128.1, 127.7, 126.3, 125.5,

119.7, 80.2, 27.8, 21.4, 21.4. Anal. calcd for $C_{21}H_{24}O_2$ (308.41): C, 81.78; H, 7.84. Found: C, 81.73; H, 7.96.

***Tert*-butyl 3,3-di(4-tolyl)acrylate (58).** Following procedure D (4 mol% **1**), **58** (258 mg, 84 %) was obtained from 4-bromotoluene (376 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55–7.50 (m, 8H), 6.22 (s, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.32 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.0, 154.8, 139.2, 138.5, 137.7, 136.5, 129.3, 129.0, 128.5, 128.3, 118.6, 80.1, 27.9, 21.4, 21.2. Anal. calcd for $C_{21}H_{24}O_2$ (308.41): C, 81.78; H, 7.84. Found: C, 81.67; H, 7.94.

(*E*)-*Tert*-butyl 3-(2-trifluoromethylphenyl)acrylate (59).[19] Following procedure D (4 mol% **1**), **59** (168 mg, 62 %) was obtained from 2-bromobenzotrifluoride (300 μL, 496 mg) as a yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min).

***Tert*-butyl 3,3-di-(3-trifluoromethylphenyl)acrylate (60) and (*E*)-*Tert*-butyl 3-(3-trifluoromethylphenyl)acrylate (61).**[19] Following procedure D (4 mol% **1**), an inseparable mixture of **60** (100 mg, 24 %) and **61** (112 mg, 41 %) was obtained from 3-bromobenzotrifluoride (300 μL, 496 mg) as a yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min). The yields of **60** and **61** were determined by integration of the ^{1}H NMR spectra of the mixture. Selected resonances: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.32 (m), 6.45 (d, J = 16.0 Hz), 6.39 (s), 1.55 (s), 1.30 (s). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 165.7, 164.8, 81.2, 81.0, 28.2, 27.7. Compound **60**: HR-MS (FAB) calcd for $C_{21}H_{19}F_6O_2$ ($[M+H]^+$): 417.1284. Found: 417.1294 (δ +2.40 ppm).Compound **61**: HR-MS (FAB) calcd for $C_{14}H_{16}F_3O_2$ ($[M+H]^+$): 273.1097. Found: 273.1096 (δ -0.49 ppm).

(*E*)-*Tert*-butyl 3-(4-trifluoromethylphenyl)acrylate (13) and *tert*-butyl 3,3-di-(4-trifluoromethylphenyl)acrylate (62).[19] Following procedure D (4 mol% **1**), an inseparable mixture of **13** (161 mg, 59 %) and **62** (87 mg, 21 %) was obtained from 4-bromobenzotrifluoride (300 μL, 496 mg) as a yellow oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min). The yields of **13** and **62** were determined by integration of the ^{1}H NMR spectra of the mixture. Selected resonances: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (dd, J = 9.2, 0.8 Hz), 6.45 (d, J = 16.0 Hz), 6.40 (s), 1.55 (s), 1.30 (s). ^{13}C NMR ($CDCl_3$, 400 MHz): d 165.7, 164.7, 81.2, 81.0, 28.1; 27.7. Compound **13**: HR-MS (FAB) calcd for $C_{14}H_{16}F_3O_2$ ($[M+H]^+$): 273.1097. Found:

273.1090 (δ -2.44 ppm). Compound **62**: HR-MS (FAB) calcd for $C_{21}H_{19}F_6O_2$ ($[M+H]^+$): 417.1284. Found: 417.1289 (δ +1.27 ppm).

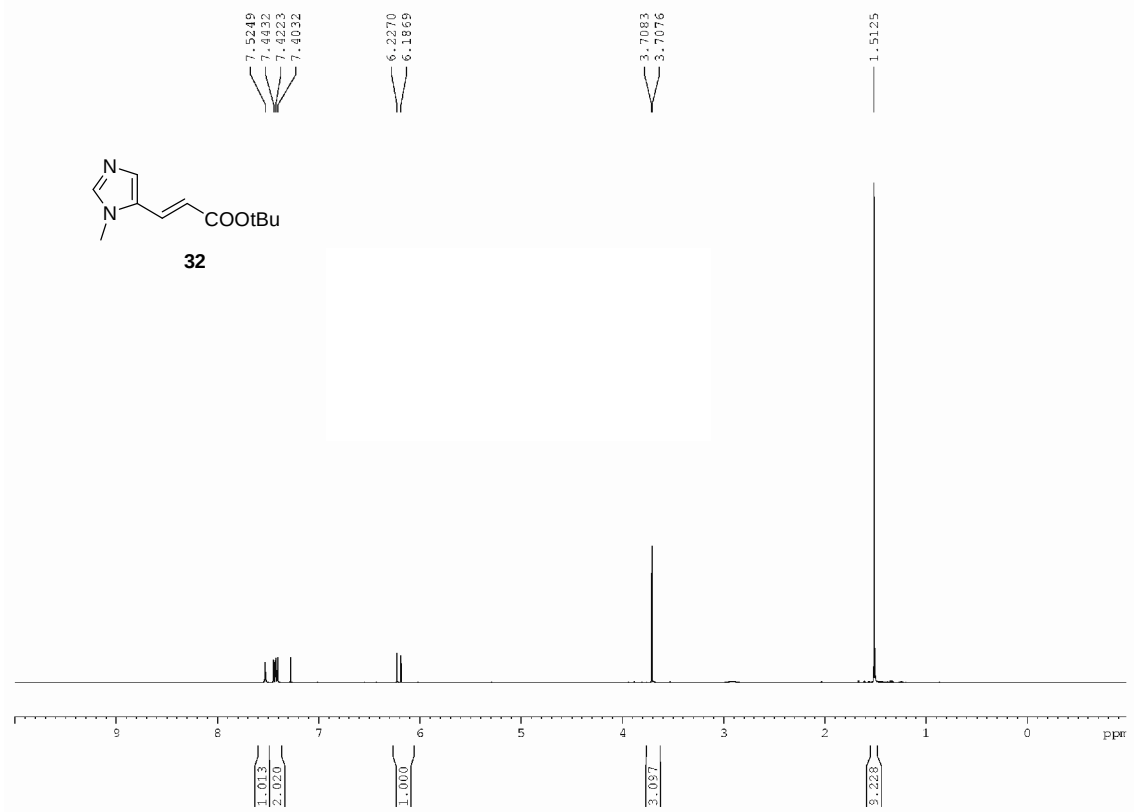
Methyl 2-((*E*)-2-(*tert*-butoxycarbonyl)vinyl)benzoate (63). Following procedure D (4 mol% **1**), **63** (233 mg, 89%) was obtained from methyl 2-bromobenzoate (473 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (d, *J* = 16.0 Hz, 1H), 7.94–7.91 (m, 1H), 7.60–7.58 (m, 1H), 7.52–7.46 (m, 1H), 7.43–7.37 (m, 1H), 6.24 (d, *J* = 15.8 Hz, 1H), 3.92 (s, 1H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 167.4, 165.9, 142.5, 136.4, 132.3, 130.7, 129.2, 127.8, 123.0, 80.6, 52.4, 28.2. HR-MS (FAB) calcd for $C_{15}H_{19}O_4$ ($[M+H]^+$): 263.1278. Found: 263.1285 (δ 2.69 ppm).

***Tert*-butyl 3,3-bis(3-(methoxycarbonyl)phenyl)acrylate (64) and methyl 3-((*E*)-2-(*tert*-butoxycarbonyl)vinyl)benzoate (17).** Following procedure D (4 mol% **1**), **17** (164 mg, 63%; eluted at 5 % ethyl acetate) and **64** (24 mg, 6 %; eluted at 10% ethyl acetate) were obtained from methyl 3-bromobenzoate (473 mg) as a colorless oil after column chromatography on silica gel (ethyl acetate gradient: 0 %, 5 min, followed by 0 to 20 %, 20 min). Compound **64**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09–8.07 (m, 1H), 8.03–8.01 (m, 1H), 7.99–7.98 (m, 1H), 7.51–7.47 (m, 1H), 7.42–7.38 (m, 3H), 6.37 (s, 1H), 3.91 (s, 6H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.8, 166.6, 165.1, 152.3, 141.0, 139.1, 133.7, 132.7, 130.5, 130.4, 130.3, 130.1, 129.4, 129.0, 128.6, 128.2, 121.6, 80.9, 52.3, 52.2, 27.8. Anal. calcd for $C_{23}H_{24}O_6$ (396.43): C, 69.68; H, 6.10. Found: C, 69.64; H, 6.26.

***Tert*-butyl 3,3-bis(4-(methoxycarbonyl)phenyl)acrylate (65) and methyl 4-((*E*)-2-(*tert*-butoxycarbonyl)vinyl)benzoate (66).** Following procedure D (4 mol % **1**), **66** (144 mg, 55 %; eluted at 10 % ethyl acetate) and **65** (24 mg, 6 %; eluted at 12 % ethyl acetate) were obtained from methyl 4-bromobenzoate (473 mg) as a white solid after column chromatography on silica gel (ethyl acetate gradient in hexane: 0 %, 5 min, followed by 0 to 20 %, 20 min). Compound **65**: mp 121.2-123.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10–8.07 (m, 2H), 8.00–7.95 (m, 2H), 7.32 (m, 4H), 6.39 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.8, 166.5, 164.9, 152.1, 144.5, 143.7, 130.7, 129.8, 129.7, 129.4, 129.2, 128.0, 127.8, 122.2, 81.1, 52.3, 52.2, 27.8. HR-MS (FAB) calcd for $C_{23}H_{25}O_6$ ($[M+H]^+$): 397.1646. Found: 397.1655 (δ 2.27 ppm). Compound **66**: mp 79.2-80.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05–8.02 (m, 2H), 7.62–7.55 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 166.5, 165.8, 142.1, 131.0, 130.5,

127.8, 122.6, 80.9, 52.3, 28.2. For $C_{15}H_{18}O_4$ (262.3): C, 68.68; H, 6.92. Found: C, 68.63; H, 6.85.

NMR Spectra



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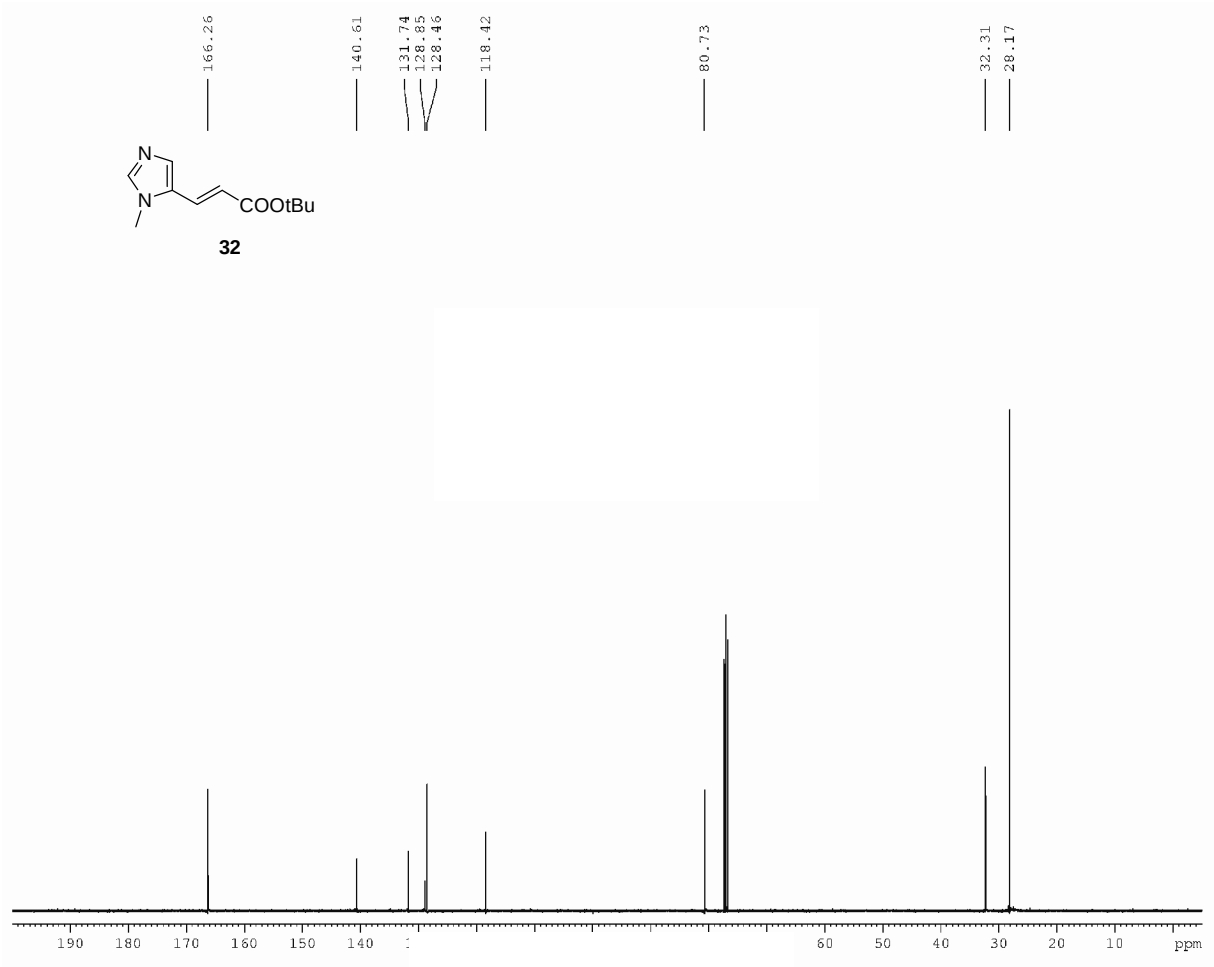

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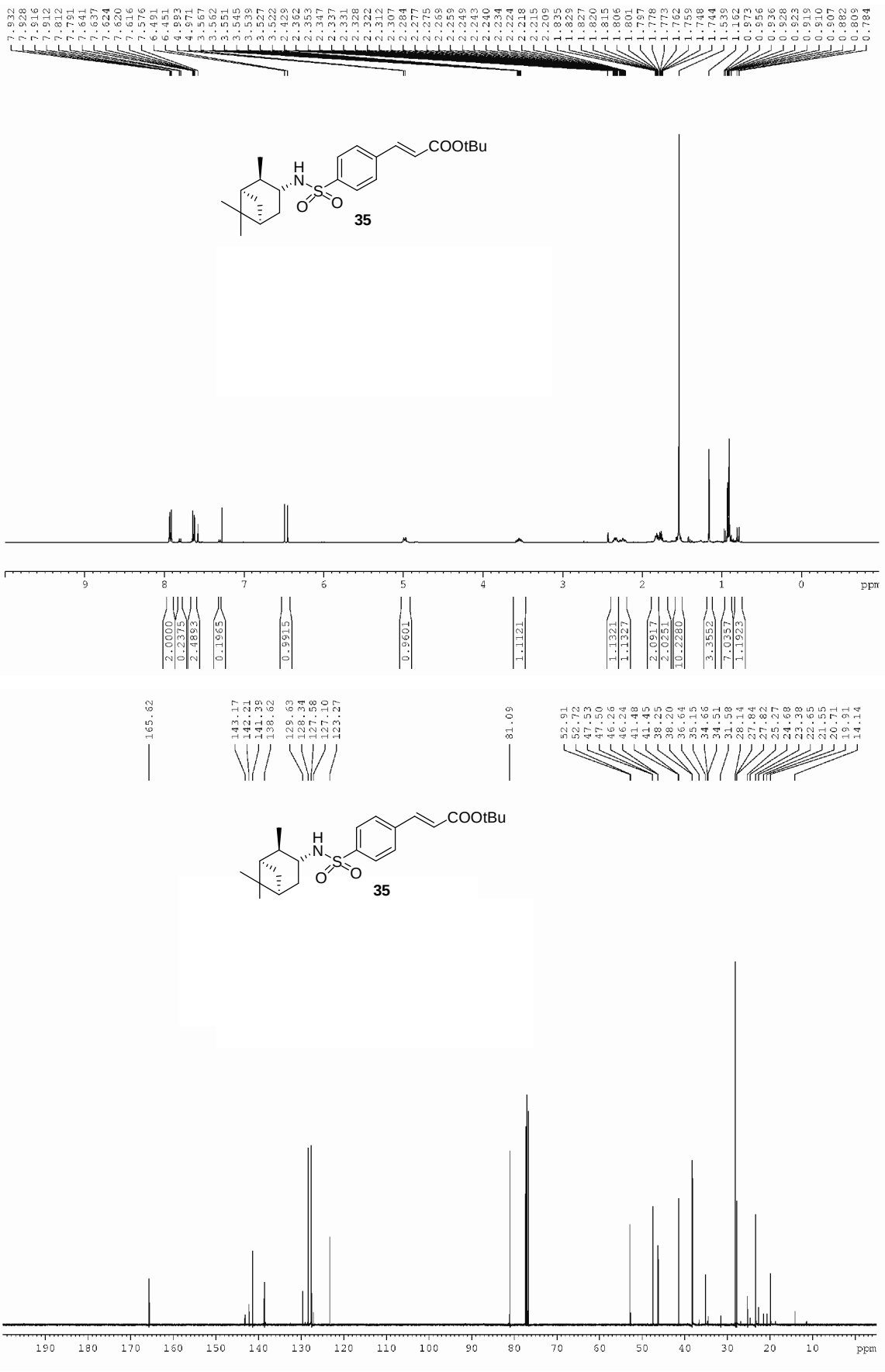
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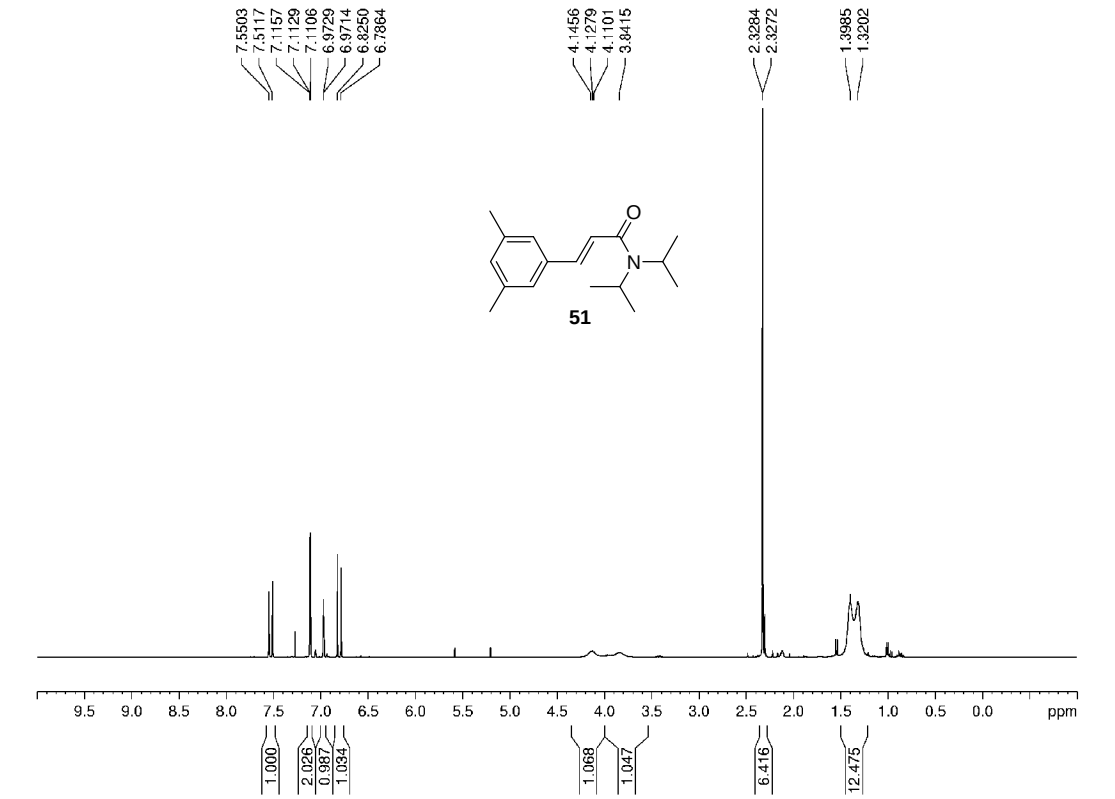
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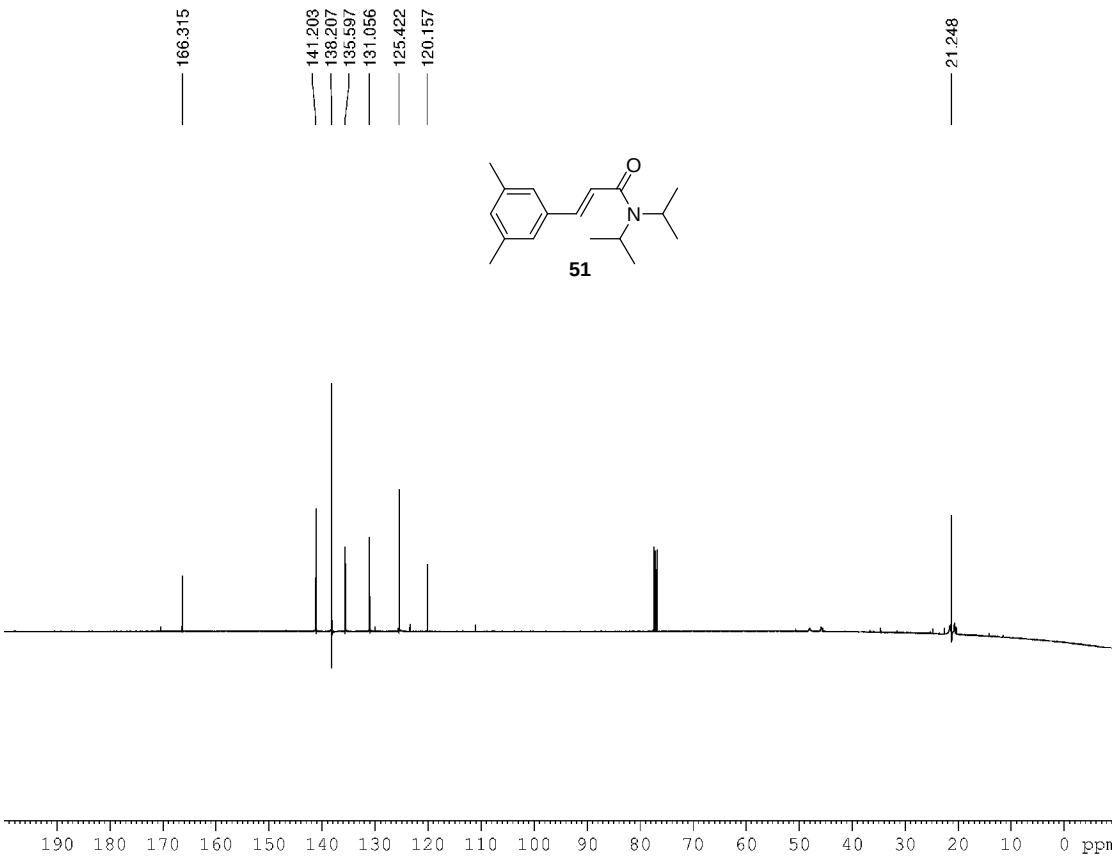
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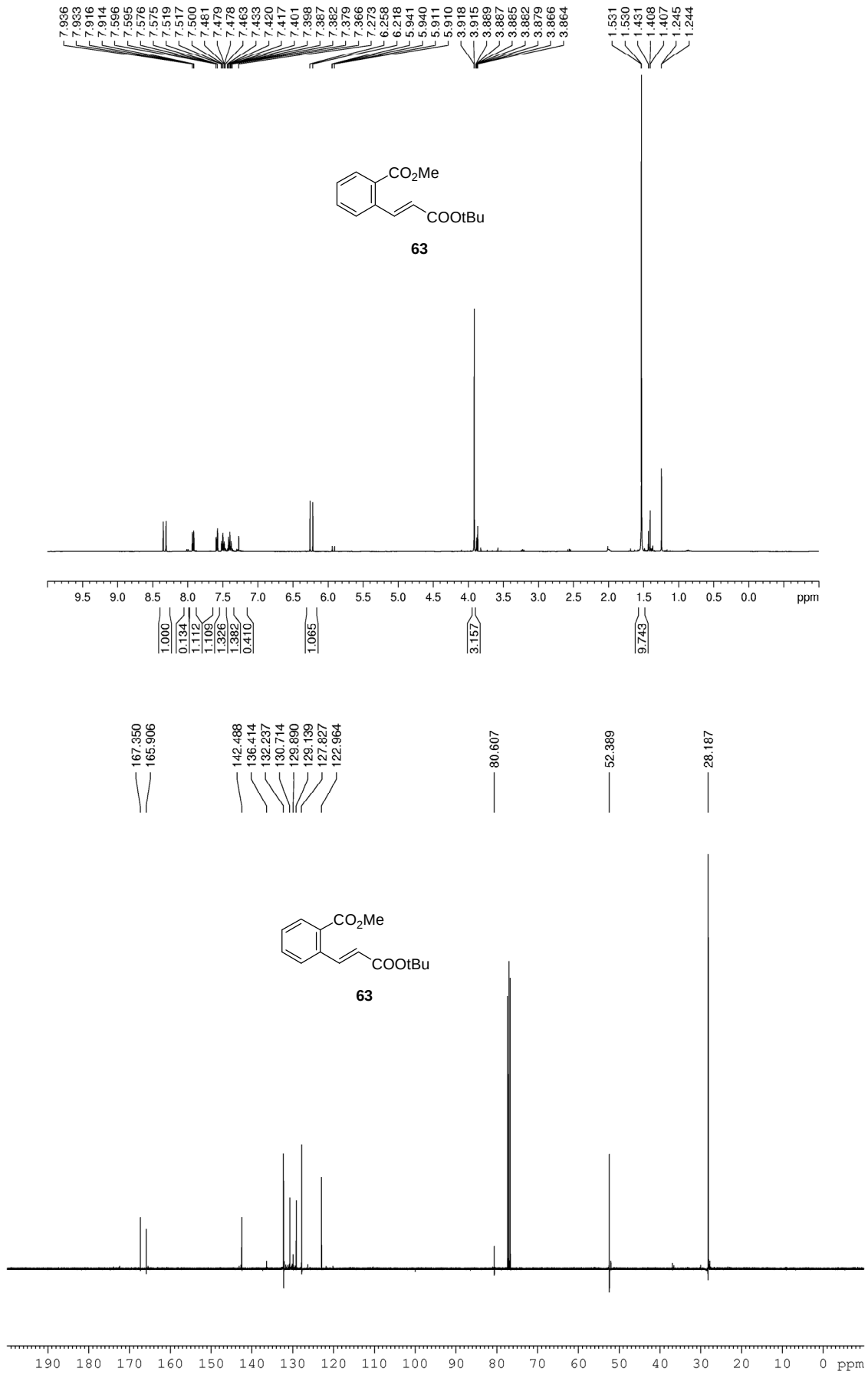
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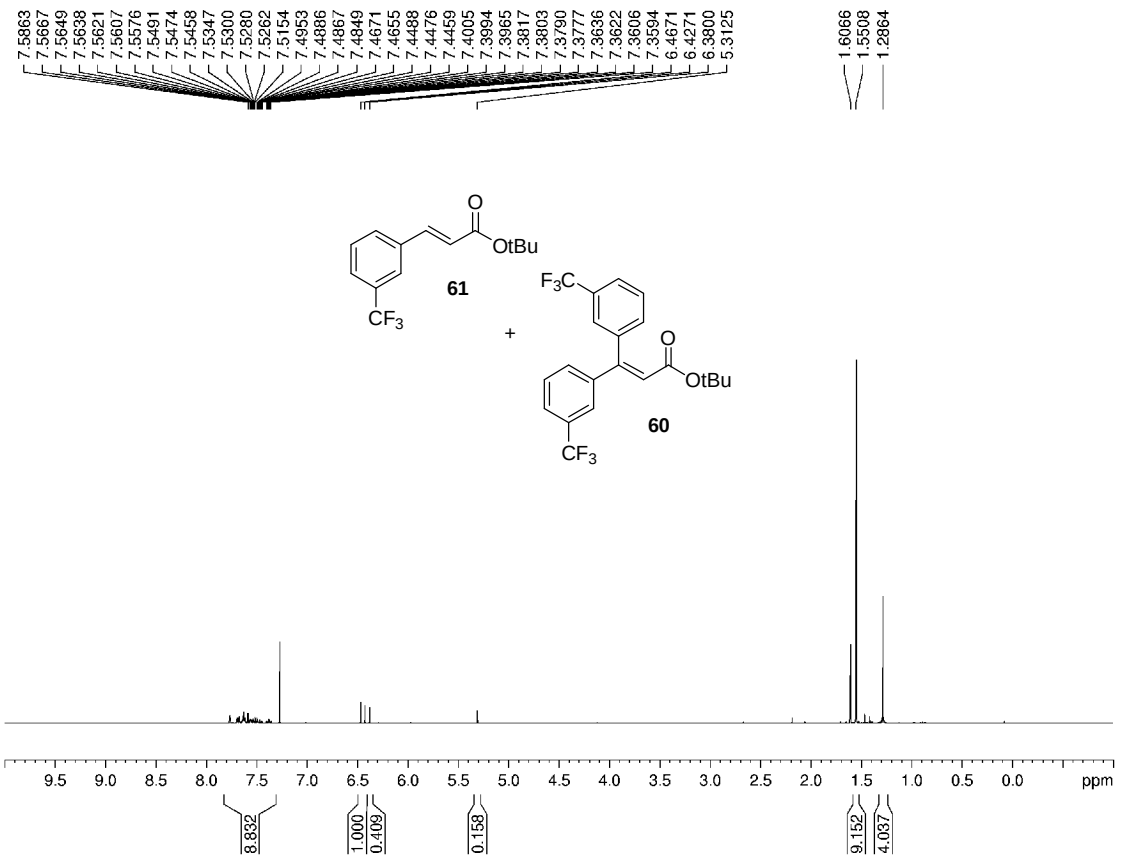
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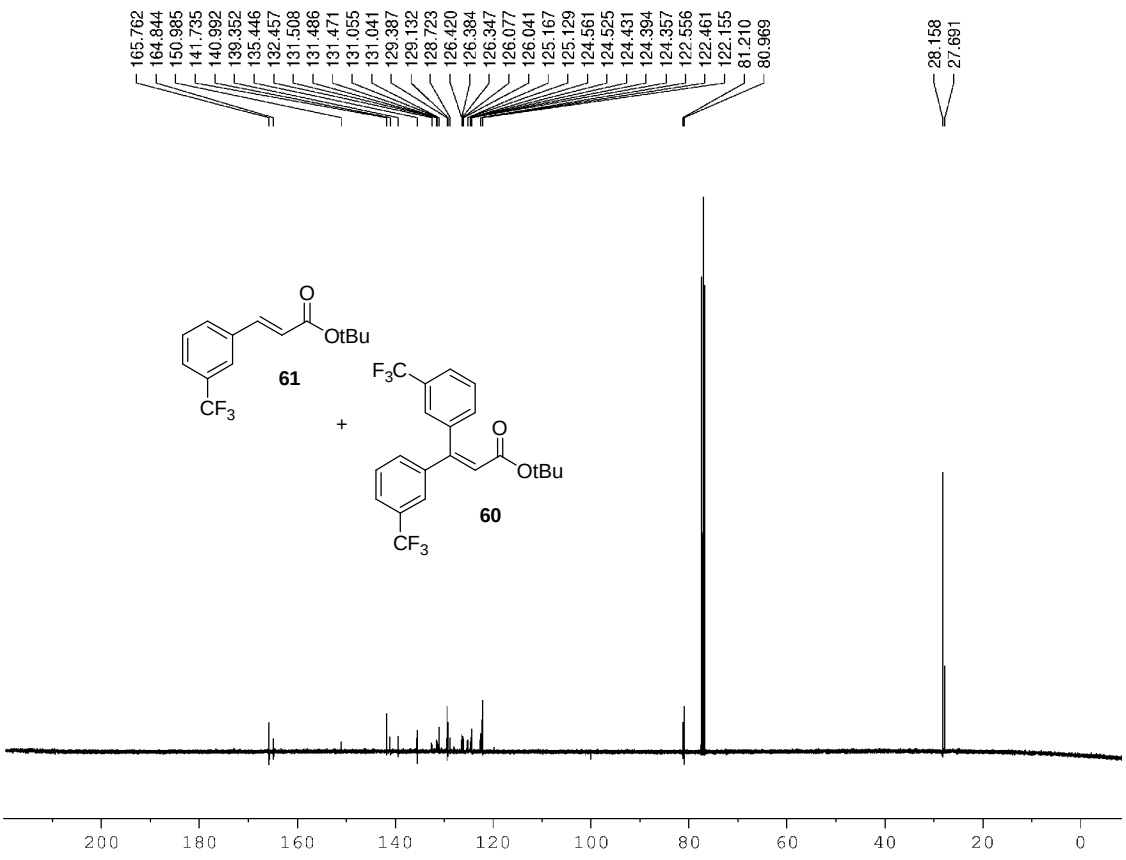
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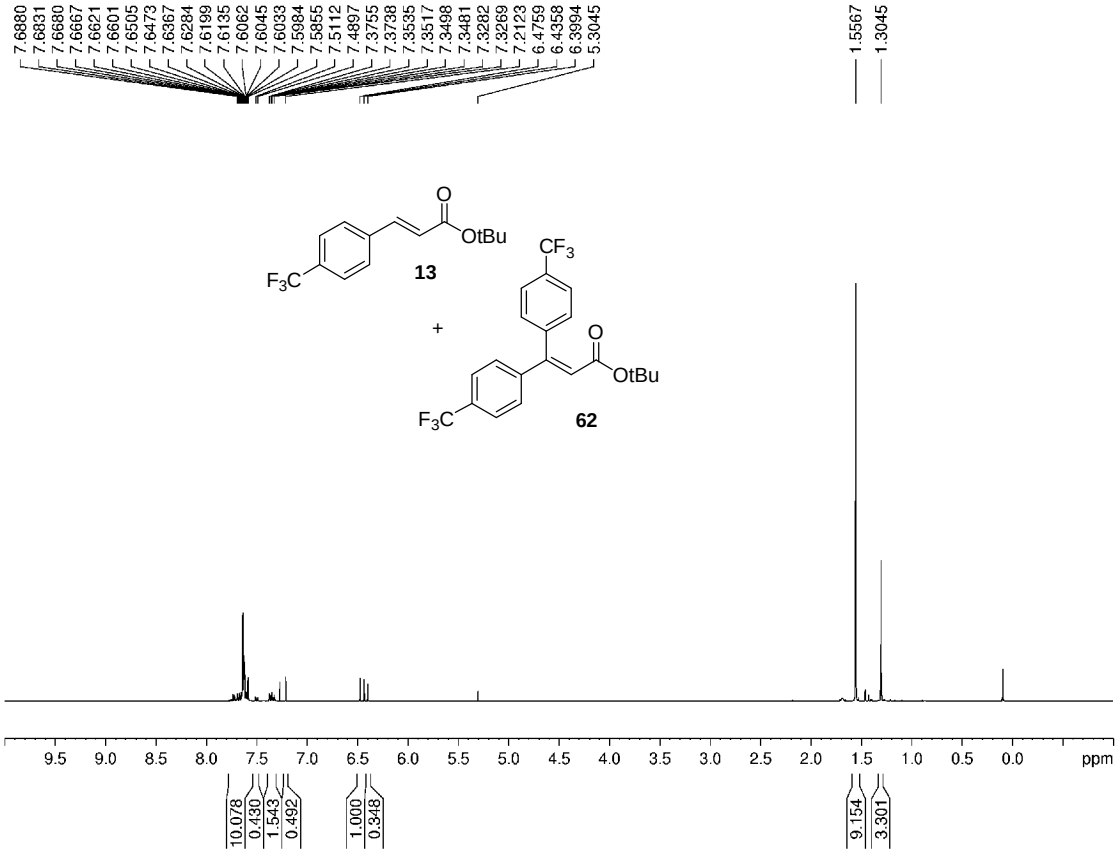
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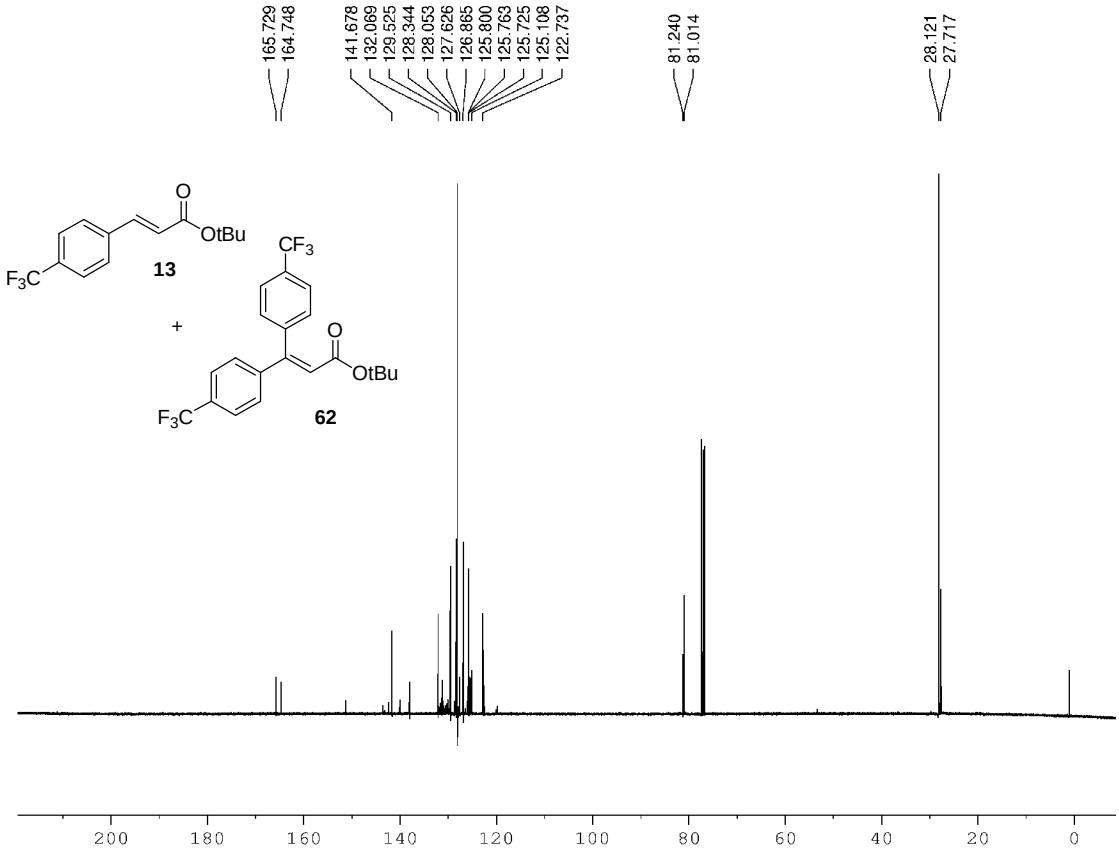
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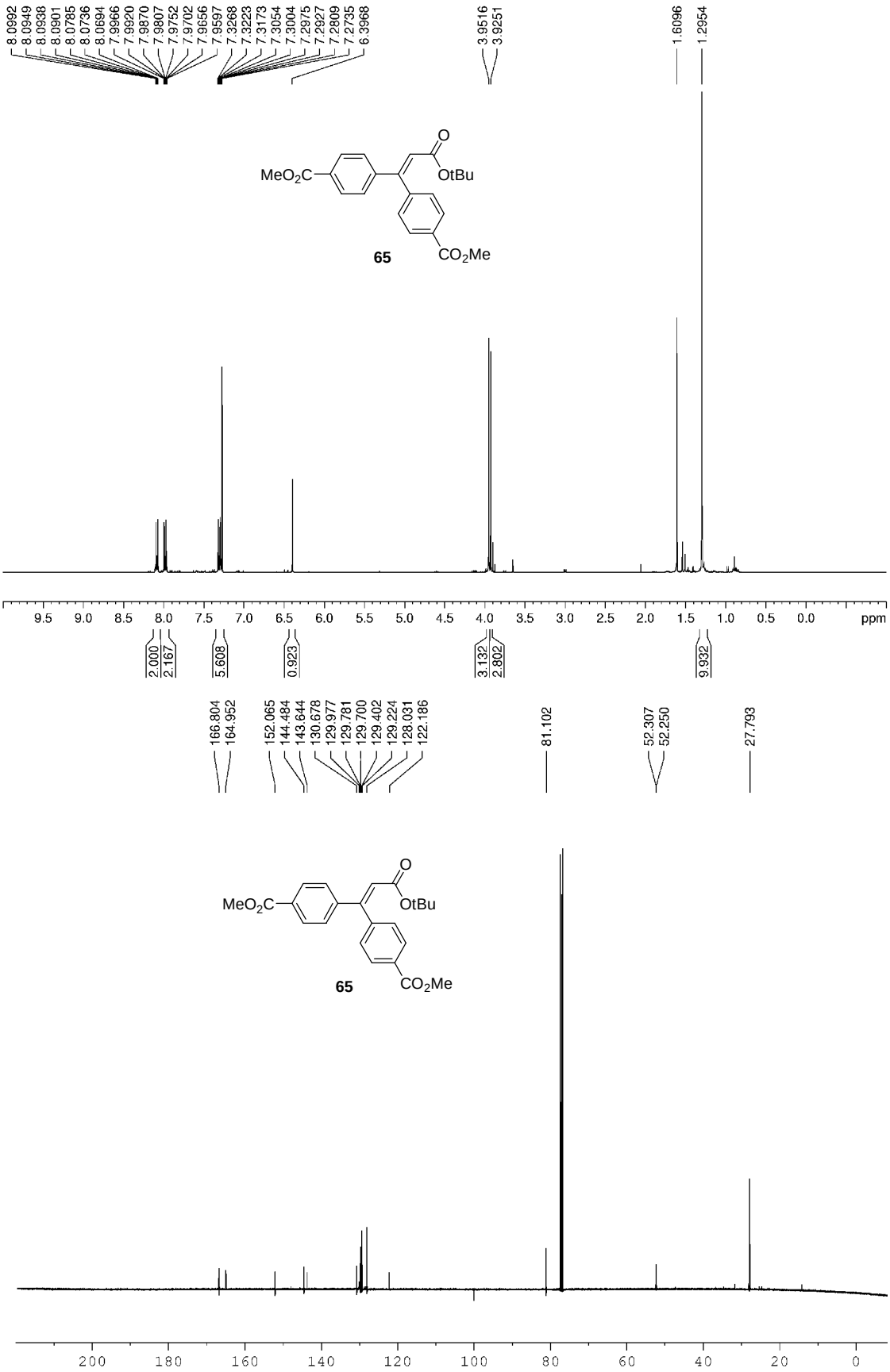
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References

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