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Copper Catalyzed Cross-Coupling Reactions of Diaryl Ditellurides with Potassium Aryltrifluoroborate Salts

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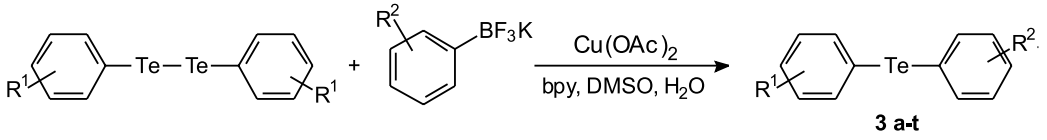
General informations

All air-sensitive and/or water-sensitive reactions were carried out under nitrogen atmosphere with dry solvents and anhydrous conditions. Standard syringe techniques were applied for transfer of dry solvents and some air-sensitive reagents; needles were introduced into reaction vessels through a rubber septum. The reactions were monitored by TLC carried out on Merck silica gel (60 F_{254}) by using UV light as visualizing agent and 5% vanillin in 10% H_2SO_4 and heat as developing agents. Merck silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. THF was distilled from sodium-benzophenone before use. NMR spectra were recorded with Bruker DPX 300 (300 MHz) instrument using $CDCl_3$ as solvent and calibrated using tetramethylsilane as internal standard. Chemical shifts are reported in δ (ppm) relative to $(CH_3)_4Si$ for ^1H and $CDCl_3$ for ^{13}C NMR. Coupling constants (*J*) are reported in Hertz. Mass spectra (MS) were measured on a Shimadzu GCMS-QP5050A mass spectrometer. The HRMS spectra were measured on a Bruker Daltonics Micro TOF (direct inlet probe).

Experimental

General procedure for the cross-coupling reaction of diaryl ditellurides with potassium aryltrifluoroborates

To a round-bottomed flask containing diaryl ditelluride (0.25 mmol), potassium aryltrifluoroborate salt (0.5 mmol), $Cu(OAc)_2$ (1 mol%) and bpy (1 mol%), DMSO (1 mL) and H_2O (0.5 mL) were added. The reaction mixture was allowed to stir at reflux for 12 h. After this time, the solution was cooled to room temperature, diluted with dichloromethane (20 mL) and washed with saturated aqueous NH_4Cl (3 × 20 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent.



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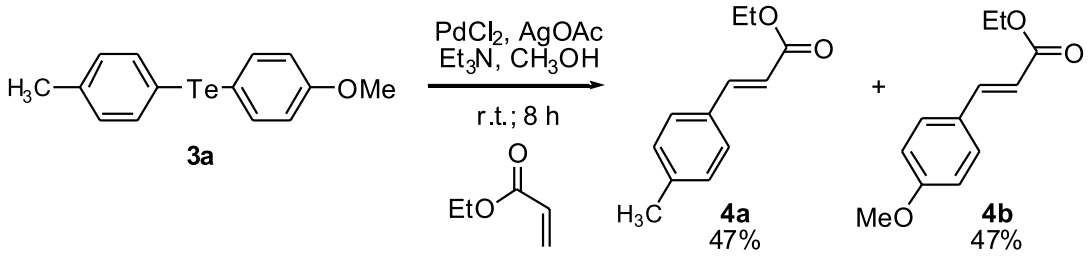
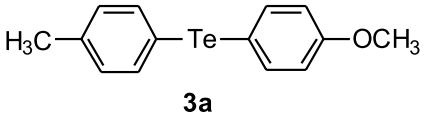
*General procedure for the Heck cross-coupling reaction of unsymmetrical diaryl telluride (**3a**) with ethyl acrylate*

Into a two-necked 25 mL round-bottomed flask containing $PdCl_2$ (0.05 mmol), AgOAc (2.00 mmol) and unsymmetrical diaryl telluride **3a** (0.50 mmol), dry methanol (10 mL), Et_3N (2.00 mmol) and ethyl acrylate (1.00 mmol) were added. After the heterogeneous reaction mixture had been stirred at 25 °C for 8 h, the solid part was filtered. The filtrate was poured into brine (60 mL) and extracted with ethyl acetate (3 × 20 mL). The organic phase was separated, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent.



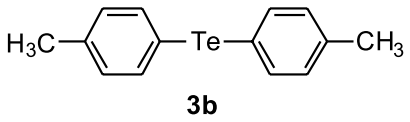
Description of the products

*4-Methoxyphenyl-p-tolyl-telluride (**3a**)*



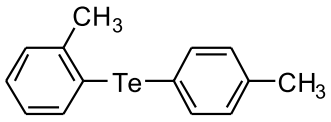
Yield: 90%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69 (d, *J* 8.5 Hz, 2H), 7.53 (d, *J* 7.8 Hz, 2H), 7.02 (d, *J* 7.8 Hz, 2H), 6.79 (d, *J* 8.5 Hz, 2H), 3.80 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.64, 140.36, 137.25, 137.02, 130.10, 115.26, 111.21, 103.48, 54.96, 20.96. MS (relative intensity) *m/z*: 328 (28), 198 (100), 183 (74), 155 (25), 91 (23), 65 (17). HRMS calculated for $C_{14}H_{14}OTe$: 328.0107. Found: 328.0111.

*Bis-(p-Tolyl)-telluride (**3b**)*



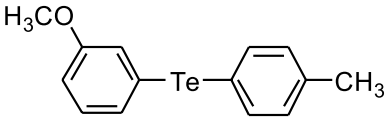
Yield: 94%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (d, *J* 7.7 Hz, 4H), 7.01 (d, *J* 7.7 Hz, 4H), 2.33 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.2 (2C), 136.9 (4C), 131.4 (4C), 110.7 (2C), 22.0. MS (relative intensity) *m/z*: 312 (34), 182 (100), 167 (72), 91 (59), 65 (36). HRMS calculated for $C_{14}H_{14}Te$: 312.0157. Found: 312.0169.

*p-Tolyl-o-tolyl-telluride (**3c**)*



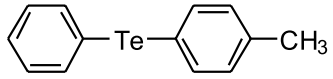
Yield: 89%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64 (d, *J* 7.5 Hz, 2H), 7.49 (d, *J* 7.5 Hz, 1H), 7.13-7.22 (m, 2H), 7.07 (d, *J* 7.5 Hz, 2H), 6.93 (t, *J* 7.5 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.4, 139.5 (2C), 138.1, 136.4, 130.6 (2C), 129.3, 127.7, 126.7, 119.7, 109.6, 25.8, 21.3. MS (relative intensity) *m/z*: 312 (54), 220 (10), 182 (38), 167 (100), 91 (81), 65 (40). HRMS calculated for $C_{14}H_{14}Te$: 312.0157. Found: 312.0167.

*3-Methoxyphenyl-p-tolyl-telluride (**3d**)*



Yield: 88 %. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, *J* 7.8 Hz, 2H), 7.18-7.22 (m, 1H), 7.15-7.17 (m, 1H), 7.07 (s, 1H), 7.03 (d, *J* 7.8 Hz, 2H), 6.76 (d, *J* 7.5 Hz, 1H), 3.72 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.6, 138.7 (2C), 137.9, 130.2 (2C), 129.9, 129.2, 122.2, 115.8, 113.1, 109.9, 55.0, 21.0. MS (relative intensity) *m/z*: 328 (28), 198 (100), 167 (23), 155 (17), 91 (36), 77 (17), 65 (21). HRMS calculated for $C_{14}H_{14}OTe$: 328.0107. Found: 328.0118.

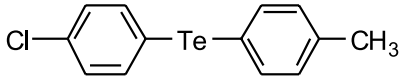
*Phenyl-p-tolyl-telluride (**3e**)*



3e

Yellow oil: Yield: 91%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, *J* 7.8 Hz, 2H), 7.19-7.24 (m, 3H), 7.15 (d, *J* 7.8 Hz, 2H), 7.00 (t, *J* 7.8 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.6 (2C), 137.9, 137.1 (2C), 130.3 (2C), 129.2 (2C), 127.3, 115.1, 110.1, 21.0. MS (relative intensity) *m/z*: 298 (31), 168 (100), 167 (83), 153 (20), 91 (39), 77 (24), 65 (25). HRMS calculated for $C_{13}H_{12}Te$: 298.0001. Found: 298.0018.

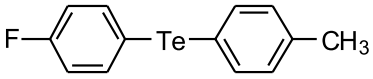
*4-Chlorophenyl-p-tolyl-telluride (**3f**)*



3f

Yield: 84%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, *J* 7.2 Hz, 2H), 7.49 (d, *J* 7.2 Hz, 2H), 7.11 (d, *J* 7.2 Hz, 2H), 7.02 (d, *J* 7.2 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.4, 138.9 (2C), 138.5 (2C), 134.0, 130.6 (2C), 129.6 (2C), 113.0, 110.0, 21.3. MS (relative intensity) *m/z*: 332 (31), 202 (100), 167 (62), 91 (48), 65 (33). HRMS calculated for $C_{13}H_{11}ClTe$: 331.9611. Found: 331.9627.

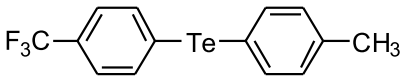
*4-Fluorophenyl-p-tolyl-telluride (**3g**)*



3g

Yield: 68%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65 (d, *J* 7.8 Hz, 2H), 7.56 (d, *J* 7.5 Hz, 2H), 7.02 (d, *J* 7.8 Hz, 2H), 6.88 (d, *J* 7.5 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.5, 161.2, 140.1 (2C), 138.0 (2C), 130.5 (2C), 117.2 (2C), 110.5, 108.6, 21.3. MS (relative intensity) *m/z*: 316 (35), 186 (100), 165 (13), 91 (47), 65 (32). HRMS calculated for $C_{13}H_{11}FTe$: 315.9907. Found: 315.9918.

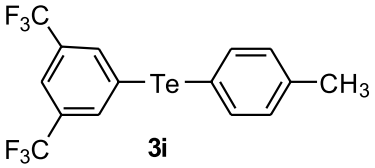
*4-(Trifluoromethyl)-phenyl-p-tolyl-telluride (**3h**)*



3h

Yield: 66%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72 (d, *J* 7.8 Hz, 2H), 7.60 (d, *J* 7.8 Hz, 2H), 7.37 (d, *J* 7.5 Hz, 2H), 7.11 (d, *J* 7.5 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.0 (2C), 139.1, 138.0, 135.8 (2C), 130.8 (2C), 126.2, 125.8 (2C), 121.6, 109.1, 21.3. MS (relative intensity) *m/z*: 366 (43), 236 (97), 221 (17), 167 (67), 126 (16), 91 (100), 65 (61). HRMS calculated for $C_{14}H_{11}F_3Te$: 365.9875. Found: 365.9890.

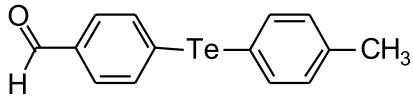
*3,5-Bis-(trifluoromethyl)-phenyl-p-tolyl-telluride (**3i**)*



3i

Yield: 68%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.90 (s, 2H), 7.72 (d, *J* 7.8 Hz, 2H), 7.67 (s, 1H), 7.12 (d, *J* 7.8 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.0 (2C), 139.7, 135.4 (2C), 132.1, 131.7 (2C), 130.1 (2C), 121.0, 118.4, 108.5, 21.3. MS (relative intensity) *m/z*: 434 (29), 304 (54), 235 (24), 219 (16), 91 (100), 65 (67). HRMS calculated for $C_{15}H_{10}F_6Te$: 433.9748. Found: 433.9748.

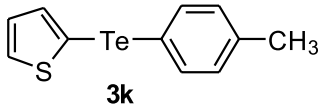
*4-Formylphenyl-p-tolyl-telluride (**3j**)*



3j

Yield: 72%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.88 (s, 1H), 7.73 (d, *J* 7.5 Hz, 2H), 7.51-7.60 (m, 4H), 7.12 (d, *J* 7.5 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 191.7, 140.4 (2C), 139.4, 138.0, 135.1 (2C), 130.9 (2C), 130.6, 129.9 (2C), 127.5, 21.4. MS (relative intensity) *m/z*: 326 (37), 219 (11), 195 (100), 167 (21), 91 (59), 65 (29). HRMS calculated for $C_{14}H_{12}OTe$: 325.9950. Found: 325.9968.

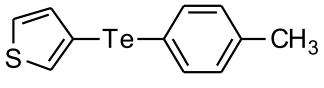
*2-Thiophenyl-p-tolyl-telluride (**3k**)*



3k

Yield: 81%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50 (d, *J* 8.1 Hz, 2H), 7.44-7.47 (m, 2H), 7.01 (d, *J* 8.1 Hz, 2H), 6.96 (dd, *J* 5.2, 3.6 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.3, 137.8, 136.2 (2C), 134.6, 130.1 (2C), 128.8, 111.9, 100.6, 20.9. MS (relative intensity) *m/z*: 304 (30), 174 (100), 141 (11), 91 (25), 65 (27). HRMS calculated for $C_{11}H_{10}STe$: 303.9565. Found: 303.9579.

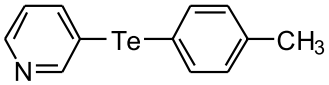
*3-Thiophenyl-p-tolyl-telluride (**3l**)*



3l

Yield: 83%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.47-7.49 (m, 2H), 7.19-7.22 (m, 2H), 7.17 (s, 1H), 6.96 (d, *J* 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.9, 137.4, 137.0 (2C), 136.2, 133.4, 130.2 (2C), 126.8, 110.6, 104.1, 21.0. MS (relative intensity) *m/z*: 304 (30), 174 (100), 141 (17), 91 (40), 65 (29). HRMS calculated for $C_{11}H_{10}STe$: 303.9565. Found: 303.9582.

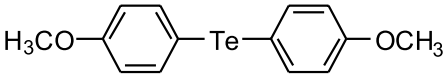
*3-Pyridinyl-telluride (**3m**)*



3m

Yield: 78%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.78 (s, 1H), 8.43 (d, *J* 6.5 Hz, 1H), 7.87 (d, *J* 6.5 Hz, 1H), 7.61 (d, *J* 7.8 Hz, 2H), 7.01-7.12 (m, 1H), 6.99 (d, *J* 7.8 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.4, 148.3, 144.3, 139.1 (2C), 138.0, 130.7 (2C), 124.6, 113.0, 109.0, 21.2. MS (relative intensity) *m/z*: 299 (35), 169 (100), 91 (58), 65 (33), 51 (21). HRMS calculated for $C_{12}H_{11}NTe$: 298.9953, Found: 298.9971.

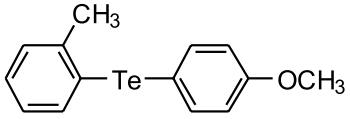
*Bis-(4-Methoxyphenyl)-telluride (**3n**)*



3n

Yield: 89 %. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.64 (d, *J* 6.2 Hz, 4H), 6.77 (d, *J* 6.2 Hz, 4H), 3.76 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.7 (2C), 139.7 (4C), 115.4 (4C), 104.3 (2C), 55.2 (2C). MS (relative intensity) *m/z*: 344 (24), 214 (93), 199 (100), 171 (21), 107 (19), 63 (24). HRMS calculated for $C_{14}H_{14}O_2Te$: 344.0056, Found: 344.0067.

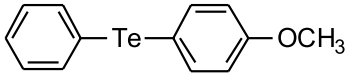
*4-Methoxyphenyl-o-tolyl-telluride (**3o**)*



3o

Yield: 91%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (d, *J* 8.5 Hz, 2H), 7.23 (d, *J* 7.5 Hz, 1H), 7.05-7.14 (m, 2H), 6.88 (t, *J* 7.5 Hz, 1H), 6.76 (d, *J* 8.5 Hz, 2H), 3.76 (s, 3H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.2, 141.9 (2C), 140.8, 135.3, 129.4, 127.4, 126.7, 120.3, 115.7 (2C), 102.5, 55.2, 25.4. MS (relative intensity) *m/z*: 328 (61), 220 (25), 198 (100), 183 (51), 91 (74), 65 (47). HRMS calculated for $C_{14}H_{14}OTe$: 328.0106, Found: 328.0123.

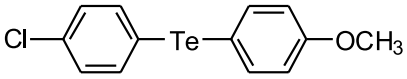
*4-Methoxyphenyl-phenyl-telluride (**3p**)*



3p

Yield: 94%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, *J* 8.7 Hz, 2H), 7.54 (dd, *J* 7.8, 1.5 Hz, 2H), 7.11-7.23 (m, 3H), 6.77 (d, *J* 8.7 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.0, 141.2 (2C), 136.4 (2C), 129.4 (2C), 127.3, 116.0, 115.5 (2C), 103.3, 55.2. MS (relative intensity) *m/z*: 314 (27), 184 (100), 169 (60), 141 (38), 115 (17), 77 (29). HRMS calculated for $C_{13}H_{12}OTe$: 313.9950, Found: 313.9968.

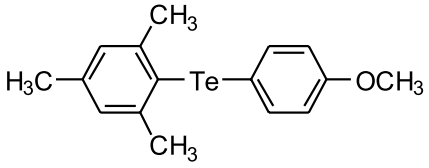
*4-Methoxyphenyl-4-chlorophenyl-telluride (**3q**)*



3q

Yield: 91%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.70 (d, *J* 8.7 Hz, 2H), 7.44 (d, *J* 8.1 Hz, 2H), 7.11 (d, *J* 8.1 Hz, 2H), 6.78 (d, *J* 8.7 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.3, 141.5 (2C), 137.8 (2C), 133.8, 129.8 (2C), 115.7 (2C), 113.8, 103.2, 55.3. MS (relative intensity) *m/z*: 348 (29), 218 (100), 203 (51), 175 (24), 63 (19). HRMS calculated for $C_{13}H_{11}ClOTe$: 347.9570, Found: 347.9587.

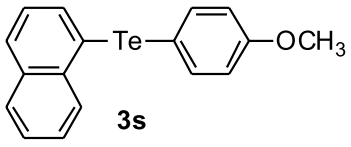
*4-Methoxyphenyl-mesityl-telluride (**3r**)*



3r

Yield: 79%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (d, *J* 8.4 Hz, 2H), 6.95 (s, 2H), 6.68 (d, *J* 8.4 Hz, 2H), 3.75 (s, 3H), 2.52 (s, 6H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.1, 145.2 (2C), 139.1, 137.3 (2C), 127.5 (2C), 118.8, 115.4 (2C), 104.7, 55.1, 29.4 (2C), 21.0. MS (relative intensity) *m/z*: 356 (100), 248 (65), 226 (74), 211 (61), 119 (97), 91 (76), 77 (61), 65 (27). HRMS calculated for $C_{16}H_{18}OTe$: 356.0419, Found: 356.0435.

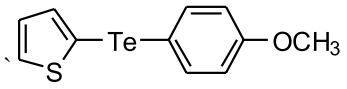
*4-Methoxyphenyl-(1-naphthalenyl)-telluride (**3s**)*



3s

Yield: 87%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.04 (d, *J* 7.5 Hz, 1H), 7.73-7.78 (m, 3H), 7.68 (d, *J* 8.1 Hz, 2H), 7.46-7.52 (m, 2H), 7.19-7.24 (m, 1H), 6.75 (d, *J* 8.1 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.0, 140.9 (2C), 136.4, 135.5, 133.7, 130.8, 128.7, 128.6, 126.7, 126.5, 126.2, 118.8, 115.6 (2C), 103.0, 55.1. MS (relative intensity) *m/z*: 364 (21), 234 (100), 219 (40), 127 (33), 77 (14). HRMS calculated for $C_{17}H_{14}OTe$: 364.0106, Found: 364.0135.

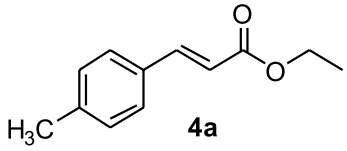
*2-Thiophenyl-4-methoxyphenyl-telluride (**3t**)*



3t

Yield: 79%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (d, *J* 7.8 Hz, 2H), 7.36-7.39 (m, 2H), 6.88 (dd, *J* 5.1, 3.3 Hz, 1H), 6.69 (d, *J* 7.8 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.8, 140.9, 139.0 (2C), 134.5, 129.0, 115.4 (2C), 105.2, 101.6, 55.2. MS (relative intensity) *m/z*: 320 (27), 190 (100), 175 (89), 147 (31), 63 (18). HRMS calculated for $C_{11}H_{10}OSTe$: 319.9514, Found: 319.9535.

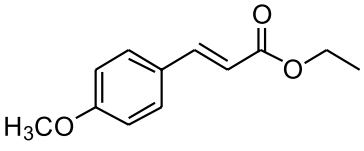
*(E)-Ethyl 3-p-tolylacrylate (**4a**)*



4a

Yield: 47%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65 (d, *J* 16.0 Hz, 1H), 7.39 (d, *J* 8.1 Hz, 2H), 7.28 (d, *J* 8.1 Hz, 2H), 6.42 (d, *J* 16.0 Hz, 1H), 4.25 (q, *J* 7.3 Hz, 2H), 2.33 (s, 3H), 1.26 (t, *J* 7.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.0, 144.5, 134.4, 130.2, 128.8 (2C), 128.0 (2C), 118.3, 60.5, 24.3, 14.5. MS (relative intensity) *m/z*: 190 (24), 117 (45), 91 (23).

*(E)-Ethyl 3-(4-methoxyphenyl)acrylate (**4b**)*



4b

Yield: 47%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, *J* 16.2 Hz, 1H), 7.37 (d, *J* 8.3 Hz, 2H), 7.25 (d, *J* 8.3 Hz, 2H), 6.40 (d, *J* 16.2 Hz, 1H), 4.23 (q, *J* 7.3 Hz, 2H), 3.67 (s, 3H), 1.25 (t, *J* 7.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.2, 144.2, 134.0, 130.1, 128.6 (2C), 128.2 (2C), 118.2, 60.1, 55.7, 14.9. MS (relative intensity) *m/z*: 206 (23), 107 (43), 99 (36).