Supporting Information

Oxidative Alkenylation of Aromatic Esters by Ruthenium-Catalyzed Twofold C−H Bond Cleavages

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General Remarks

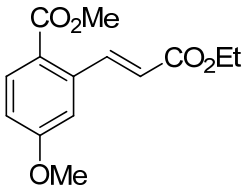
Catalytic reactions were carried out under air. 1,2-Dichloroethane was distilled over CaH_2. The esters **1** were obtained from commercial sources or were prepared from carboxylic acids or chlorides with the corresponding alcohol.[1,2] The following starting material was synthesized according to previously described methods: **$[D]_5$-1s**.[3] Yields refer to isolated compounds, estimated to be >95 % pure as determined by ^{1}H-NMR and GC. TLC: Macherey-Nagel, TLC plates Alugram® Sil G/UV254. Detection under UV light at 254 nm. Chromatography: Separations were carried out on Merck Silica 60 (0.040–0.063 mm, 70–230 mesh ASTM). All IR spectra were recorded on a BRUKER ALPHA-P spectrometer. MS: EI-MS: Finnigan MAT 95, 70 eV; ESI-MS: Finnigan LCQ. High resolution mass spectrometry (HRMS): APEX IV 7T FTICR, Bruker Daltonic. M. p.: Stuart® Melting Point Apparatus SMP3 melting point apparatus, values are uncorrected. ^{1}H, ^{13}C, ^{19}F NMR-spectra were recorded at 300 (^{1}H), 75 {^{13}C, APT (Attached Proton Test)} and 283 MHz (^{19}F), respectively, on Varian Unity-300 and AMX 300 instruments in $CDCl_3$ solutions. If not otherwise specified, chemical shifts (δ) are given in ppm.

General Procedure A: Ruthenium Catalyzed Oxidative Alkenylation of Aromatic Esters

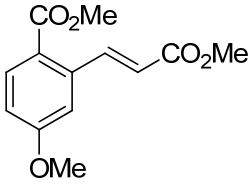
A suspension of methyl 4-methoxybenzoate (**1a**) (83.3 mg, 0.50 mmol), ethyl acrylate (**2a**) (110 mg, 1.10 mmol), $[RuCl_2(p\text{-cymene})]_2$ (15.9 mg, 5.2 mol %), $AgSbF_6$ (68.3 mg, 40 mol %) and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.00 mmol) in DCE (2.0 mL) was at ambient temperature for 5 min, and then stirred at 100 °C for 16 h under an atmosphere of ambient air. At ambient temperature, the reaction mixture was diluted with sat. aq. NH_4Cl/NH_3 (1:1, 10 mL) and extracted with EtOAc (4 x 25 mL). The combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1→25/1) to yield **3a** (81.9 mg, 62%) as a colorless solid.

General Procedure B: Ruthenium Catalyzed Oxidative Aerobic Alkenylation of Aromatic Esters and Heteroaromatic Esters with Cocatalytic Amounts of $Cu(OAc)_2 \cdot H_2O$

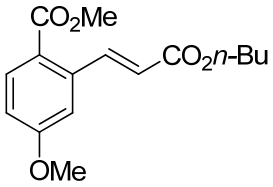
A suspension of methyl 4-methoxybenzoate (**1a**) (83.4 mg, 0.50 mmol), ethyl acrylate (**2a**) (107 mg, 1.07 mmol), $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %), $AgSbF_6$ (35.3 mg, 20 mol %) and $Cu(OAc)_2 \cdot H_2O$ (29.7 mg, 30 mol %) in DCE (2.0 mL) was pre-stirred at ambient temperature for 5 min under N_2. Thereafter, the reaction mixture was stirred at 100 °C for 16 h under an atmosphere of ambient air. At ambient temperature, the reaction mixture was diluted with sat. aq. NH_4Cl/NH_3 (1:1, 10 mL) and extracted with EtOAc (4 x 25 mL). The combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 50/1→25/1) to yield **3a** (72.4 mg, 55%) as a colorless solid.



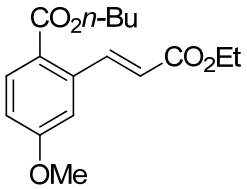
(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (3a): M. p. = 44−48 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.48 (d, J = 15.9 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 2.6 Hz, 1H), 6.91 (dd, J = 8.8, 2.6 Hz, 1H), 6.25 (d, J = 15.9 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.7 (C_q), 166.5 (C_q), 162.5 (C_q), 144.2 (CH), 139.0 (C_q), 133.1 (CH), 121.8 (C_q), 121.2 (CH), 114.6 (CH), 113.0 (CH), 60.6 (CH_2), 55.5 (CH_3), 52.1 (CH_3), 14.3 (CH_3). IR (neat): 2950, 2844, 1701, 1234, 1173, 1123, 1021, 974, 849 cm^{-1}. MS (EI): *m/z* (relative intensity) 264 ([M^+] 7), 219 (9), 191 (99), 177 (8), 161 (12), 159 (8) 148 (14), 77 (4). HR-MS (ESI) *m*/*z* calcd for $C_{14}H_{16}O_5$ [M^+] 264.0998, found 264.0999.



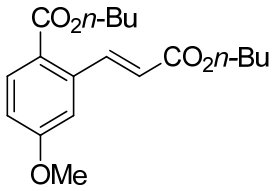
(*E*)-Methyl 4-methoxy-2-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (3b): The general procedure A was followed using methyl 4-methoxybenzoate (83.8 mg, 0.50 mmol) and methyl acrylate (87.7 mg, 1.01 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1) yielded **3b** (78.0 mg, 62%) as a colorless solid. M. p. = 68−70 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.51 (d, J = 15.9 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.03 (d, J = 2.6 Hz, 1H), 6.93 (dd, J = 8.7, 2.6 Hz, 1H), 6.26 (d, J = 15.9 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.9 (C_q), 166.7 (C_q), 162.5 (C_q), 144.5 (CH), 139.0 (C_q), 133.1 (CH), 121.8 (C_q), 120.8 (CH), 114.6 (CH), 113.1 (CH), 55.5 (CH_3), 52.1 (CH_3), 51.8 (CH_3). IR (neat): 2954, 1708, 1253, 1175, 1123, 1019, 851, 780 cm^{-1}. MS (EI): *m/z* (relative intensity) 250 ([M^+] 5), 219 (7), 191 (99), 176 (8), 160 (12), 148 (16), 89 (17), 77 (5). HR-MS (ESI) *m*/*z* calcd for $C_{13}H_{14}O_5$ [M^+] 250.0841, found 250.0842.



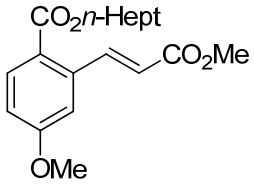
(*E*)-Methyl 2-(3-*n*-butoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (3c): The general procedure A was followed using methyl 4-methoxybenzoate (83.9 mg, 0.50 mmol) and *n*-butyl acrylate (133 mg, 1.04 mmol). Purification by column chromatography (*n*-pentane/EtOAc: 50/1) yielded **3c** (86.6 mg, 59%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.49 (d, J = 15.9 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.04 (d, J = 2.6 Hz, 1H), 6.92 (dd, J = 8.8, 2.6 Hz, 1H), 6.26 (d, J = 15.9 Hz, 1H), 4.22 (t, J = 6.7 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 1.77−1.63 (m, 2H), 1.51−1.37 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.7 (C_q), 166.6 (C_q), 162.5 (C_q), 144.2 (CH), 139.0 (C_q), 133.1 (CH), 121.9 (C_q), 121.2 (CH), 114.6 (CH), 113.0 (CH), 64.5 (CH_2), 55.5 (CH_3), 52.1 (CH_3), 30.7 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (neat): 2957, 1708, 1599, 1254, 1168, 1126, 1088, 1032 cm^{-1}. MS (EI): *m/z* (relative intensity) 292 ([M^+] 3), 219 (6), 191 (99), 177 (8), 161 (7), 148 (11), 89 (5), 77 (4). HR-MS (ESI) *m/z* calcd for $C_{16}H_{20}O_5$ [M^+] 292.1311, found 292.1313.



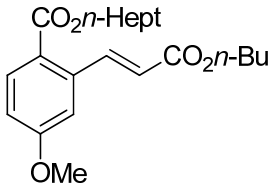
(*E*)-*n*-Butyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (3d): The general procedure A was followed using *n*-butyl 4-methoxybenzoate (106 mg, 0.51 mmol) and ethyl acrylate (99.5 mg, 0.94 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1→25/1) yielded **3d** (87.5 mg, 61%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.47 (d, J = 15.8 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.00 (s, 1H), 6.91 (d, J = 8.7 Hz, 1H), 6.24 (d, J = 15.8 Hz, 1H), 4.35−4.10 (m, 4H), 3.85 (s, 3H), 1.83−1.65 (m, 2H), 1.53−1.39 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.4 (C_q), 166.4 (C_q), 162.3 (C_q), 144.4 (CH), 138.8 (C_q), 133.0 (CH), 122.2 (C_q), 121.0 (CH), 114.6 (CH), 113.0 (CH), 65.0 (CH_2), 60.5 (CH_2), 55.5 (CH_3), 30.7 (CH_2), 19.3 (CH_2), 14.3 (CH_3), 13.7 (CH_3). IR (neat): 2960, 2935, 1706, 1251, 1251, 1171, 1126, 1086, 1031 cm^{-1}. MS (EI): *m/z* (relative intensity) 306 ([M^+] 4), 233 (35), 203 (10), 177 (99), 161 (20), 118 (5), 89 (6), 77 (5). HR-MS (ESI) *m/z* calcd for $C_{17}H_{22}O_5$ [M^+] 306.1467, found 306.1466.



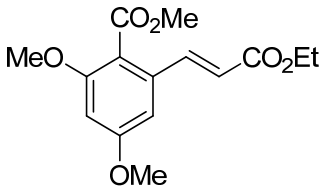
(*E*)-*n*-Butyl 2-(3-*n*-butoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (3e): The general procedure A was followed using *n*-butyl 4-methoxybenzoate (107 mg, 0.52 mmol) and *n*-butyl acrylate (128 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1→25/1) yielded **3e** (97.4 mg, 57%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.48 (d, J = 15.9 Hz, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 2.5 Hz, 1H), 6.92 (dd, J = 8.8, 2.5 Hz, 1H), 6.25 (d, J = 15.9 Hz, 1H), 4.30 (t, J = 6.6 Hz, 2H), 4.21 (t, J = 6.7 Hz, 2H), 3.87 (s, 3H), 1.80−1.62 (m, 4H), 1.54−1.33 (m, 4H), 0.96 (t, J = 7.3 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.6 (C_q), 166.4 (C_q), 162.4 (C_q), 144.4 (CH), 138.9 (C_q), 133.1 (CH), 122.4 (C_q), 121.1 (CH), 114.6 (CH), 113.0 (CH), 65.0 (CH_2), 64.5 (CH_2), 55.5 (CH_3), 30.8 (CH_2), 30.7 (CH_2), 19.3 (CH_2), 19.2 (CH_2), 13.7 (CH_3), 13.7 (CH_3). IR (neat): 2959, 2873, 1707, 1599, 1251, 1169, 1126, 1085, 1032 cm^{-1}. MS (EI): *m/z* (relative intensity) 334 ([M^+] 3), 261 (4), 233 (36), 203 (7), 178 (13), 177 (99) 161 (21), 77 (4). HR-MS (ESI) *m/z* calcd for $C_{19}H_{26}O_5$ [M^+] 334.1780, found 334.1784.



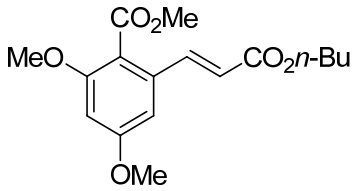
(*E*)-*n*-Heptyl 4-methoxy-2-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (3f): The general procedure A was followed using *n*-heptyl 4-methoxybenzoate (134 mg, 0.54 mmol) and methyl acrylate (128 mg, 1.01 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1→25/1) yielded **3f** (121 mg, 68%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.50 (d, J = 15.9 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 2.6 Hz, 1H), 6.92 (dd, J = 8.7, 2.6 Hz, 1H), 6.25 (d, J = 15.9 Hz, 1H), 4.28 (t, J = 6.7 Hz, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 1.82−1.64 (m, 2H), 1.49−1.18 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.9 (C_q), 166.3 (C_q), 162.4 (C_q), 144.6 (CH), 138.8 (C_q), 133.0 (CH), 122.2 (C_q), 120.6 (CH), 114.6 (CH), 113.0 (CH), 65.3 (CH_2), 55.5 (CH_3), 51.7 (CH_3), 31.7 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 26.0 (CH_2), 22.6 (CH_2), 14.0 (CH_3). IR (neat): 2929, 2856, 1707, 1251, 1192, 1168, 1126, 1033 cm^{-1}. MS (EI): *m/z* (relative intensity) 334 ([M^+] 7), 275 (26), 203 (7), 191 (7), 178 (15) 177 (99), 161 (8), 77 (2). HR-MS (ESI) *m/z* calcd for $C_{19}H_{26}O_5$ [M^+] 334.1780, found 334.1781.



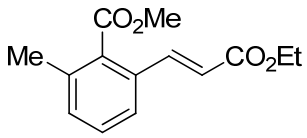
(*E*)-*n*-Heptyl 2-(3-*n*-butoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (3g): The general procedure A was followed using *n*-heptyl 4-methoxybenzoate (115 mg, 0.46 mmol) and *n*-butyl acrylate (131 mg, 1.02 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1) yielded **3g** (106 mg, 84%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.48 (d, *J* = 15.9 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.25 (d, *J* = 15.9 Hz, 1H), 4.29 (t, *J* = 6.7 Hz, 2H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 1.79−1.61 (m, 4H), 1.52 – 1.25 (m, 10H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.5 (C_q), 166.4 (C_q), 162.4 (C_q), 144.4 (CH), 138.9 (C_q), 133.0 (CH), 122.4 (C_q), 121.1 (CH), 114.6 (CH), 113.0 (CH), 65.3 (CH_2), 64.5 (CH_2), 55.5 (CH_3), 31.7 (CH_2), 30.8 (CH_2), 29.0 (CH_2), 28.7 (CH_2), 26.0 (CH_2), 22.6 (CH_2), 19.2 (CH_2), 14.0 (CH_3), 13.7 (CH_3). IR (neat): 2956, 2929, 2857, 1708, 1252, 1169, 1126, 10832 cm^{-1}. MS (EI): *m/z* (relative intensity) 376 ([M^+] 2), 275 (32), 203 (17), 178 (14, 177 (99), 161 (22) 43 (9), 44 (16). HR-MS (ESI) *m/z* calcd for $C_{22}H_{32}O_5$ [M^+] 376.2250, found 376.2249.



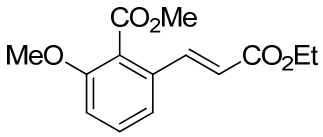
(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4,6-dimethoxybenzoate (3h): The general procedure A was followed using methyl 2,4-dimethoxybenzoate (102 mg, 0.52 mmol) and ethyl acrylate (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1) yielded **3g** (82.5 mg, 54%) as a colorless solid. M. p. = 88−90 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 15.9 Hz, 1H), 6.67 (d, *J* = 2.2 Hz, 1H), 6.49 (d, *J* = 2.2 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 167.5 (C_q), 166.3 (C_q), 161.6 (C_q), 158.4 (C_q), 141.4 (CH), 134.8 (C_q), 121.3 (CH), 117.1 (C_q), 102.2 (CH), 100.2 (CH), 60.6 (CH_2), 56.0 (CH_3), 55.5 (CH_3), 52.5 (CH_3), 14.2 (CH_3). IR (neat): 2962, 1703, 1267, 1202, 1157, 1096, 1045, 979 cm^{-1}. MS (EI): *m/z* (relative intensity) 294 ([M^+] 7), 263 (5), 249 (6), 233 (5), 222 (15), 221 (99), 207 (10), 191 (13). HR-MS (ESI) *m/z* calcd for $C_{15}H_{18}O_6$ [M^+] 294.1103, found 294.1101.



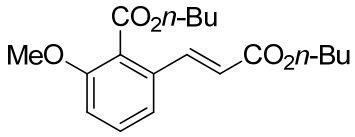
(*E*)-Methyl 2-(3-*n*-butoxy-3-oxoprop-1-en-1-yl)-4,6-dimethoxybenzoate (3i): The general procedure A was followed using methyl 2,4-dimethoxybenzoate (97.3 mg, 0.50 mmol) and *n*-butyl acrylate (130 mg, 1.01 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1) yielded **3i** (90.2 mg, 56%) as a colorless solid. M. p. = 69−71 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.66 (d, J = 15.8 Hz, 1H), 6.68 (d, J = 2.2 Hz, 1H), 6.50 (d, J = 2.2 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 4.19 (t, J = 6.6 Hz, 2H), 3.91 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 1.76−1.59 (m, 2H), 1.51−1.32 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 167.5 (C_q), 166.4 (C_q), 161.6 (CH), 158.4 (C_q), 141.4 (CH), 134.8 (C_q), 121.3 (CH), 117.1 (C_q), 102.2 (CH), 100.2 (CH), 64.6 (CH_2), 56.1 (CH_3), 55.5 (CH_3), 52.5 (CH_3), 30.7 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (neat): 2984, 2841, 1711, 1266, 1235, 1202, 1041, 832 cm^{-1}. MS (EI): *m/z* (relative intensity) 322 ([M^+] 4), 249 (5), 222 (16), 221 (99), 207 (15), 191 (15) 178 (6), 41 (11). HR-MS (ESI) *m/z* calcd for $C_{17}H_{22}O_6$ [M^+] 322.1416, found 322.1415.



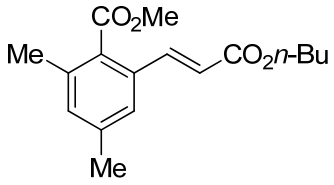
(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-6-methylbenzoate (3j): The general procedure A was followed using methyl 2-methylbenzoate (75.2 mg, 0.50 mmol) and ethyl acrylate (130 mg, 1.03 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1→25/1) yielded **3j** (59.8 mg, 48%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.68 (d, J = 15.8 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.30 (dd, J = 7.6, 7.4, Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 2.33 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$) δ = 169.2 (C_q), 166.4 (C_q), 141.6 (CH), 135.8 (C_q), 134.0 (C_q), 132.3 (C_q), 131.6 (CH), 129.7 (CH), 123.9 (CH), 120.7 (CH), 60.5 (CH_2), 52.3 (CH_3), 19.6 (CH_3), 14.2 (CH_3). IR (neat): 2983, 2953, 1711, 1267, 1229, 1165, 1116, 1072 cm^{-1}. MS (EI): *m/z* (relative intensity) 248 ([M^+] 5), 203 (12), 189 (35), 175 (99), 161 (32), 147 (80) 132 (18), 115 (37). HR-MS (ESI) *m/z* calcd for $C_{14}H_{16}O_4$ [M^+] 248.1049, found 248.1048. The analytical data are in accordance with those reported in the literature.[4]



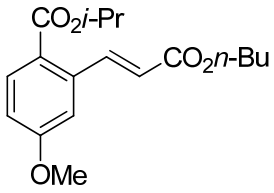
(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-6-methoxybenzoate (3k): The general procedure A was followed using methyl 2-methoxybenzoate (88.9 mg, 0.53 mmol) and ethyl acrylate (103 mg, 1.02 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1→25/1→17/1) yielded **3k** (73.5 mg, 51%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.61 (d, J = 15.9 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.39 (d, J = 15.9 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 3.85 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 167.6 (C_q), 166.3 (C_q), 156.7 (C_q), 140.9 (CH), 133.3 (C_q), 130.8 (CH), 124.1 (C_q), 121.4 (CH), 118.6 (CH), 112.3 (CH), 60.6 (CH_2), 56.1 (CH_3), 52.6 (CH_3), 14.3 (CH_3). IR (neat): 2981, 2951, 1709, 1258, 1173, 1113, 1066, 1030 cm^{-1}. MS (EI): *m/z* (relative intensity) 264 ([M^+] 7), 219 (7), 203 (9), 191 (99), 177 (19), 161 (13) 89 (6), 77 (5). HR-MS (ESI) *m/z* calcd for $C_{14}H_{16}O_5$ [M^+] 264.0998, found 264.1001.



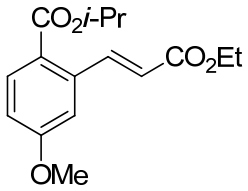
(*E*)-*n*-Butyl 2-(3-*n*-butoxy-3-oxoprop-1-en-1-yl)-6-methoxybenzoate (3l): The general procedure A was followed using *n*-butyl 2-methoxybenzoate (106 mg, 0.51 mmol) and *n*-butyl acrylate (200 mg, 1.56 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 25/1→10/1→6/1) yielded **3l** (106 mg, 63%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.64 (d, J = 15.9 Hz, 1H), 7.35 (dd, J = 8.2, 7.8 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.38 (d, J = 15.9 Hz, 1H), 4.37 (t, J = 6.7 Hz, 2H), 4.18 (t, J = 6.7 Hz, 2H), 3.84 (s, 3H), 1.87−1.55 (m, 4H), 1.54−1.30 (m, 4H), 0.95 (t, J = 7.4 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 167.2 (C_q), 166.3 (C_q), 156.6 (C_q), 140.9 (CH), 133.3 (C_q), 130.6 (CH), 124.5 (C_q), 121.4 (CH), 118.6 (CH), 112.3 (CH), 65.5 (CH_2), 64.5 (CH_2), 56.0 (CH_3), 30.7 (CH_2), 30.6 (CH_2), 19.2 (CH_2), 19.1 (CH_2), 13.7 (CH_3), 13.6 (CH_3). IR (neat): 2959, 2935, 2873, 1713, 1260, 1168, 1112, 1066 cm^{-1}. MS (EI): *m/z* (relative intensity) 334 ([M^+] 5), 261 (8), 233 (35), 203 (8), 178 (14), 177 (99), 161 (18), 41 (14). HR-MS (ESI) *m/z* calcd for $C_{19}H_{26}O_5$ [M^+] 334.1780, found 334.1781.



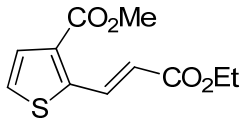
(*E*)-Methyl 2-(3-*n*-butoxy-3-oxoprop-1-en-1-yl)-4,6-dimethylbenzoate (3m): The general procedure A was followed using methyl 2,4-dimethylbenzoate (82.9 mg, 0.50 mmol) and *n*-butyl acrylate (129 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1→25/1) yielded **3m** (83.3 mg, 57%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.70 (d, J = 15.9 Hz, 1H), 7.27 (s, 1H), 7.05 (s, 1H), 6.35 (d, J = 15.9 Hz, 1H), 4.19 (t, J = 6.7 Hz, 2H), 3.93 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H), 1.77−1.60 (m, 2H), 1.52−1.37 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$) δ = 169.4 (C_q), 166.6 (C_q), 142.0 (CH), 139.7 (C_q), 136.0 (C_q), 132.6 (CH), 132.5 (C_q), 131.3 (C_q), 124.6 (CH), 120.4 (CH), 64.4 (CH_2), 52.2 (CH_3), 30.7 (CH_2), 21.2 (CH_3), 19.7 (CH_3), 19.2 (CH_2), 13.7 (CH_3). IR (neat): 2957, 2873, 1711, 1258, 1165, 1083, 975, 853 cm^{-1}. MS (EI): *m/z* (relative intensity) 290 ([M^+] 5), 231 (15), 189 (99), 175 (46), 159 (14), 146 (13) 115 (12), 77 (5). HR-MS (ESI) *m/z* calcd for $C_{17}H_{22}O_4$ [M^+] 290.1518, found 290.1516.



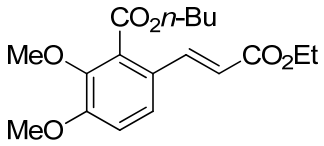
(*E*)-*iso*-Propyl 2-(3-*n*-butoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (3n): The general procedure A was followed using *iso*-propyl 4-methoxybenzoate (98.9 mg, 0.51 mmol) and *n*-butyl acrylate (132 mg, 1.03 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 100/1→50/1) yielded **3n** (102 mg, 63%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.47 (d, J = 15.9 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 2.6 Hz, 1H), 6.92 (dd, J = 8.8, 2.6 Hz, 1H), 6.25 (d, J = 15.9 Hz, 1H), 5.24 (hept, J = 6.2 Hz, 1H), 4.22 (t, J = 6.7 Hz, 2H), 3.87 (s, 3H), 1.78−1.59 (m, 2H), 1.53−1.39 (m, 2H), 1.37 (d, J = 6.3 Hz, 6H), 0.96 (t, J = 7.4 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.5 (C_q), 165.8 (C_q), 162.2 (C_q), 144.3 (CH), 138.5 (C_q), 132.9 (CH), 122.8 (C_q), 120.8 (CH), 114.6 (CH), 112.9 (CH), 68.7 (CH), 64.5 (CH_2), 55.5 (CH_3), 30.8 (CH_2), 22.0 (CH_3), 19.3 (CH_2), 13.8 (CH_3). IR (neat): 2960, 2873, 1704, 1254, 1169, 1135, 1104, 1031 cm^{-1}. MS (EI): *m/z* (relative intensity) 320 ([M^+] 4), 278 (4), 219 (13), 205 (6), 178 (16), 177 (99) 161 (14), 77 (3). HR-MS (ESI) *m/z* calcd for $C_{18}H_{24}O_5$ [M^+] 320.1624, found 320.1629.



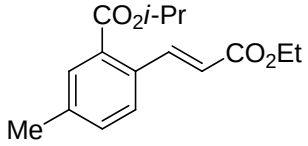
(*E*)-*iso*-Propyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (3o): The general procedure was followed using *iso*-propyl 4-methoxylbenzoate (96.1 mg, 0.50 mmol) and ethyl acrylate (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **3o** (75 mg, 52%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.47 (d, J = 15.5 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.02 (d, J = 2.6 Hz, 1H), 6.92 (dd, J = 8.7, 2.6 Hz, 1H), 6.24 (d, J = 15.5 Hz, 1H), 5.24 (hept, J = 6.2 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.37 (d, J = 6.2 Hz, 6H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.4 (C_q), 165.8 (C_q), 162.2 (C_q), 144.4 (CH), 138.5 (C_q), 132.9 (CH), 122.8 (C_q), 120.8 (CH), 114.6 (CH), 112.8 (CH), 68.7 (CH), 60.6 (CH_2), 55.5 (CH_3), 22.1 (CH_3), 14.4 (CH_3). IR (neat): 2980, 2939, 1703, 1254, 1171, 1135, 1104, 1030 cm^{-1}. MS (EI) *m/z* (relative intensity): 292 ([M^+] 3), 250 (3), 233 (5), 219 (11), 205 (6), 177 (100), 161 (17), 89 (6), 77 (5). HR-MS (EI) *m/z* calcd for $C_{16}H_{20}O_5$ [M^+] 292.1311, found: 292.1316.



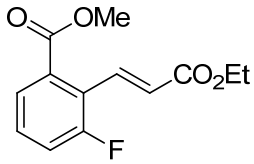
(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)thiophene-3-carboxylate (3p): The general procedure B was followed using methyl thiophene-3-carboxylate (71.0 mg, 0.50 mmol) and ethyl acrylate (98.1 mg, 0.98 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 20/1) yielded **3p** (56 mg, 47%) as a colorless solid. M. p. = 42−44 ^{o}C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.60 (d, J = 15.9 Hz, 1H), 7.48 (d, J = 5.3 Hz, 1H), 7.25 (d, J = 5.3 Hz, 1H), 6.36 (d, J = 15.9 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.90 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.2 (C_q), 163.2 (C_q), 145.1 (C_q), 135.7 (CH), 131.8 (C_q), 130.5 (CH), 125.8 (CH), 121.1 (CH), 60.7 (CH_2), 52.0 (CH_3), 14.3 (CH_3). IR (neat): 3114, 3071, 2984, 2949, 1705, 1247, 1168, 982, 857, 710. MS (EI) *m/z* (relative intensity): 240 ([M^+] 6), 195 (13), 167 (100), 152 (10), 135 (16), 108 (6), 96 (5), 82 (5), 63 (14). HR-MS (EI) *m/z* calcd for $C_{11}H_{12}O_4S$ [M^+] 240.0456, found: 240.0453.



(*E*)-*n*-Butyl 6-(3-ethoxy-3-oxoprop-1-en-1-yl)-2,3-dimethoxybenzoate (3q): The general procedure B was followed using *n*-butyl 4-methoxybenzoate (98.9 mg, 0.51 mmol) and ethyl acrylate (132 mg, 1.03 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 20/1→15/1→8/1) yielded **3q** (126 mg, 72%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.58 (d, J = 15.9 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 6.95 (d, J = 8.7 Hz, 1H), 6.27 (d, J = 15.9 Hz, 1H), 4.39 (t, J = 6.7 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 1.84−1.65 (m, 2H), 1.54−1.38 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.8 (C_q), 166.6 (C_q), 154.0 (C_q), 146.0 (C_q), 140.6 (CH), 130.2 (C_q), 124.8 (C_q), 123.0 (CH), 118.8 (CH), 113.4 (CH), 65.6 (CH_2), 61.6 (CH_3), 60.4 (CH_2), 56.0 (CH_3), 30.6 (CH_2), 19.1 (CH_2), 14.3 (CH_3), 13.6 (CH_3). IR (neat): 2960, 2938, 1709, 1490, 1246, 1176, 1158, 1055 cm^{-1}. MS (EI): *m/z* (relative intensity) 336 ([M^+] 13), 263 (29), 235 (19), 233 (49), 207 (99), 192 (24) 176 (9), 147 (9). HR-MS (ESI) *m*/*z* calcd for $C_{18}H_{24}O_6$ [M^+] 336.1573, found 336.1585.



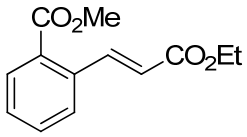
(*E*)-*iso*-Propyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-methybenzoate (3r): The general procedure A was followed using *iso*-propyl 3-methylbenzoate (78.1 mg, 0.44 mmol) and ethyl acrylate (103.2 mg, 1.03 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 20/1) yielded **3r** (86.6 mg, 71%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.37 (d, J = 15.9 Hz, 1H), 7.71 (m, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.32 (dm, J = 8.1 Hz, 1H), 6.27 (d, J = 15.9 Hz, 1H), 5.28 (hept, J = 6.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.39 (d, J = 6.4 Hz, 6H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.6 (C_q), 166.6 (C_q), 143.5 (CH), 139.6 (C_q), 132.9 (C_q), 132.6 (CH), 131.0 (CH), 130.8 (C_q), 127.5 (CH), 119.8 (CH), 69.1 (CH), 60.5 (CH_2), 22.0 (CH_3), 21.2 (CH_3), 14.4 (CH_3). IR (neat): 2981, 2836, 1709, 1261, 1201, 1171, 1107, 1073 cm^{-1}. MS (EI): *m/z* (relative intensity) 276 ([M^+] 5): 234 (10), 217 (8), 189 (10), 161 (100), 145 (15), 115 (10), 89 (3), 77 (3). HR-MS (EI) *m/z* calcd for $C_{16}H_{20}O_4$ [M^+] 276.1362, found: 276.1367.



(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-fluorobenzoate (3s): The general procedure was followed using methyl 3-fluorobenzoate (76.1 mg, 0.49 mmol) and ethyl acrylate (99.3 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/3) yielded **3s** (37 mg, 30%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.02 (d, J =16.3 Hz, 1H), 7.68 (dd, J =7.5 Hz, 0.8 Hz, 1H), 7.38−7.22 (m, 2H), 6.47 (dd, J = 16.3 Hz, 2.0 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.6 (C_q), 166.5 (C_q), 161.9 (d, J_{CF} = 253 Hz, C_q), 136.1 (d, J_{CF} = 1 Hz, CH), 132.5 (d, J_{CF} = 3 Hz, C_q), 129.9 (d, J_{CF} = 9 Hz, CH), 126.3 (d, J_{CF} = 4 Hz, CH), 125.2 (d, J_{CF} = 12 Hz, CH), 123.6 (d, J_{CF} = 13 Hz, C_q), 119.8 (d, J_{CF} = 24 Hz, CH), 60.6 (CH_2), 52.6 (CH_3), 14.3 (CH_3). IR (neat): 2983, 2956, 1713, 1264, 1178, 1141, 1006, 758 cm^{-1}. ^{19}F-NMR (283 MHz, $CDCl_3$): δ = -110.9 (ddd, J = 10 Hz, 5 Hz, 2 Hz). MS (EI) *m/z* (relative intensity): 252 ([M^+] 3), 207 (13), 191 (15), 165 (10), 149 (12), 136 (13), 120 (13), 108 (9), 59 (13). HR-MS (EI) *m/z* calcd for $C_{13}H_{13}FO_4$ [M^+] 252.0798, found: 252.0807.

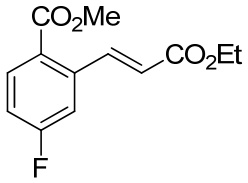
Intermolecular Competition Experiments

General Procedure C: Intermolecular Competition Experiment between Substrates 1a and 1t: A suspension of methyl 4-methoxybenzoate (250 mg, 1.50 mmol), methyl benzoate (208 mg, 1.53 mmol), ethyl acrylate (103 mg, 1.02 mmol), $[RuCl_2(p\text{-cymene})]_2$ (16.0 mg, 5.2 mol %), $AgSbF_6$ (70.0 mg, 41 mol %) and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.00 mmol) in DCE (2.0 mL) was pre-stirred at ambient temperature for 5 min. Thereafter, the reaction mixture was stirred at 100 °C for 16 h under an atmosphere of ambient air. The reaction mixture was diluted with sat. aq. NH_4Cl/NH_3 (1:1, 10 mL) and extracted with EtOAc (4 x 25 mL). The combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 60/1→30/1→15/1) to yield **3a** (79.7 mg, 29%) and **3t** (31.6 mg, 13%) as a colorless oil.



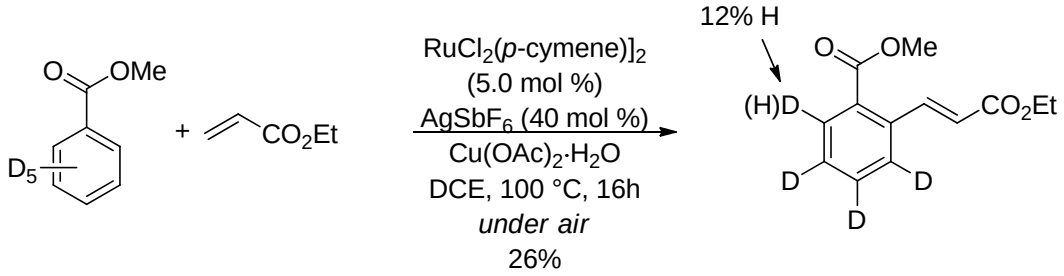
(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (3t): ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 15.9 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 (ddd, *J* = 7.8, 7.5, 1.4 Hz, 1H), 7.42 (ddd, *J* = 7.8, 7.5, 1.5 Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 167.1 (C_q), 166.5 (C_q), 143.6 (CH), 136.4 (C_q), 132.3 (CH), 130.7 (CH), 129.8 (C_q), 129.3 (CH), 127.9 (CH), 121.1 (CH), 60.5 (CH_2), 52.3 (CH_3), 14.3 (CH_3). IR (neat): 2983, 2953, 1710, 1255, 1175, 1129, 1076, 763 cm^{-1}. MS (EI): *m/z* (relative intensity) 234 ([M^+] 3), 173 (10), 161 (99), 147 (8), 129 (9), 118 (8) 101 (8), 76 (7). HR-MS (ESI) *m*/*z* calcd for $C_{13}H_{14}O_4$ [M^+] 234.0892, found 234.0890. The analytical data are in accordance with those reported in the literature.[5]

Intermolecular Competition Experiment between Substrates 1a and 1u: The general procedure C was followed using methyl 4-methoxybenzoate (250 mg, 1.50 mmol), methyl 4-fluorobenzoate (236 mg, 1.53 mmol), ethyl acrylate (105 mg, 1.05 mmol), $[RuCl_2(p\text{-cymene})]_2$ (16.8 mg, 5.5 mol %), $AgSbF_6$ (70.0 mg, 41 mol %) and $Cu(OAc)_2 \cdot H_2O$ (201 mg, 1.01 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 50/1→25/1) yielded **3a** (113 mg, 44%) and **3u** (23.4 mg, 9%) as a colorless oil.



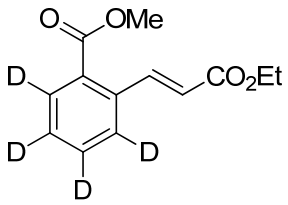
(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-fluorobenzoate (3u): ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.43 (d, J = 15.9 Hz, 1H), 8.01 (dd, J = 8.7, 5.8 Hz, 1H), 7.30−7.21 (m, 1H), 7.11 (ddd, J = 8.7, 7.7, 2.6 Hz, 1H), 6.28 (dd, J = 15.9, 0.9 Hz, 1H), 4.28 (qd, J = 7.1, 1.0 Hz, 2H), 3.92 (d, J = 1.0 Hz, 3H), 1.34 (td, J = 7.1, 1.0 Hz, 3H).^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.2 (C_q), 166.2 (C_q), 164.7 (d, J_{CF} = 254.0 Hz, C_q), 142.5 (d, J_{CF} = 1.8 Hz, CH), 139.6 (d, J_{CF} = 8.8 Hz, C_q), 133.5 (d, J_{CF} = 9.3 Hz, CH), 125.8 (d, J_{CF} = 3.0 Hz, C_q), 122.2 (CH), 116.3 (d, J_{CF} = 21.7 Hz, CH), 114.8 (d, J_{CF} = 22.9 Hz, CH), 60.7 (CH_2), 52.4 (CH_3), 14.3 (CH_3).
^{19}F-NMR (285 MHz, $CDCl_3$) δ = -106.15 (dddd, J = 9.4, 7.4, 5.8, 1.5 Hz). IR (neat): 2984, 2955, 1711, 1251, 1213, 1176, 1117, 1077 cm^{-1}. MS (EI): *m/z* (relative intensity) 264 ([M^+] 7), 252 (3), 207 (12), 180 (26), 179 (99), 151 (19) 136 (12), 94 (9). HR-MS (ESI) *m/z* calcd for $C_{13}H_{13}FO_4$ [M^+] 252.0798, found 252.0800.

Experiments with Isotopically-Labeled Substrate



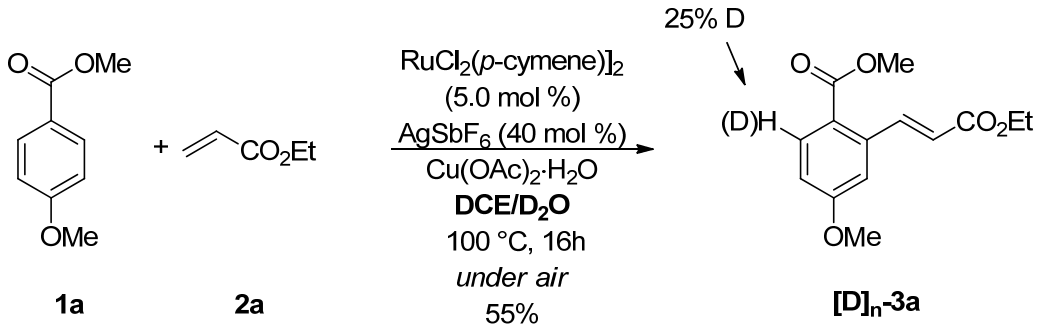
$[D]_5$-1t **2a** **$[D]_n$-3t**

A mixture of methyl 1,2,3,4,5-pentadeuteriobenzoate (**$[D]_5$-1t**) (75.1 mg, 0.53 mmol), ethyl acrylate (**2a**) (107 mg, 1.07 mmol), $[RuCl_2(p\text{-cymene})]_2$ (16.1 mg, 2.6 mol %), $AgSbF_6$ (70.0 mg, 40 mol %) and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.00 mmol) in DCE (2.0 mL) was stirred at ambient temperature for 5 min. Thereafter, the reaction mixture was stirred at 100 °C for 16 h under an atmosphere of ambient air. The reaction mixture was diluted with a solution of saturated aq. NH_4Cl/NH_3 (1:1, 20 mL) and extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with brine (50 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc: 60/1→30/1→10/1) to yield **$[D]_n$-3t** (32.6 mg, 26%) as a colorless oil. The H-incorporation in **$[D]_n$-3t** was estimated by ^{1}H-NMR spectroscopy.



(*E*)-methyl 2-(3-ethoxy-3-oxoprop-1-en-1-yl) 3,4,5-pentadeuteriobenzoate ($[D]_n$-3t):
^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.43 (d, J = 15.9 Hz, 1H), 6.30 (d, J = 15.9 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.93 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 167.0 (C_q), 166.4 (C_q), 143.5 (CH), 136.2 (C_q), 131.7 (t, J = 24 Hz, CD), 130.3 (t, J = 24 Hz, CD), 129.6 (C_q), 128.7 (t, J = 24 Hz, CD), 127.4 (t, J = 24 Hz, CD), 121.1 (CH), 60.6 (CH_2), 52.4 (CH_3), 14.4 (CH_3). IR (neat): 2982, 2954, 1710, 1264, 1218, 1174, 1151, 1075 cm^{-1}. MS (EI): *m/z* (relative intensity) 302 ([M^+] 100), 274 (34), 224 (33), 169 (30), 105 (67), 77 (55), 51 (14). HR-MS (ESI) *m/z* calcd for $C_{13}H_{10}D_4O_4$ [M^+] 238.1143, found 238.1153.

Ruthenium-Catalyzed H/D Exchange in 1a with D_2O as Cosolvent



The general procedure A was followed using methyl 4-methoxybenzoate (85.4 mg, 0.51 mmol), ethyl acrylate (105 mg, 1.05 mmol), $[RuCl_2(p\text{-cymene})]_2$ (16.8 mg, 5.5 mol %), $AgSbF_6$ (70.0 mg, 41 mol %) and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.00 mmol) in a solvent mixture of DCE and D_2O (1.8/0.2 mL). Purification by column chromatography (*n*-hexane/EtOAc: 25/1) yielded **$[D]_n$-3a** (74.1 mg, 55%) as a colorless oil. The D-incorporation in **$[D]_n$-3a** was estimated by ^{1}H-NMR spectroscopy.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.49 (d, J = 15.8 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 2.6 Hz, 1H), 6.91 (dd, J = 8.8, 2.6 Hz, 1H), 6.25 (d, J = 15.8 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.7 (C_q), 166.5 (C_q), 162.5 (C_q), 144.2 (CH), 139.0 (C_q), 133.1 (CH), 121.8 (C_q), 121.2 (CH), 114.6 (CH), 113.0 (CH), 60.6 (CH_2), 55.5 (CH_3), 52.1 (CH_3), 14.3 (CH_3). MS (EI): *m/z* (relative intensity) 302 ([M^+] 100), 274 (34), 224 (33), 169 (30), 105 (67), 77 (55), 51 (14). IR (neat): 2981, 2952, 1255, 1172, 1126, 1089, 1031 cm^{-1}. HR-MS (ESI) *m/z* calcd for $C_{14}H_{15}DO_5$ [M^+] 265.1065, found 265.1073.

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[2] Fatemeh, T.; Mohammad, A. A.; Leily, S. *Tetrahedron Lett*. **2005**, *46*, 7841–7844.
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[4] Park, S. H.; Kim, J. Y.; Chang, S. *Org. Lett.* **2011**, *13*, 2373–2375.
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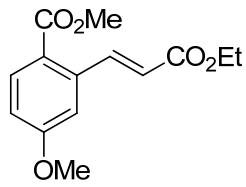
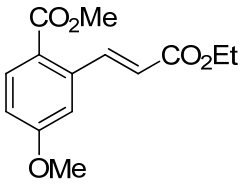


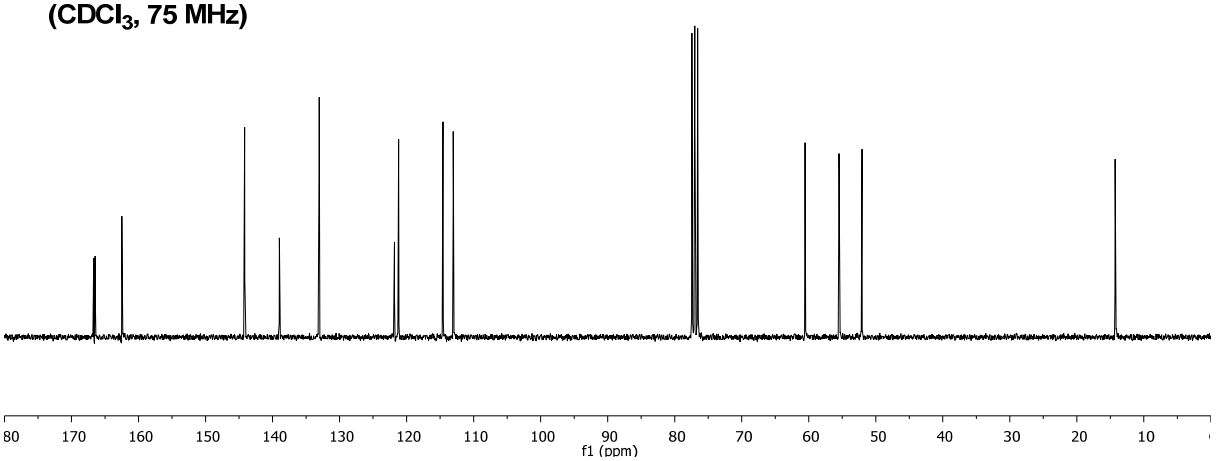
3a

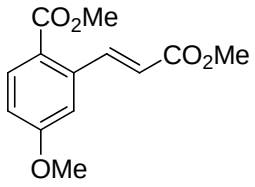
($CDCl_3$, 300 MHz)



3a

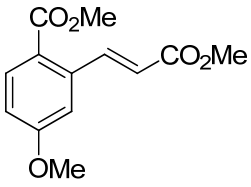
($CDCl_3$, 75 MHz)





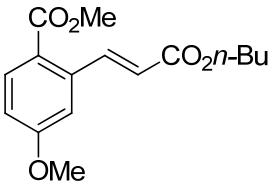
3b

($CDCl_3$, 300 MHz)



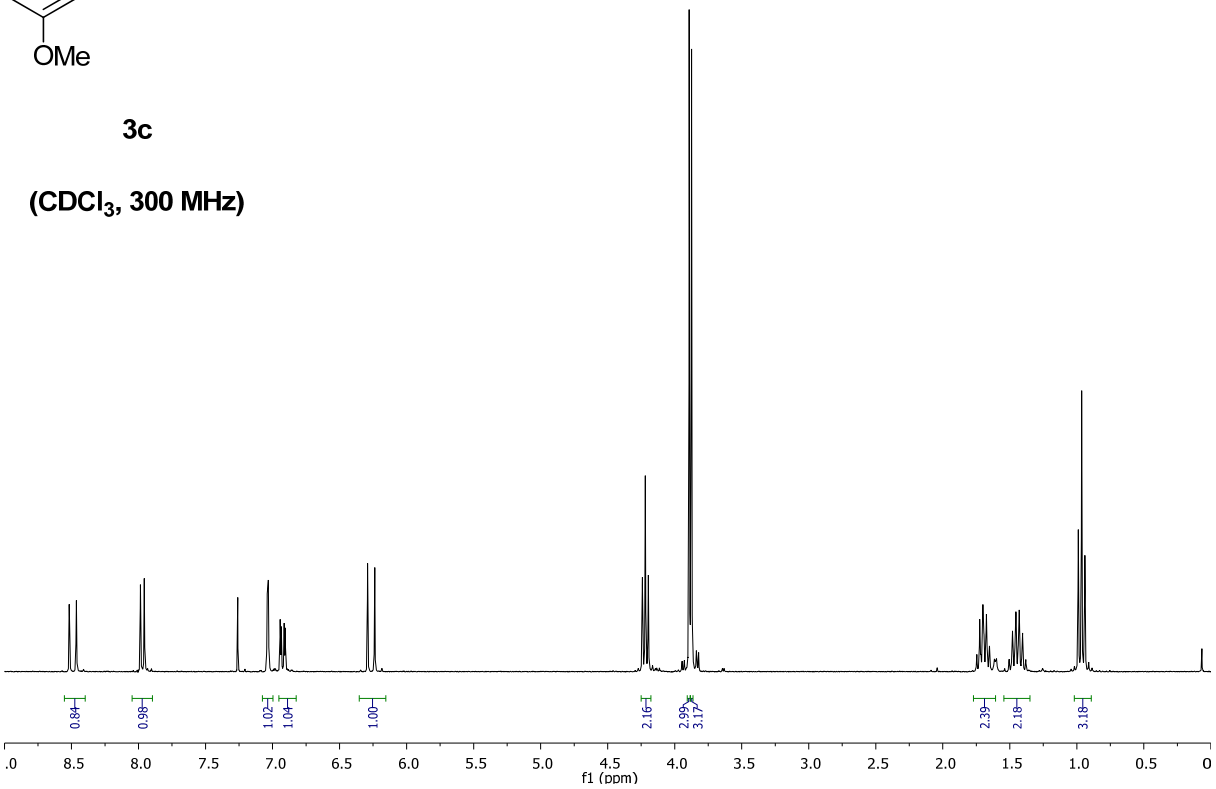
3b

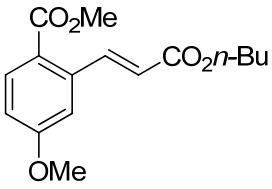
($CDCl_3$, 75 MHz)



3c

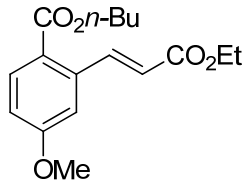
($CDCl_3$, 300 MHz)





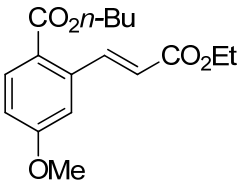
3c

($CDCl_3$, 75 MHz)



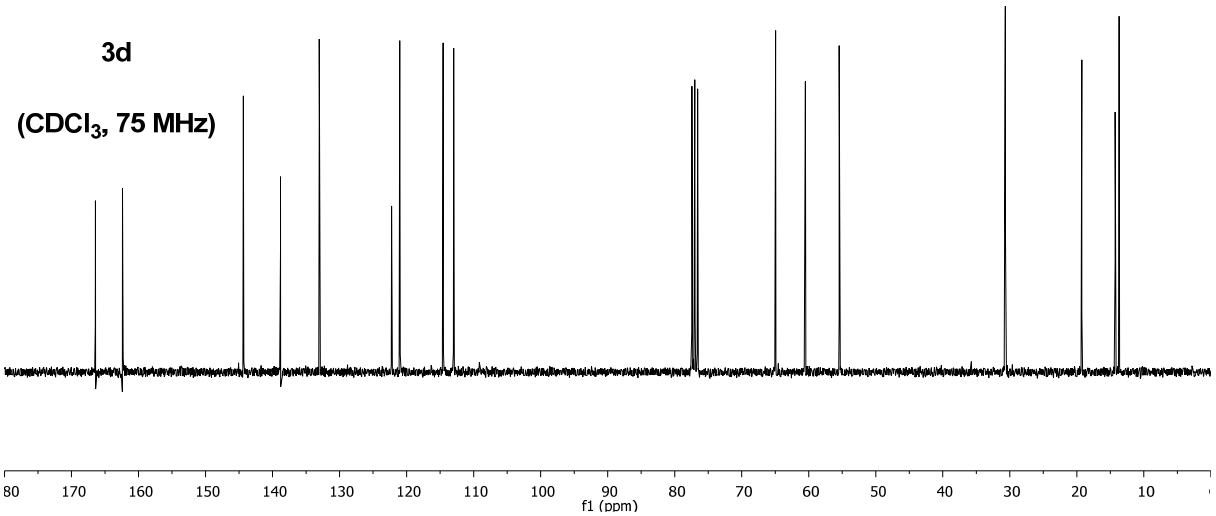
3d

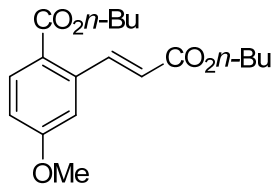
($CDCl_3$, 300 MHz)



3d

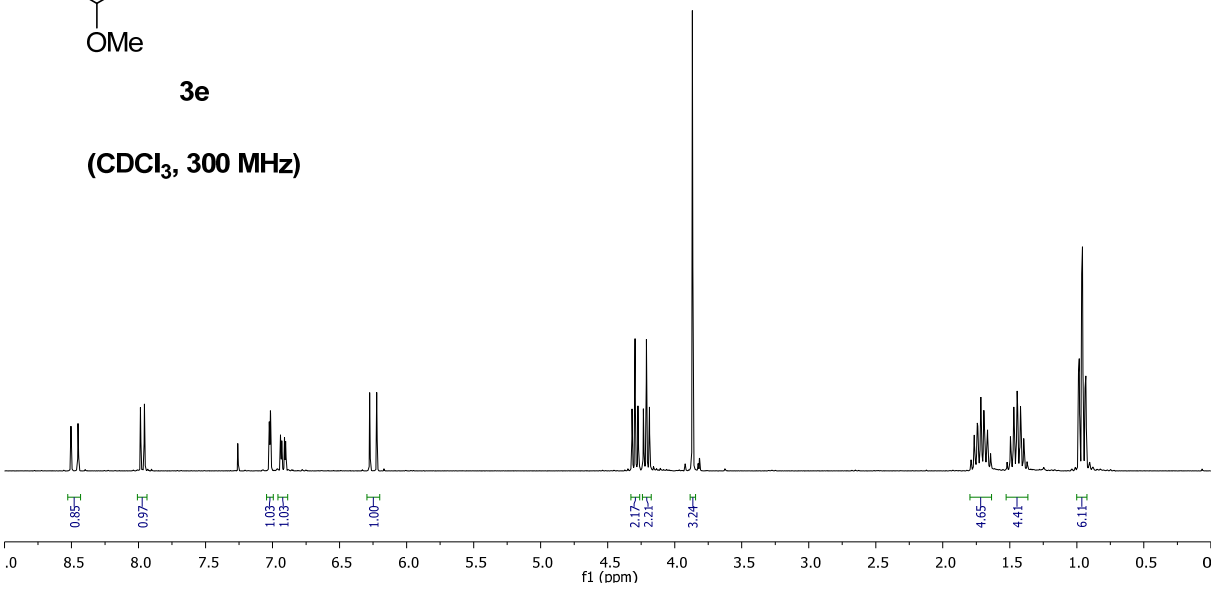
($CDCl_3$, 75 MHz)

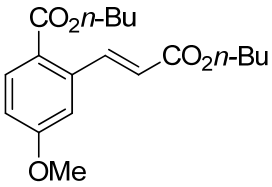




3e

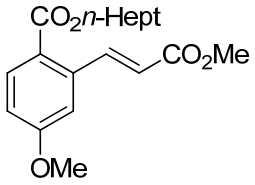
($CDCl_3$, 300 MHz)





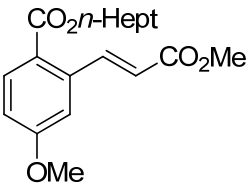
3e

($CDCl_3$, 75 MHz)



3f

($CDCl_3$, 300 MHz)



3f

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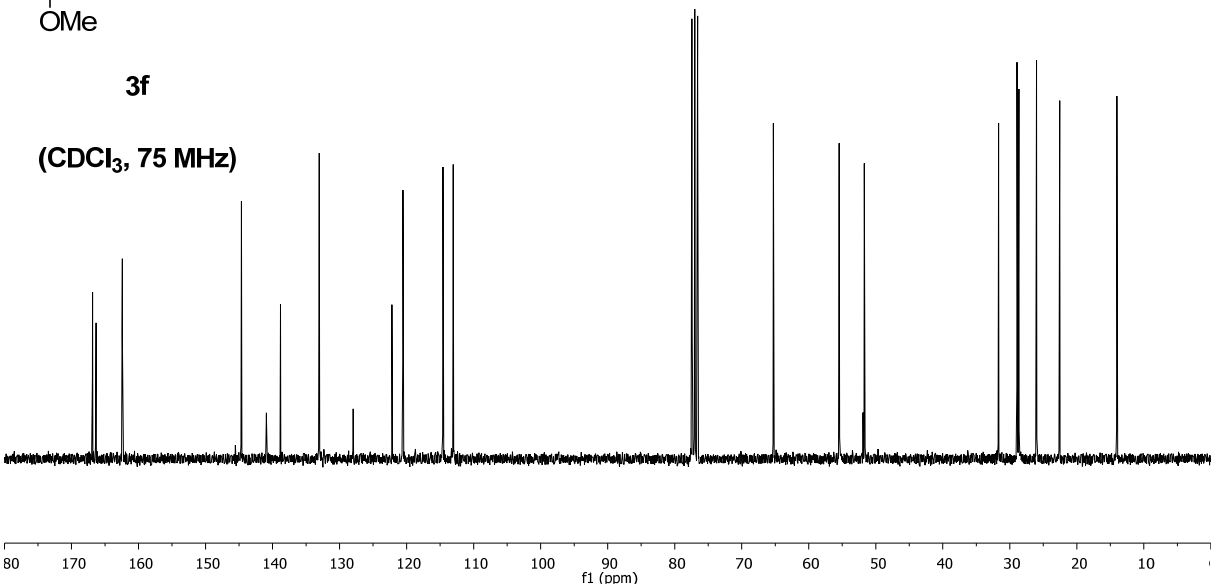

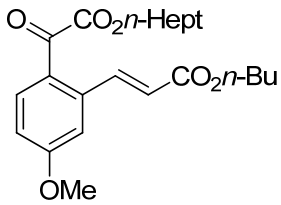

3g

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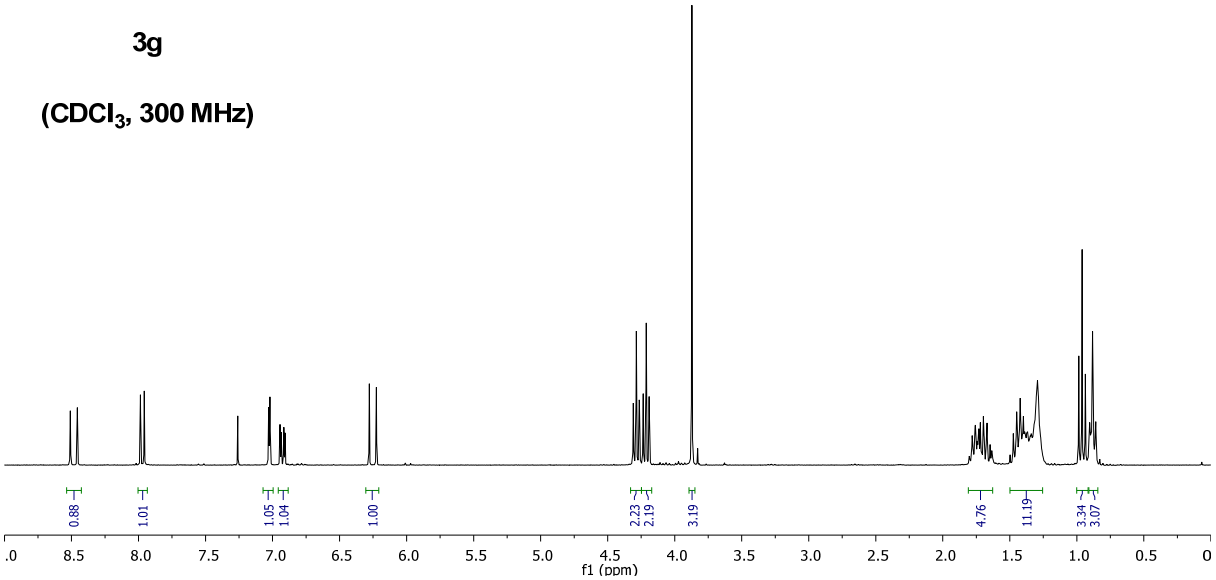

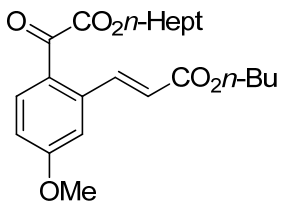

3g

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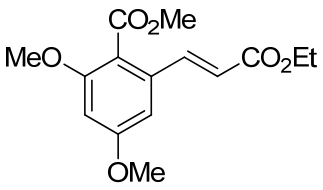

3h

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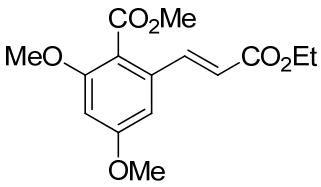

3h

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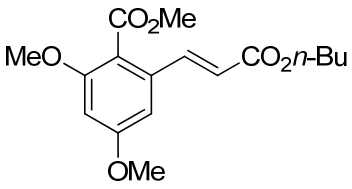

3i

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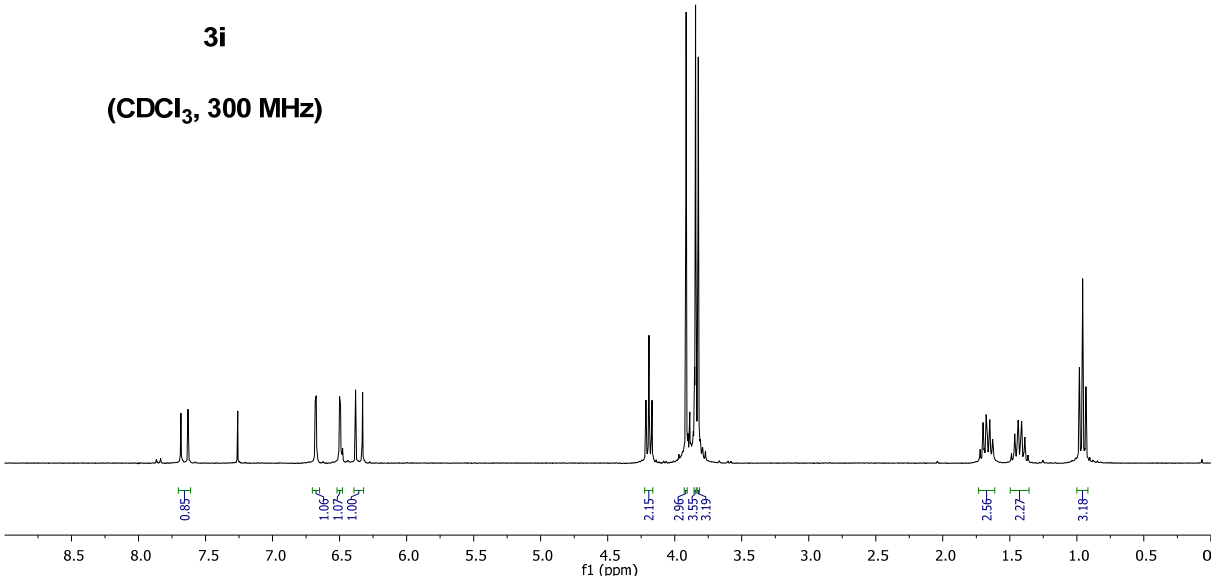

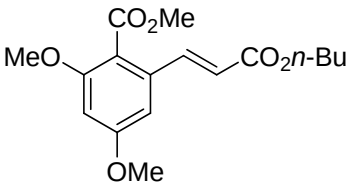

3i

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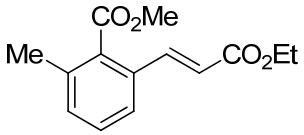

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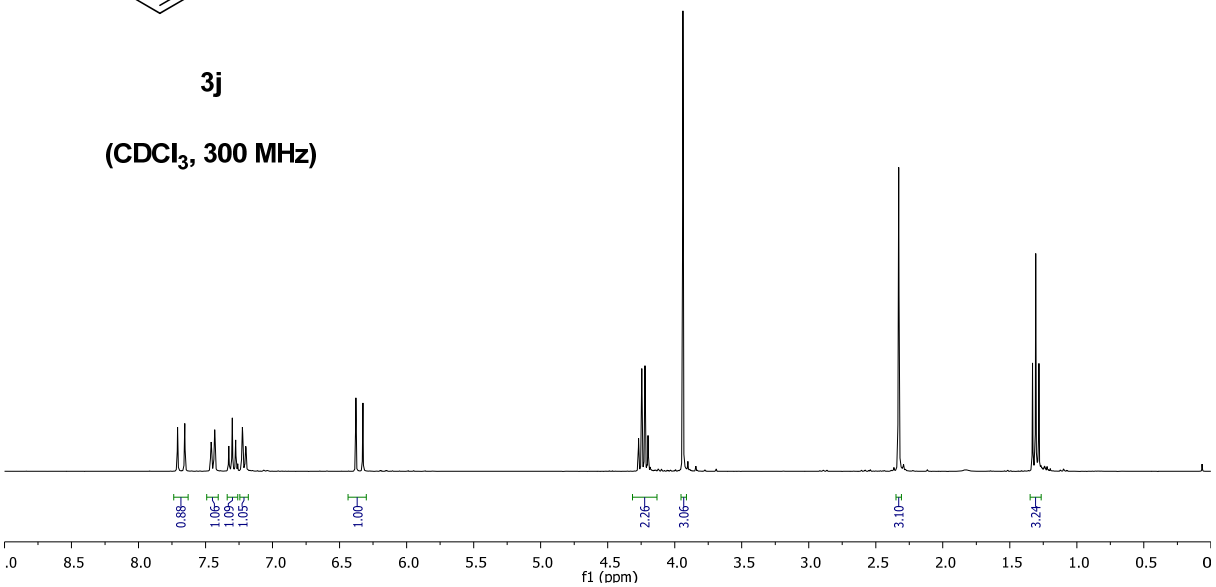

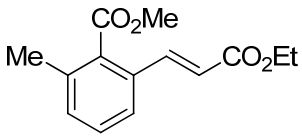

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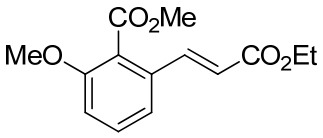

3k

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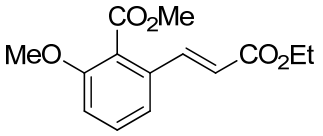

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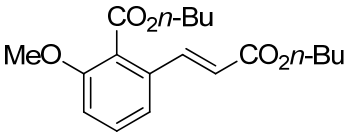
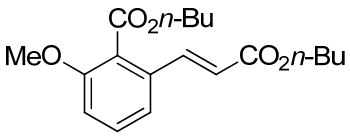


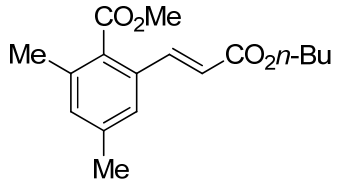
3l

($CDCl_3$, 300 MHz)



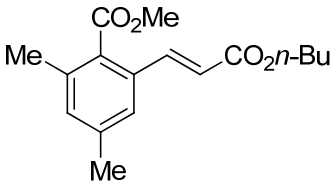
3l

($CDCl_3$, 75 MHz)



3m

($CDCl_3$, 300 MHz)



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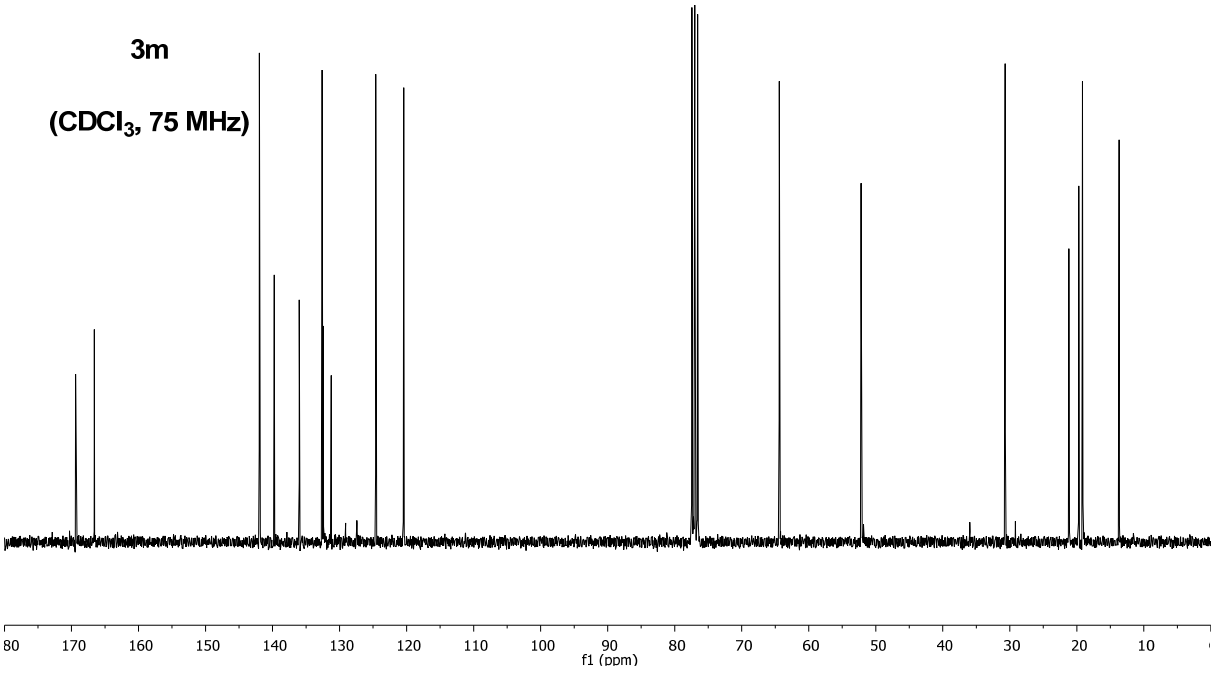
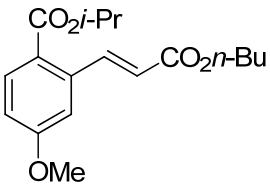
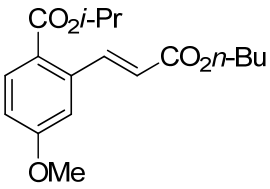




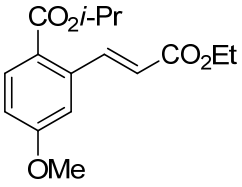
3n

($CDCl_3$, 300 MHz)



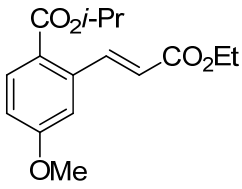
3n

($CDCl_3$, 75 MHz)



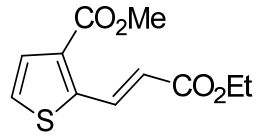
3o

($CDCl_3$, 300 MHz)



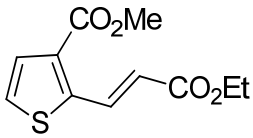
3o

($CDCl_3$, 75 MHz)



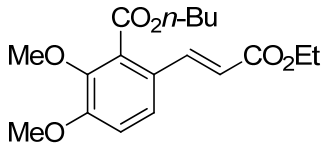
3p

($CDCl_3$, 300 MHz)



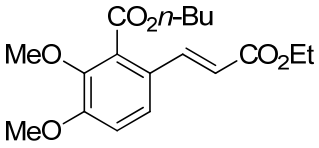
3p

($CDCl_3$, 75 MHz)



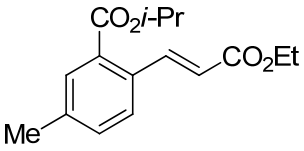
3q

($CDCl_3$, 300 MHz)



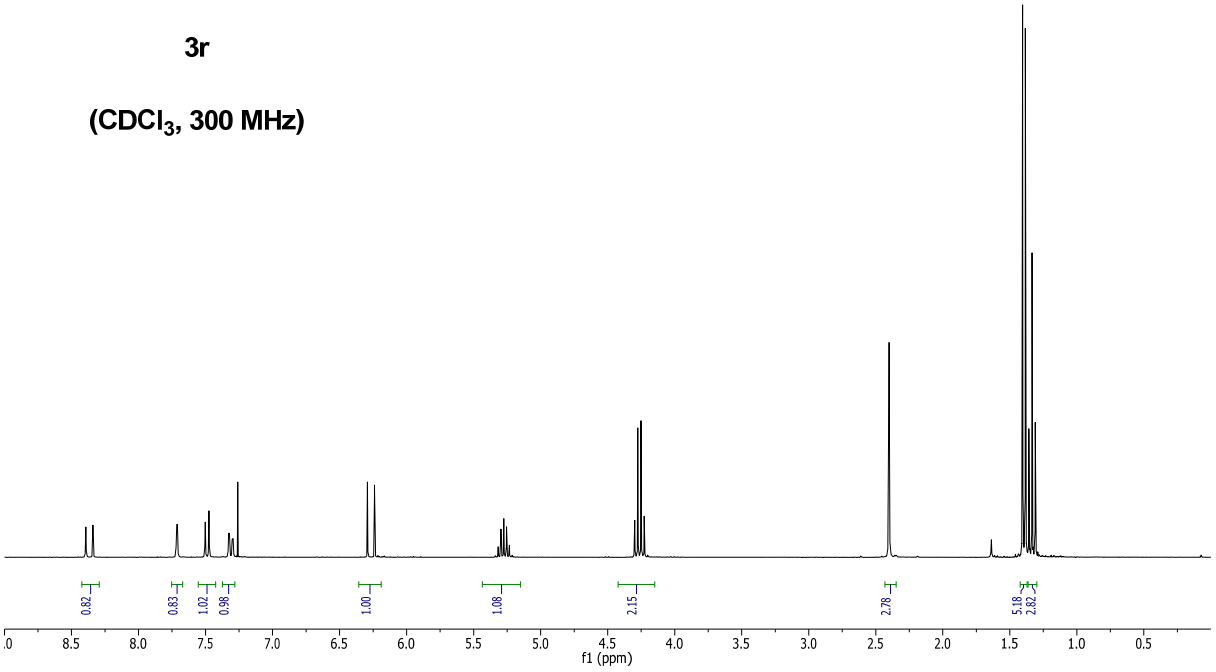
3q

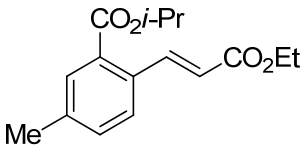
($CDCl_3$, 75 MHz)



3r

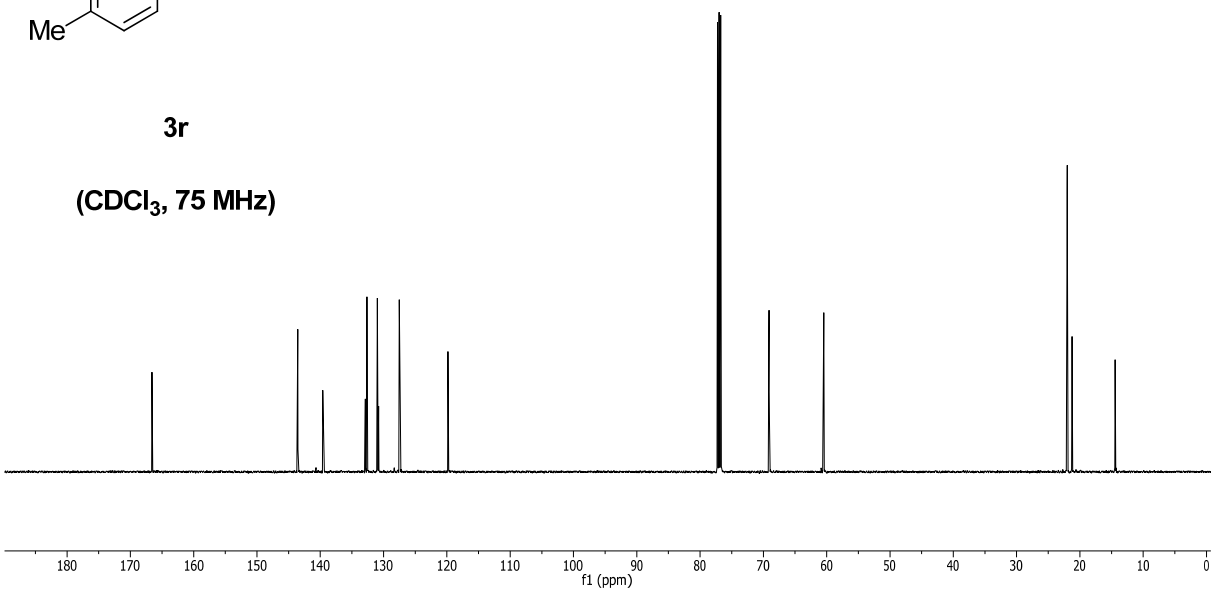
($CDCl_3$, 300 MHz)

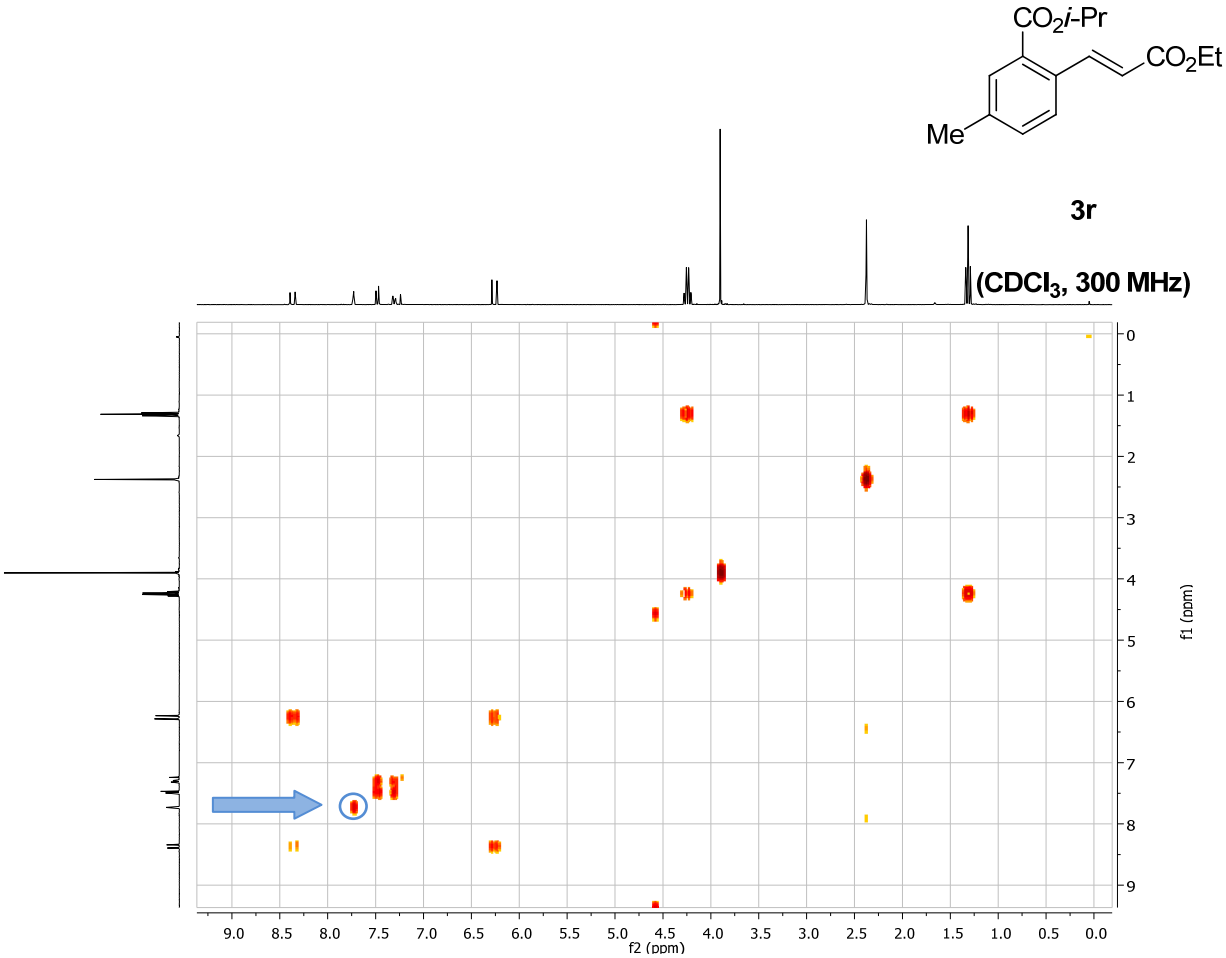


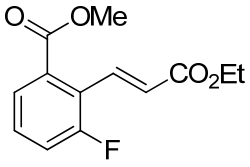


3r

($CDCl_3$, 75 MHz)

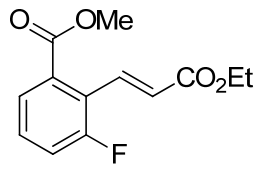



CO2i-Pr
CO2Et
Me
3r
(CDCl3, 300 MHz)
f2 (ppm)
f1 (ppm)



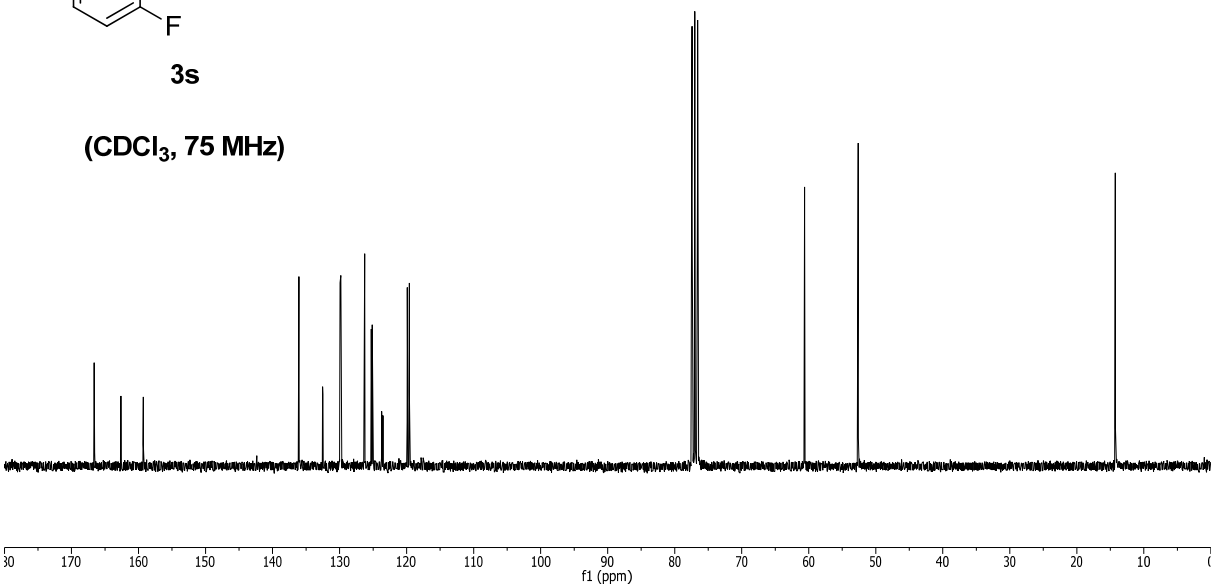
3s

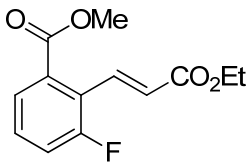
($CDCl_3$, 300 MHz)



3s

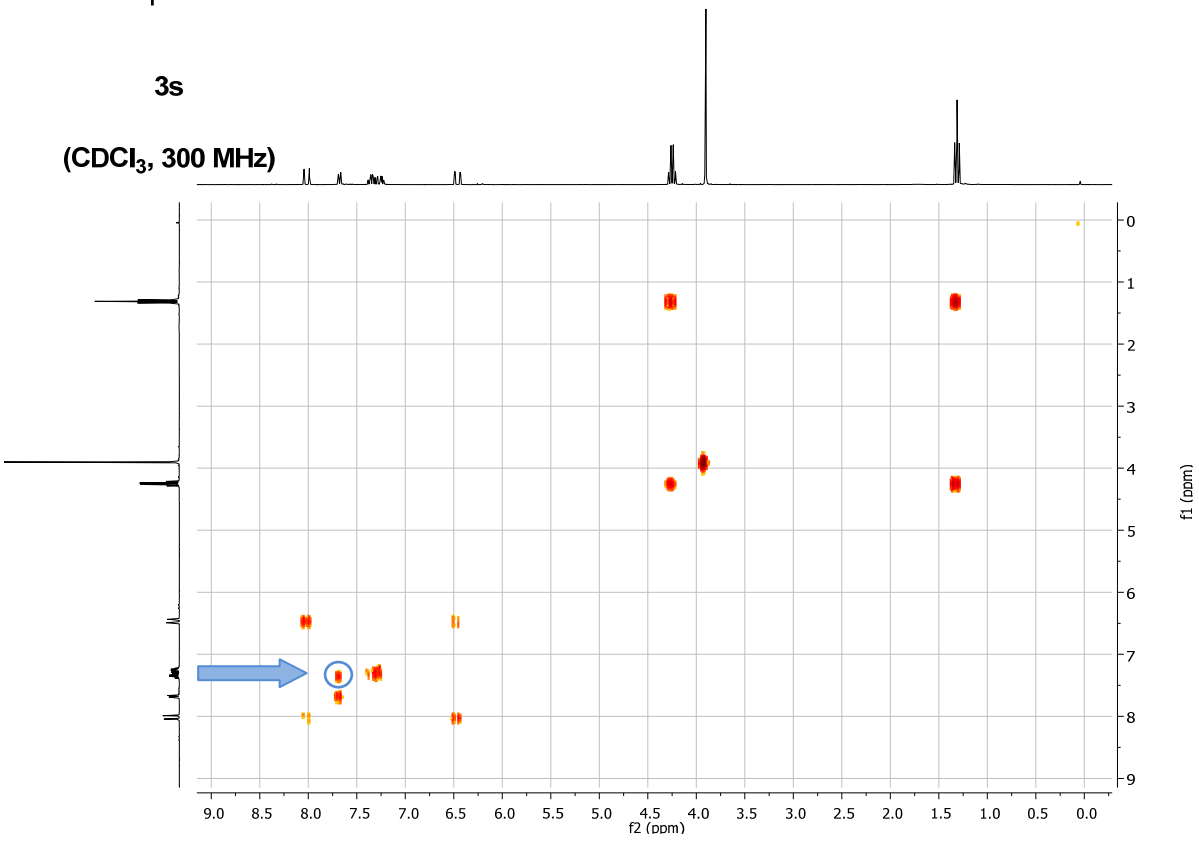
($CDCl_3$, 75 MHz)

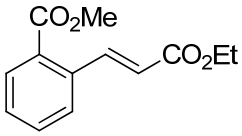




3s

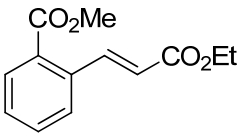
($CDCl_3$, 300 MHz)





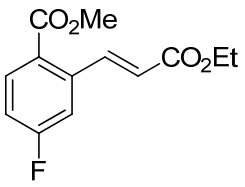
3t

($CDCl_3$, 300 MHz)



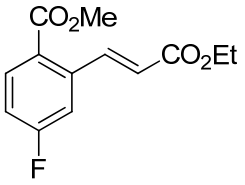
3t

($CDCl_3$, 75 MHz)



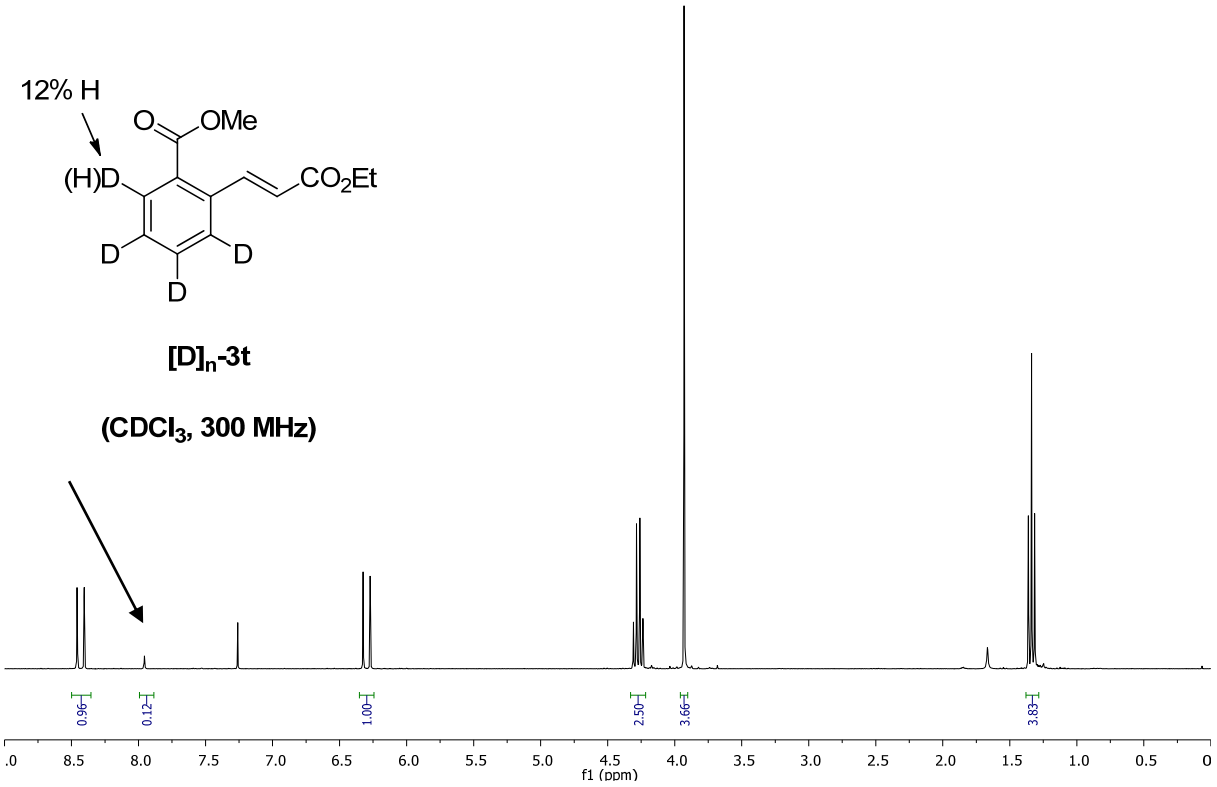
3u

($CDCl_3$, 300 MHz)



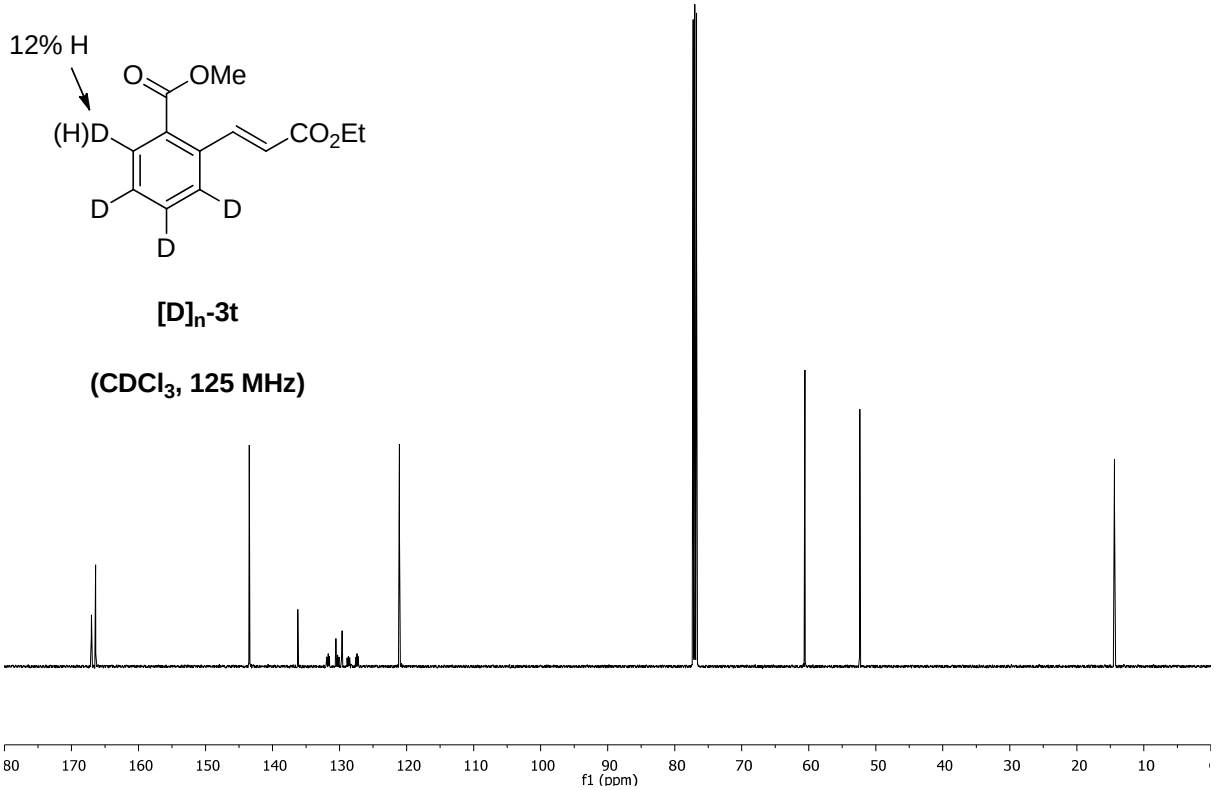
3u

($CDCl_3$, 75 MHz)



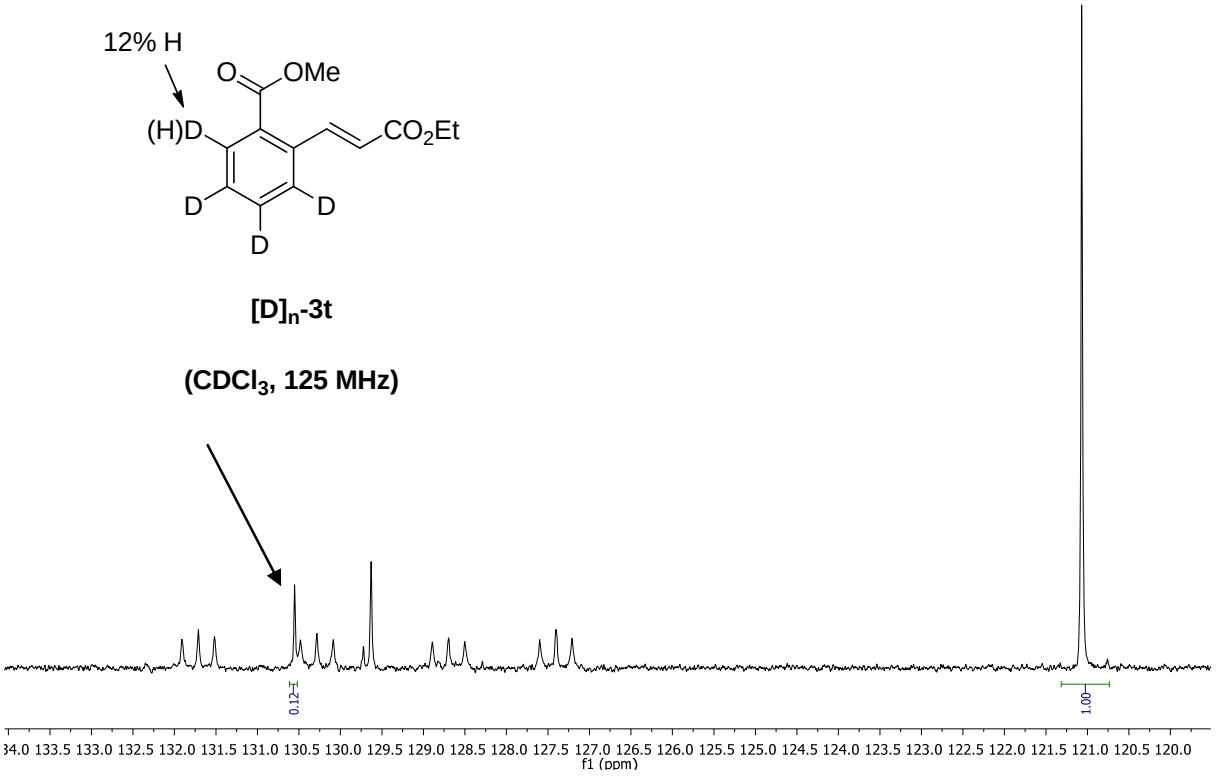
$[D]_n$-3t

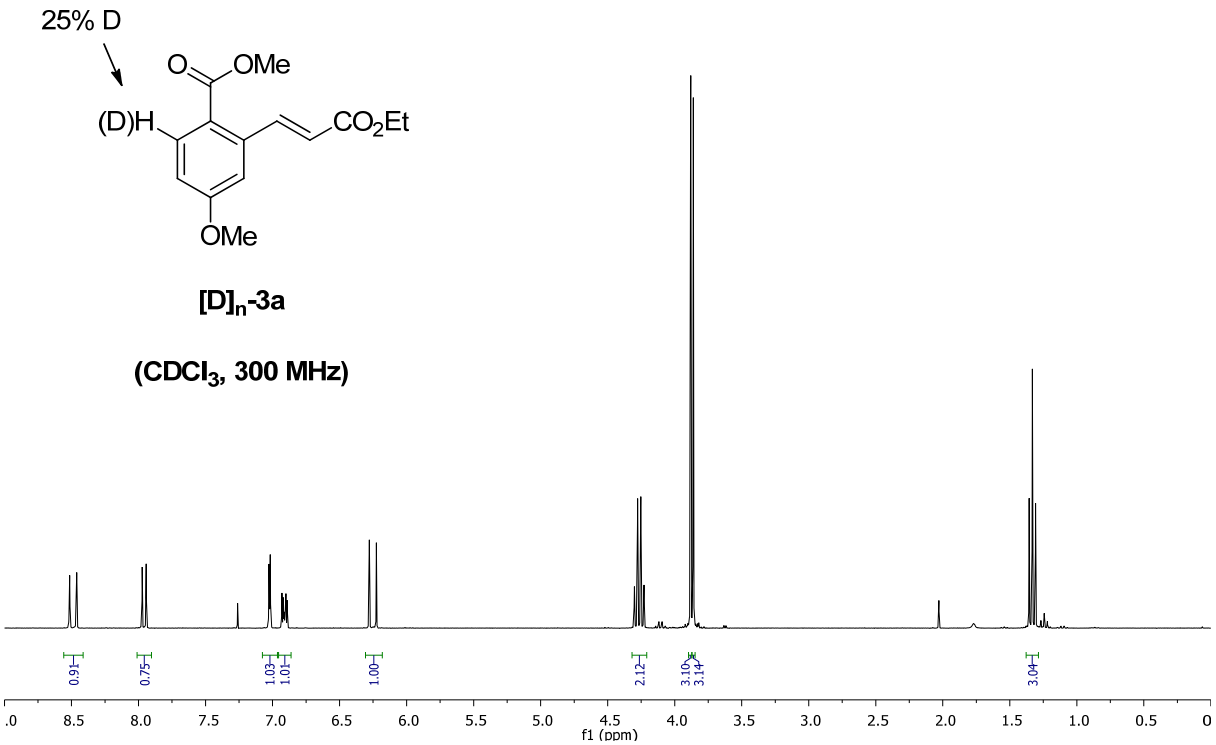
($CDCl_3$, 300 MHz)

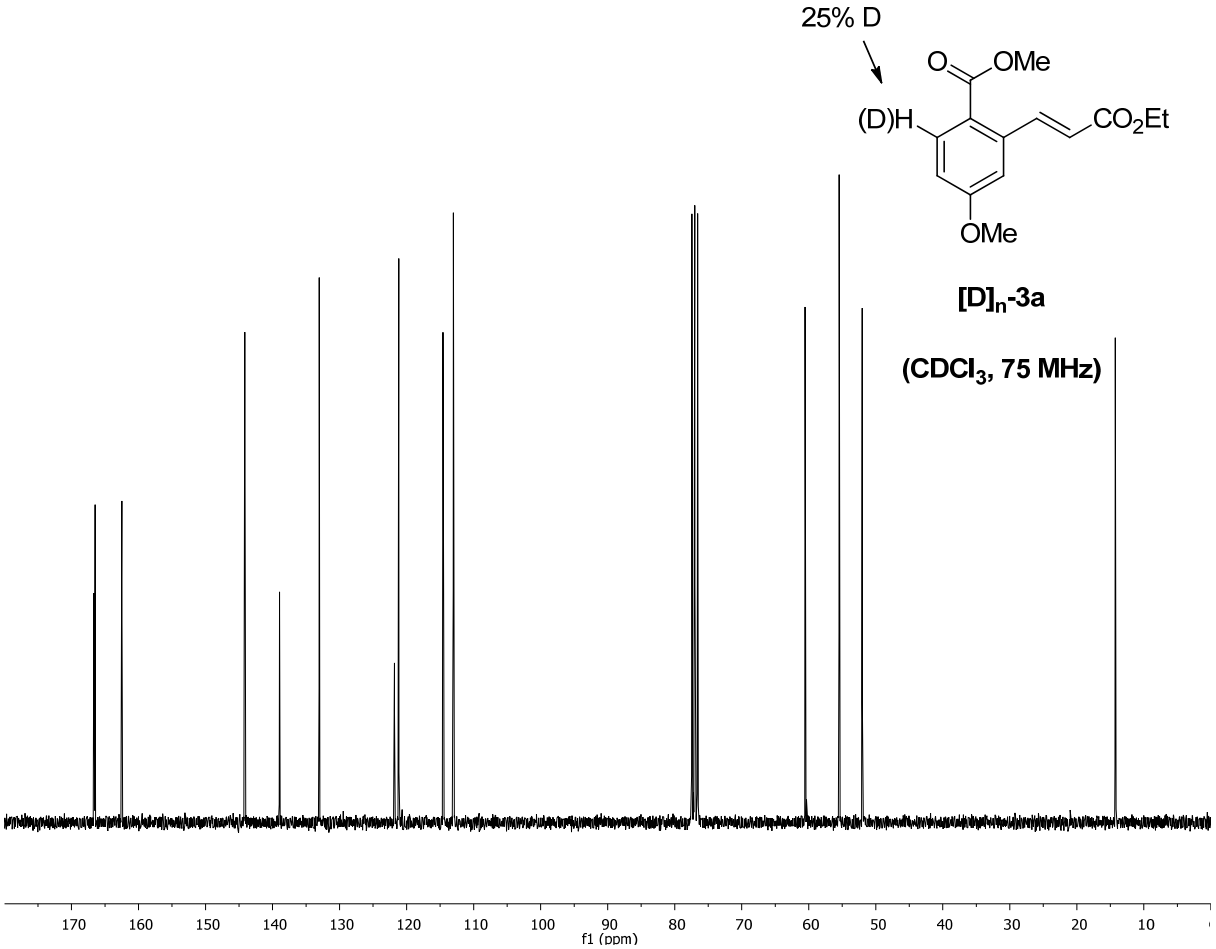


$[D]_n$-3t

($CDCl_3$, 125 MHz)


12% H
O
OMe
(H)D
CO2Et
D
D
D
[D]n-3t
(CDCl3, 125 MHz)
0.12
1.00
34.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5 122.0 121.5 121.0 120.5 120.0
f1 (ppm)


25% D
O
OMe
(D)H
CO2Et
OMe
[D]n-3a
(CDCl3, 300 MHz)
0.91
0.75
1.03
1.01
1.00
2.12
3.10
3.14
3.04
f1 (ppm)


25% D
O
OMe
(D)H
CO2Et
OMe
[D]n-3a
(CDCl3, 75 MHz)
f1 (ppm)