Supporting Information

Ruthenium-Catalyzed Oxidative C–H Alkenylation of Aryl Carbamates

Jie Li, Christoph Kornhaaß and Lutz Ackermann*

Institut für Organische und Biomolekulare Chemie, Georg-August-Universität,

Tammannstrasse 2, D-37077 Göttingen (Germany)

Fax: +49/ 551-39-6777

E-mail: Lutz.Ackermann@chemie.uni-goettingen.de

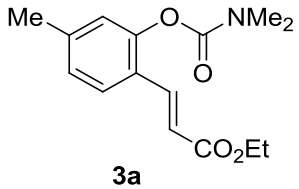
http://www.org.chemie.uni-goettingen.de/ackermann/

General remarks

Catalytic reactions were carried out under a N_2 atmosphere using pre-dried glassware. Aerobic catalytic reactions were carried out under air. 1,2-Dimethoxylethane (DME) was dried and distilled over Sodium. All aryl carbamates were synthesized according to a previously described procedure.[1] Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR and GC-analysis. Chromatography: Merck silica gel 60 (40-63 µm). NMR: Spectra were recorded on Varian Unity 300, Mercury 300 or Inova 500 in the solvent indicated; chemical shifts (δ) are reported in ppm. All IR spectra were taken on a Bruker FT-IR Alpha device. MS: EI-MS-spectra were recorded with Finnigan MAT 95, 70 eV; High resolution mass spectrometry (HRMS) with APEX IV 7T FTICR, ESI-MS: Finnigan LCQ, Bruker Daltonic. M.p.: Stuart melting point apparatus SMP3, Barlworld Scientific, values are uncorrected.

General Procedure A: Ruthenium-Catalyzed Oxidative Alkenylation of Aryl Carbamates

A suspension of *m*-tolyl *N*,*N*-dimethylcarbamate (**1a**) (89.6 mg, 0.50 mmol), ethyl acrylate (**2a**) (100 mg, 1.00 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.00 mmol) in DME (3.0 mL) was stirred at 110 °C for 24 h under an atmosphere of N_2. At ambient temperature, EtOAc (15 mL) was added and the mixture was filtered through silica. The solvents were removed *in vacuo*. Purification of the remaining residue by column chromatography (*n*-hexane/EtOAc: 10/1→*5*/1) yielded **3a** (117 mg, 84%) as a colorless oil.

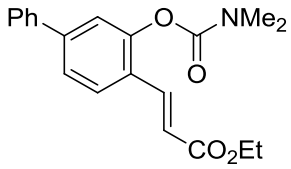


3a

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy)]}-4-methylphenyl}acrylate (3a): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 16.1 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.34 (d, *J* = 16.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.11 (s, 3H), 2.97 (s, 3H), 2.30 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 154.2 (C_q), 149.9 (C_q), 141.7 (C_q), 138.1 (CH), 126.9 (CH), 126.5 (CH), 124.3 (C_q), 123.7 (CH), 118.5 (CH), 60.2 (CH_2), 36.6 (CH_3), 36.3 (CH_3), 21.2 (CH_3), 14.1 (CH_3). IR (ATR): 2934, 1708, 1632, 1381, 1149, 884, 619 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 277 (5) [M^+], 189 (25), 132 (5), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{15}H_{19}NO_4$ 277.1314, found 277.1316. The analytical data are in accordance with those reported in the literature.[2]

General Procedure B: Ruthenium-Catalyzed Oxidative Aerobic Alkenylation of Aryl Carbamates with Cocatalytic Amounts of $Cu(OAc)_2 \cdot H_2O$

A suspension of [1,1'-biphenyl]-3-yl *N*,*N*-dimethylcarbamate (**1w**) (121 mg, 0.50 mmol), ethyl acrylate (**2a**) (100 mg, 1.00 mmol), $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %), $AgSbF_6$ (34.4 mg, 20 mol %) and $Cu(OAc)_2 \cdot H_2O$ (29.7 mg, 30 mol %) in DME (3.0 mL) was pre-stirred at ambient temperature for 10 min under N_2. Thereafter, the reaction mixture was purged with air for 10 min. Then, the tube was sealed and the reaction mixture was stirred at 110 °C for 24 h under an atmosphere of ambient air. At ambient temperature, EtOAc (15 mL) was added and the mixture was filtered through silica. The solvents were removed *in vacuo*. Purification of the remaining residue by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3w** (116 mg, 68%) as a white solid (M.p.: 110–112 °C).

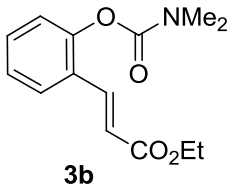


3w

(*E*)-Ethyl 3-{3-[(*N*,*N*-dimethylcarbamoyl)oxy]-[1,1'-biphenyl]-4-yl}acrylate (3w):

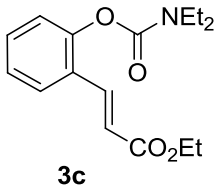
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 16.0 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.60–7.56 (m, 2H), 7.47–7.37 (m, 4H), 7.36–7.30 (m, 1H), 6.46 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.18 (s, 3H), 3.03 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 154.2 (C_q), 150.4 (C_q), 144.0 (C_q),139.3 (C_q), 137.9 (CH), 128.8 (CH), 128.0 (CH), 127.6 (CH), 127.0 (CH), 126.0 (C_q), 124.3 (CH), 121.8

(CH), 119.4 (CH), 60.4 (CH_2), 36.8 (CH_3), 36.5 (CH_3), 14.2 (CH_3). IR (ATR): 2982, 1631, 1610, 1483, 1383, 1157, 893, 762 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 339 (5) [M^+], 251 (20), 194 (8), 165 (10),72 (100). HR-MS (EI): *m*/*z* calcd for $C_{20}H_{21}NO_4$ 339.1471, found 339.1470.



3b

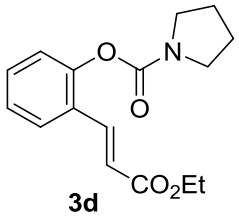
(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]phenyl}acrylate (3b): The general procedure A was followed using **1b** (83 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3b** (89 mg, 68%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, J = 16.1 Hz, 1H), 7.58 (dd, J = 7.8, 1.7 Hz, 1H), 7.35 (dd, J = 7.8, 7.8 Hz, 1H), 7.21–7.12 (m, 2H), 6.41 (d, J = 16.1Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.14 (s, 3H), 2.99 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 154.2 (C_q), 150.0 (C_q), 138.2 (CH), 130.9 (CH), 127.2 (CH), 127.2 (C_q), 125.6 (CH), 123.3 (CH), 119.7 (CH), 60.4 (CH_2), 36.8 (CH_3), 36.4 (CH_3), 14.2 (CH_3). IR (ATR): 2938, 1708, 1635, 1149, 1094, 754 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 263 (5) [M^+], 175 (25), 118 (6), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{14}H_{17}NO_4$ 263.1158, found 263.1159. The analytical data are in accordance with those reported in the literature.[2]



3c

(*E*)-Ethyl 3-{2-[(*N*,*N*-diethylcarbamoyl)oxy]phenyl}acrylate (3c): The general procedure A was followed using **1c** (97 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3c** (98 mg, 67%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ =

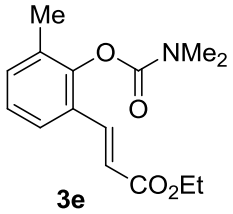
7.82 (d, J = 16.1Hz, 1H), 7.60 (dd, J = 7.8, 1.7 Hz, 1H), 7.35 (ddd, J = 7.8, 7.8, 1.7 Hz, 1H), 7.21–7.13 (m, 2H), 6.40 (d, J = 16.1Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.49 (q, J =7.1 Hz, 2H), 3.37 (q, J = 7.1 Hz, 2H), 1.33–1.25 (m, 6H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.7 (C_q), 153.5 (C_q), 150.1 (C_q), 138.2 (CH), 130.9 (CH), 127.3 (C_q), 127.1 (CH), 125.5 (CH), 123.3 (CH), 119.6 (CH), 60.4 (CH_2), 42.3 (CH_2), 41.9 (CH_2), 14.2 (CH_3), 14.2 (CH_3), 13.2 (CH_3). IR (ATR): 2978, 1708, 1636, 1148, 1038, 881 cm^{-1}. MS (EI) m/z (relative intensity) 291 (5) [M^+], 175 (10), 118 (10), 100 (100), 72 (55), 44 (15). HR-MS (ESI): m/z calcd for $C_{16}H_{21}NO_4$+Na^+ 314.1368, found 314.1367.



3d

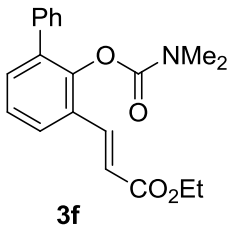
(*E*)-2-(3-Ethoxy-3-oxoprop-1-en-1-yl)phenyl pyrrolidine-1-carboxylate (3d): The general procedure A was followed using **1d** (96 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3d** (79 mg, 55%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 16.1Hz, 1H), 7.58 (dd, J = 7.8, 1.7 Hz, 1H), 7.34 (ddd, J = 7.8, 7.8, 1.7 Hz, 1H), 7.21–7.13 (m, 2H), 6.40 (d, J = 16.1Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.61 (t, J = 6.7 Hz, 2H), 3,46 (t, J = 6.7 Hz, 2H), 2.01–1.83 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 152.3 (C_q), 149.9 (C_q), 138.4 (CH), 130.9 (CH), 127.1 (C_q), 127.1 (CH), 125.4 (CH), 123.3 (CH), 119.5 (CH), 60.4 (CH_2), 46.5

(CH_2), 46.4 (CH_2), 25.7 (CH_2), 24.8 (CH_2), 14.2 (CH_3). IR (ATR): 2978, 1708, 1635, 1392, 1170, 757 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 289 (5) [M^+], 175 (13), 118 (14), 98 (100), 55 (50), 43 (44). HR-MS (ESI): *m*/*z* calcd for $C_{16}H_{19}NO_4$+Na^+ 312.1212, found 312.1207.



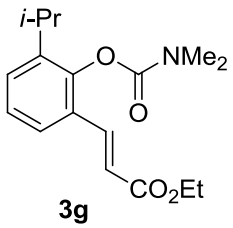
3e

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-3-methylphenyl}acrylate (3e): The general procedure A was followed using **1e** (90 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3e** (97 mg, 70%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 16.1 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H) , 7.10 (dd, *J* = 7.6, 8.0 Hz, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.17 (s, 3H), 3.00 (s, 3H), 2.18 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 153.7 (C_q), 148.8 (C_q), 138.6 (CH), 132.7 (CH), 131.9 (C_q), 127.9 (C_q), 125.7 (CH), 124.8 (CH), 119.7 (CH), 60.3 (CH_2), 36.8 (CH_3), 36.4 (CH_3), 16.1 (CH_3), 14.2 (CH_3). IR (ATR): 2934, 1708, 1635, 1463, 1149, 1035, 847 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 277 (5) [M^+], 189 (25), 160 (6), 131 (6), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{15}H_{19}NO_4$ 277.1314, found 277.1316. The analytical data are in accordance with those reported in the literature.[2]



3f

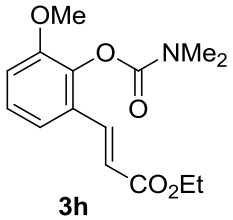
(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-[1,1'-biphenyl]-3-yl}acrylate (3f): The general procedure A was followed using **1f** (121 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3f** (130 mg, 77%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, J = 16.1 Hz, 1H), 7.61 (dd, J = 7.8, 1.9 Hz, 1H), 7.41–7.25 (m, 7H), 6.47 (d, J = 16.1 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 2.90 (s, 3H), 2.77 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.6 (C_q), 153.6 (C_q), 147.3 (C_q), 138.5 (CH), 137.3 (C_q), 136.4 (C_q), 132.3 (CH), 128.8 (CH), 128.7 (C_q), 127.9 (CH), 127.4 (CH), 126.3 (CH), 125.9 (CH), 120.0 (CH), 60.3 (CH_2), 36.5 (CH_3), 36.2 (CH_3), 14.2 (CH_3). IR (ATR): 2934, 1709, 1635, 1429, 1382, 1148, 841 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 339 (5) [M^+], 251 (25), 194 (10), 165 (10), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{20}H_{21}NO_4$ 339.1471, found 339.1468. The analytical data are in accordance with those reported in the literature.[2]



3g

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-3-isopropylphenyl}acrylate (3g): The general procedure A was followed using **1g** (104 mg, 0.50 mmol) and ethyl

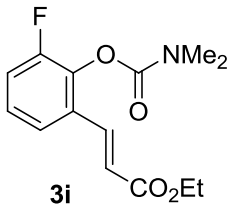
acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3g** (119 mg, 79%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 16.0 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.18 (dd, *J* = 7.8, 7.7 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.09 (s, 3H), 3.07–2.95 (m, 1H), 3.01 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). 1.20 (d, *J* = 6.9 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.2 (C_q), 154.7 (C_q), 148.0 (C_q), 142.4 (C_q), 139.4 (CH), 128.7 (CH), 128.6 (C_q), 126.5 (CH), 125.1 (CH), 120.1 (CH), 60.8 (CH_2), 37.3 (CH_3), 36.9 (CH_3), 27.8 (CH_3), 23.4 (CH), 14.7 (CH_3). IR (ATR): 2979, 1708, 1636, 1392, 1170, 1056, 911, 757 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 305 (5) [M^+] 217 (15), 72 (100). HR-MS (ESI): *m*/*z* calcd for $C_{17}H_{23}NO_4$+Na^+ 328.1525, found 328.1521.



3h

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-3-methoxyphenyl}acrylate (3h): The general procedure A was followed using **1h** (98 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3h** (96 mg, 65%) as a white solid (M.p.: 99–101 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 16.1 Hz, 1H), 7.16 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.11 (dd, *J* = 7.6, 8.0 Hz, 1H), 6.91 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.40 (d, *J* = 16.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.12 (s, 3H), 2.97 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

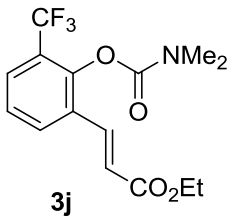
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.6 (C_q), 153.9 (C_q), 152.1 (C_q), 139.5 (C_q), 138.2 (CH), 128.7 (C_q), 125.9 (CH), 120.0 (CH), 118.5 (CH), 113.4 (CH), 60.3 (CH_2), 56.0 (CH_3), 36.7 (CH_3), 36.5 (CH_3), 14.1 (CH_3). IR (ATR): 2984, 1715, 1634, 1580, 1181, 1059, 781 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 293 (5) [M^+], 205 (12), 176 (5), 148 (5), 105 (5), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{15}H_{19}NO_5$ 293.1263, found 293.1253.



3i

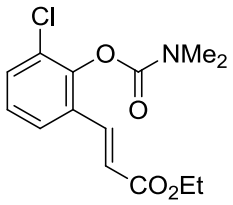
(*E*)-ethyl 3-[2-(*N*,*N*-dimethylcarbamoyloxy)-3-fluorophenyl]acrylate (3i): The general procedure A was followed using **1i** (92 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3i** (102 mg, 73%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, J = 16.2 Hz, 1H), 7.37–7.32 (m, 1H), 7.17–7.10 (m, 2H), 6.42 (d, J = 16.2 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.14 (s, 3H), 3.00 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.4 (C_q), 155.1 (d, $^1J_{C\text{-}F}$ = 250 Hz, C_q), 153.1 (C_q), 138.8 (d, $^2J_{C\text{-}F}$ = 13 Hz, C_q), 137.1 (d, $^4J_{C\text{-}F}$ = 3 Hz, CH), 130.0 (C_q), 126.2 (d, $^3J_{C\text{-}F}$ = 8 Hz, CH), 122.4 (d, $^4J_{C\text{-}F}$ = 3 Hz, CH), 121.0 (CH), 117.6 (d, $^2J_{C\text{-}F}$ = 19 Hz, CH), 60.5 (CH_2), 36.9 (CH_3), 36.5 (CH_3), 14.2 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): -(128.1–128.2) (m). IR (ATR): 2938, 1709, 1639, 1584, 1259, 1145, 845 cm^{-1}. MS (EI)

m/*z* (relative intensity) 281 (5) [M^+], 193 (18), 164 (5), 136 (5), 107 (5), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{14}H_{16}FNO_4$ 281.1063, found 281.1060.



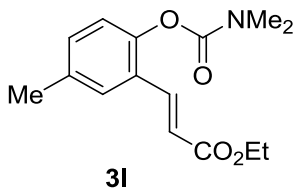
3j

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-3-[trifluoromethyl]phenyl} acrylate (3j): The general procedure A was followed using **1j** (117 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3j** (107 mg, 65%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 16.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.29 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.13 (s, 3H), 2.98 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.2 (C_q), 153.3 (C_q), 147.6 (q, $^4J_{C\text{-}F}$ = 2 Hz, C_q), 136.8 (CH), 130.7 (CH), 130.7 (C_q), 128.0 (q, $^3J_{C\text{-}F}$ = 5 Hz, CH), 125.9 (CH), 124.5 (q, $^2J_{C\text{-}F}$ = 31 Hz, C_q), 122.8 (q, $^1J_{C\text{-}F}$ = 272 Hz, C_q), 121.4 (CH), 60.3 (CH_2), 36.5 (CH_3), 36.2 (CH_3), 14.2 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): -62.1 (s). IR (ATR): 2940, 1713, 1640, 1443, 1329, 1127, 1034, 979, 848 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 331 (5) [M^+], 243 (20), 186 (5), 72 (100). HR-MS (ESI): *m*/*z* calcd for $C_{15}H_{16}F_3NO_4$+Na^+ 354.0929, found 354.0924.



3k

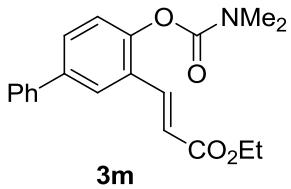
(*E*)-Ethyl 3-{3-chloro-2-[(*N*,*N*-dimethylcarbamoyl)oxy]phenyl}acrylate (3k): The general procedure A was followed using **1k** (100 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3k** (76 mg, 51%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 16.1 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.13 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.41 (d, *J* = 16.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.17 (s, 3H), 3.00 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.4 (C_q), 153.0 (C_q), 146.4 (C_q), 137.6 (CH), 131.3 (CH), 130.2 (C_q), 128.7 (C_q), 126.4 (CH), 125.6 (CH), 121.1 (CH), 60.5 (CH_2), 36.9 (CH_3), 36.5 (CH_3), 14.2 (CH_3). IR (ATR): 2938, 1709, 1637, 1567, 1438, 1148, 842 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 297 (5) [M^+], 209 (12), 152 (8), 89 (8), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{14}H_{16}ClNO_4$ 297.0768, found 297.0761. The analytical data are in accordance with those reported in the literature.[2]



3l

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-5-methylphenyl}acrylate (3l): The general procedure A was followed using **1l** (90 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc:

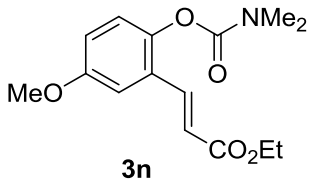
10/1→5/1) yielded **3l** (77 mg, 56%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, J = 16.1 Hz, 1H), 7.38 (d, J = 1.9 Hz, 1H), 7.15 (dd, J = 8.3, 1.9 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 6.39 (d, J = 16.1 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.13 (s, 3H), 2.99 (s, 3H), 2.30 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 154.4 (C_q), 147.9 (C_q), 138.4 (CH), 135.1 (C_q), 131.7 (CH), 127.5 (CH), 126.8 (C_q), 123.0 (CH), 119.4 (CH), 60.3 (CH_2), 36.7 (CH_3), 36.4 (CH_3), 20.8 (CH_3), 14.2 (CH_3). IR (ATR): 2984, 1707, 1607, 1497, 1158, 1035, 1035, 978, 855 cm^{-1}. MS (EI) m/z (relative intensity) 277 (3) [M^+], 189 (25), 132 (6), 72 (100). HR-MS (EI): m/z calcd for $C_{15}H_{19}NO_4$ 277.1314, found 277.1316.



3m

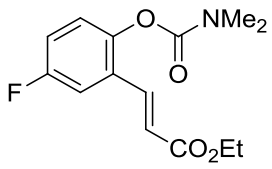
(*E*)-Ethyl 3-{4-[(*N*,*N*-dimethylcarbamoyl)oxy]-[1,1'-biphenyl]-3-yl}acrylate (3m): The general procedure A was followed using **1m** (121 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3m** (100 mg, 59%) as a white solid (M.p.: 112–114 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, J = 16.1 Hz, 1H), 7.79 (d, J = 2.2 Hz, 1H), 7.59–7.52 (m, 3H), 7.46–7.39 (m, 2H), 7.37–7.31 (m, 1H), 7.24 (d, J = 8.6 Hz, 1H), 6.51 (d, J = 16.1 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.17 (s, 3H), 3.03 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.7 (C_q), 154.2 (C_q), 149.4 (C_q), 139.8 (C_q), 138.8 (C_q), 138.2 (CH), 129.7 (CH), 128.7 (CH), 127.5 (CH), 127.4 (C_q), 127.0 (CH), 125.8 (CH), 123.6 (CH), 120.0 (CH), 60.4 (CH_2), 36.8 (CH_3),

36.4 (CH_3), 14.2 (CH_3). IR (ATR): 2927, 1720, 1700, 1477, 1386, 1154, 996, 756, 693 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 339 (8) [M^+], 251 (15), 194 (8), 165 (8), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{20}H_{21}NO_4$ 339.1471, found 339.1476.



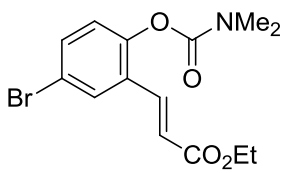
3n

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-5-methoxyphenyl}acrylate (3n): The general procedure A was followed using **1n** (98 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3n** (95 mg, 65%) as a white solid (M.p.: 52–54 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 16.1 Hz, 1H), 7.06 (d, *J* = 2.9 Hz, 1H), 7.05 (d, *J* = 8.9 Hz, 1H), 6.90 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.14 (s, 3H), 2.99 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.7 (C_q), 156.9 (C_q), 154.7 (C_q), 143.9 (C_q), 138.3 (CH), 127.9 (C_q), 124.3 (CH), 119.9 (CH), 117.1 (CH), 111.1 (CH), 60.5 (CH_2), 55.6 (CH_3), 36.8 (CH_3), 36.4 (CH_3), 14.3 (CH_3). IR (ATR): 2984, 1707, 1607, 1497, 1385, 1158, 1035, 855 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 293 (10) [M^+], 205 (20), 176 (8), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{15}H_{19}NO_5$ 293.1263, found 293.1254.



3o

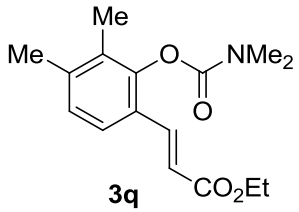
(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-5-fluorophenyl}acrylate (3o): The general procedure A was followed using **1o** (90 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3o** (84 mg, 60 %) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 16.1, 1.5 Hz, 1H), 7.25 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.12–6.99 (m, 2H), 6.37 (d, *J* = 16.1 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.13 (s, 3H), 2.99 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.4 (C_q), 159.7 (d, $^{1}J_{C\text{-}F}$ = 248 Hz, C_q), 154.1 (C_q), 145.9 (d, $^{4}J_{C\text{-}F}$ = 3 Hz, C_q), 137.1 (d, $^{4}J_{C\text{-}F}$ = 2 Hz, CH), 128.8 (d, $^{3}J_{C\text{-}F}$ = 9 Hz, C_q), 124.8 (d, $^{3}J_{C\text{-}F}$ = 9 Hz, CH), 120.9 (CH), 117.6 (d, $^{2}J_{C\text{-}F}$ = 25 Hz, CH), 113.0 (d, $^{2}J_{C\text{-}F}$ = 25 Hz, CH), 60.6 (CH_2), 36.8 (CH_3), 36.4 (CH_3), 14.2 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): -(116.6–116.7) (m). IR (ATR): 2938, 1709, 1637, 1483, 1385, 1145, 1033, 865, 751 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 281 (5) [M^+], 193 (8), 164 (5), 136 (5), 107 (5), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{14}H_{16}FNO_4$ 281.1063, found 281.1073.



3p

(*E*)-Ethyl 3-{5-bromo-2-[(*N*,*N*-dimethylcarbamoyl)oxy]phenyl}acrylate (3p): The general procedure A was followed using **1p** (122 mg, 0.50 mmol) and ethyl acrylate (**2a**)

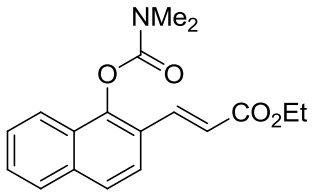
(100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3p** (103 mg, 61%) as a white solid (M.p.: 107–109 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 16.1 Hz, 1H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.42 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.11 (s, 3H), 2.97 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.3 (C_q), 153.7 (C_q), 148.9 (C_q), 136.7 (CH), 133.5 (CH), 129.8 (CH), 129.2 (C_q), 125.0 (CH), 120.9 (CH), 118.6 (C_q), 60.6 (CH_2), 36.8 (CH_3), 36.4 (CH_3), 14.2 (CH_3). IR (ATR): 2932, 1699, 1474, 1384, 1215, 1107, 973, 855 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 341 (5) [M^+], 253 (15), 196 (5), 89 (6), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{14}H_{16}BrNO_4$ 341.0263, found 341.0265.



3q

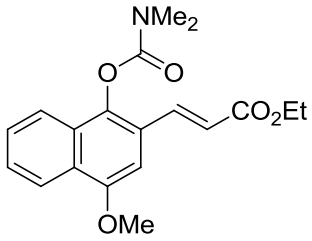
(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-3,4-dimethylphenyl}acrylate (3q): The general procedure A was followed using **1q** (97 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3q** (114 mg, 78%) as a white solid (M.p.: 63–65 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 16.1 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.18 (s, 3H), 3.00 (s, 3H), 2.26 (s, 3H), 2.06 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.9 (C_q), 154.0 (C_q), 148.5 (C_q), 140.7 (C_q), 138.9 (CH), 130.3 (C_q), 127.3 (CH),

125.4 (C_q), 123.9 (CH), 118.5 (CH), 60.2 (CH_2), 36.8 (CH_3), 36.4 (CH_3), 20.2 (CH_3), 14.2 (CH_3), 12.4 (CH_3). IR (ATR): 2926, 1704, 1631, 1453, 1313, 1156, 978, 862 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 291 (5) [M^+], 203 (15), 174 (5), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{16}H_{21}NO_4$ 291.1471, found 291.1472.



3r

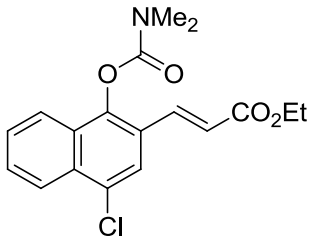
(*E*)-Ethyl 3-{1-[(*N*,*N*-dimethylcarbamoyl)oxy]naphthalen-2-yl}acrylate (3r): The general procedure A was followed using [$RuCl_2$(*p*-cymene)]$_2$ (15.3 mg, 5.0 mol %), $AgSbF_6$ (34.4 mg, 20 mol %), **1r** (108 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3r** (119 mg, 76%) as a white solid (M.p.: 86–88 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 16.1 Hz, 1H), 7.89–7.80 (m, 2H), 7.74–7.66 (m, 2H), 7.56–7.48 (m, 2H), 6.54 (d, *J* = 16.1 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 3.35 (s, 3H), 3.09 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.9 (C_q), 154.3 (C_q), 146.7 (C_q), 138.1 (CH), 135.3 (C_q), 128.0 (CH), 127.4 (CH), 127.1 (CH), 126.1 (CH), 124.0 (C_q), 124.0 (C_q), 122.8 (CH), 122.2 (CH), 119.9 (CH), 60.5 (CH_2), 37.0 (CH_3), 36.7 (CH_3), 14.3 (CH_3). IR (ATR): 2962, 1712, 1631, 1441, 1393, 1294, 1032, 872, 751 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 313 (5) [M^+], 225 (12), 196 (8), 168 (10), 139 (10), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{18}H_{19}NO_4$ 313.1314, found 313.1317. The analytical data are in accordance with those reported in the literature.[2]



3s

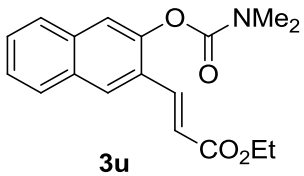
(*E*)-Ethyl 3-{1-[(*N*,*N*-dimethylcarbamoyl)oxy]-4-methoxynaphthalen-2-yl}

acrylate (3s): The general procedure A was followed using $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %), $AgSbF_6$ (34.4 mg, 20 mol %), **1s** (123 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3s** (116 mg, 68%) as a yellow solid (M.p.: 131–133 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.23–8.18 (m, 1H), 7.95 (d, J = 16.0 Hz, 1H), 7.80–7.75 (m, 1H), 7.55–7.45 (m, 2H), 6.89 (s, 1H), 6.49 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.98 (s, 3H), 3.31 (s, 3H), 3.06 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 154.6 (C_q), 153.2 (C_q), 140.7 (C_q), 138.4 (CH), 128.5 (C_q), 127.5 (CH), 127.5 (C_q), 126.8 (CH), 123.5 (C_q), 122.4 (CH), 122.0 (CH), 119.3 (CH), 99.5 (CH), 60.5 (CH_2), 55.5 (CH_3), 37.0 (CH_3), 36.7 (CH_3), 14.3 (CH_3). IR (ATR): 2937, 1717, 1702, 1633, 1511, 1446, 1288, 1088, 820 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 343 (10) [M^+], 255 (5), 226 (8), 198 (5), 183 (10), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{19}H_{21}NO_5$ 343.1420, found 343.1415.



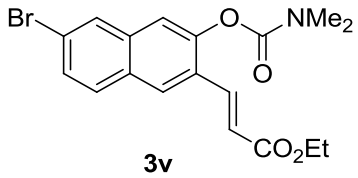
3t

(*E*)-Ethyl 3-{4-chloro-1-[(*N*,*N*-dimethylcarbamoyl)oxy]naphthalen-2-yl}acrylate (3t): The general procedure A was followed using $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %), $AgSbF_6$ (34.4 mg, 20 mol %), **1t** (123 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3t** (128 mg, 74%) as a yellow solid (M.p.: 127–129 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H), 7.88–7.84 (m, 1H), 7.77 (s, 1H), 7.65–7.54 (m, 2H), 6.50 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 3.33 (s, 3H), 3.06 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 166.6 (C_q), 154.1 (C_q), 145.6 (C_q), 136.9 (CH), 132.2 (C_q), 129.9 (C_q), 129.0 (C_q), 128.4 (CH), 127.8 (CH), 125.0 (CH), 124.4 (C_q), 122.9 (CH), 122.7 (CH), 120.7 (CH), 60.6 (CH_2), 37.0 (CH_3), 36.7 (CH_3), 14.3 (CH_3). IR (ATR): 2976, 1728, 1704, 1593, 1453, 1393, 1255, 1088, 754 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 347 (5) [M^+], 259 (5), 230 (5), 202 (8), 139 (10), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{18}H_{18}ClNO_4$ 347.0924, found 347.0920.



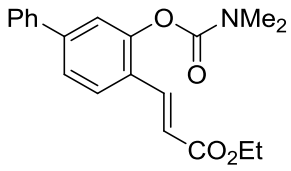
3u

(*E*)-Ethyl 3-{3-[(*N*,*N*-dimethylcarbamoyl)oxy]naphthalen-2-yl}acrylate (3u): The general procedure A was followed using $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %), $AgSbF_6$ (34.4 mg, 20 mol %), **1u** (108 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3u** (137 mg, 87%) as a white solid (M.p.: 82–84 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.92 (d, J = 16.1 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.60 (s, 1H), 7.49–7.38 (m, 2H), 6.57 (d, J = 16.1 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 3.19 (s, 3H), 3.03 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.7 (C_q), 154.4 (C_q), 147.2 (C_q), 138.9 (CH), 134.4 (C_q), 130.9 (C_q), 128.1 (CH), 128.0 (CH), 127.4 (CH), 127.3 (CH), 127.0 (C_q), 126.0 (CH), 120.2 (CH), 120.2 (CH), 60.4 (CH_2), 36.8 (CH_3), 36.5 (CH_3), 14.2 (CH_3). IR (ATR): 2987, 1711, 1638, 1440, 1270, 1157, 979, 860, 734 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 313 (10) [M^+], 225 (20), 196 (8), 168 (10), 139 (10), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{18}H_{19}NO_4$ 313.1314, found 313.1318. The analytical data are in accordance with those reported in the literature.[2]



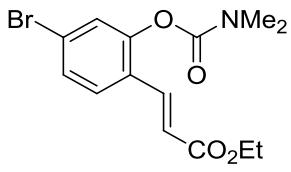
3v

(*E*)-Ethyl 3-{6-bromo-3-[(*N*,*N*-dimethylcarbamoyl)oxy]naphthalen-2-yl}acrylate (3v): The general procedure A was followed using $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 5.0 mol %), $AgSbF_6$ (34.4 mg, 20 mol %), **1v** (147 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3v** (143 mg, 73%) as a white solid (M.p.: 120–122 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.92 (s, 1H), 7.92 (s, 1H), 7.86 (d, J = 16.0 Hz, 1H), 7.59–7.53 (m, 2H), 7.49 (d, J = 8.7 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.18 (s, 3H), 3.03 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.5 (C_q), 154.1 (C_q), 147.5 (C_q), 138.3 (CH), 132.7 (C_q), 131.9 (C_q), 130.6 (CH), 130.0 (CH), 128.9 (CH), 128.0 (C_q), 126.8 (CH), 121.0 (CH), 120.2 (CH), 119.8 (C_q), 60.5 (CH_2), 36.9 (CH_3), 36.5 (CH_3), 14.2 (CH_3). IR (ATR): 2927, 1730, 1633, 1481, 1362, 1161, 1052, 884 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 391 (5) [M^+], 303 (10), 276 (5), 248 (8), 139 (13), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{18}H_{18}BrNO_4$ 391.0419, found 391.0411. The analytical data are in accordance with those reported in the literature.[2]



3w

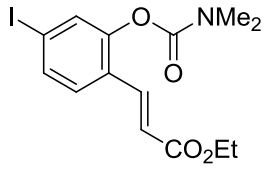
(*E*)-Ethyl 3-{3-[(*N*,*N*-dimethylcarbamoyl)oxy]-[1,1'-biphenyl]-4-yl}acrylate (3w): The general procedure A was followed using **1w** (121 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3w** (165 mg, 97%) as a white solid (M.p.: 110–112 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 16.0 Hz, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.60–7.56 (m, 2H), 7.47–7.37 (m, 4H), 7.36–7.30 (m, 1H), 6.46 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.18 (s, 3H), 3.03 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8 (C_q), 154.2 (C_q), 150.4 (C_q), 144.0 (C_q), 139.3 (C_q), 137.9 (CH), 128.8 (CH), 128.0 (CH), 127.6 (CH), 127.0 (CH), 126.0 (C_q), 124.3 (CH), 121.8 (CH), 119.4 (CH), 60.4 (CH_2), 36.8 (CH_3), 36.5 (CH_3), 14.2 (CH_3). IR (ATR): 2982, 1631, 1610, 1483, 1383, 1157, 893, 762 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 339 (5) [M^+], 251 (20), 194 (8), 165 (10),72 (100). HR-MS (EI): *m*/*z* calcd for $C_{20}H_{21}NO_4$ 339.1471, found 339.1470.



3x

(*E*)-Ethyl 3-{4-bromo-2-[(*N*,*N*-dimethylcarbamoyl)oxy]phenyl}acrylate (3x): The general procedure A was followed using **1x** (122 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc:

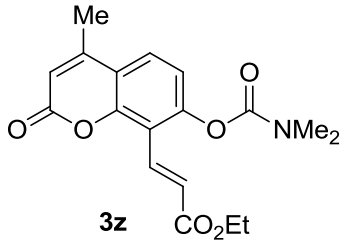
10/1→5/1) yielded **3x** (101 mg, 60%) as a white solid (M.p.: 68–70 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, J = 16.1 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.35–7.28 (m, 2H), 6.38 (d, J = 16.1 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.11 (s, 3H), 2.98 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.5 (C_q), 153.6 (C_q), 150.2 (C_q), 137.1 (CH), 128.9 (CH), 128.1 (CH), 126.7 (CH), 126.3 (C_q), 123.9 (C_q), 120.1 (CH), 60.5 (CH_2), 36.8 (CH_3), 36.4 (CH_3), 14.2 (CH_3). IR (ATR): 2939, 1713, 1636, 1590, 1370, 1146, 1032, 889, 815 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 341 (5) [M^+], 253 (15), 196 (5), 89 (8), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{14}H_{16}BrNO_4$ 341.0263, found 341.0278.



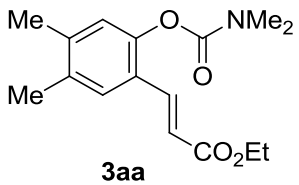
3y

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-4-iodophenyl}acrylate (3y): The general procedure A was followed using **1y** (146 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3y** (104 mg, 51%) as a yellow solid (M.p.: 84–86 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 16.1 Hz, 1H), 7.53–7.49 (m, 2H), 7.28 (d, J = 8.9 Hz, 1H), 6.40 (d, J = 16.1 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.11 (s, 3H), 2.99 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.5 (C_q), 153.7 (C_q), 149.9 (C_q), 137.3 (CH), 134.8 (CH), 132.5 (CH), 128.2 (CH), 127.0 (C_q), 120.2 (CH), 95.5 (C_q), 60.5 (CH_2), 36.8 (CH_3), 36.5 (CH_3), 14.2 (CH_3). IR (ATR): 2938, 1707,

1636, 1477, 1370, 1147, 1032, 868 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 389 (5) [M^+], 301 (20), 243 (5), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{14}H_{16}INO_4$ 389.0124, found 389.0117.

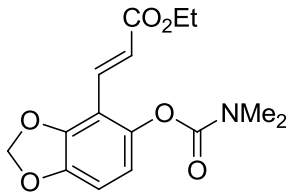


(*E*)-Ethyl 3-{7-[(*N*,*N*-dimethylcarbamoyl)oxy]-4-methyl-2-oxo-2*H*-chromen-8-yl} acrylate (3z): The general procedure A was followed using [$RuCl_2$(*p*-cymene)]$_2$ (15.3 mg, 5.0 mol %), $AgSbF_6$ (34.4 mg, 20 mol %), **1z** (117 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3z** (96 mg, 56%) as a yellow solid (M.p.: 201–203 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 16.5 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.16 (d, *J* = 8.9 Hz, 1H), 6.95 (d, *J* = 16.5 Hz, 1H), 6.27 (d, *J* = 1.2 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.17 (s, 3H), 3.02 (s, 3H), 2.42 (d, *J* = 1.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.3 (C_q), 159.7 (C_q), 153.4 (C_q), 152.7 (C_q), 152.6 (C_q), 152.2 (C_q), 132.2 (CH), 125.5 (CH), 125.5 (CH), 119.3 (CH), 117.6 (C_q), 116.6 (C_q), 114.3 (CH), 60.7 (CH_2), 37.0 (CH_3), 36.6 (CH_3), 19.0 (CH_3), 14.3 (CH_3). IR (ATR): 2980, 1726, 1703, 1629, 1382, 1296, 1152, 1032, 869 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 345 (5) [M^+], 257 (10), 228 (5), 172 (5), 72 (100), 43 (7). HR-MS (EI): *m*/*z* calcd for $C_{18}H_{19}NO_6$ 345.1212, found 345.1208.



3aa

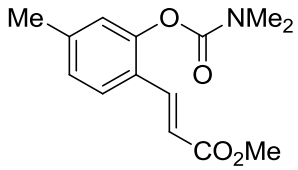
(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-4,5-dimethylphenyl}acrylate (3aa): The general procedure A was followed using **1aa** (97 mg, 0.50 mmol) and ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3aa** (126 mg, 87%) as a white solid (M.p.: 86–88 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, J = 16.1 Hz, 1H), 7.35 (s, 1H), 6.91 (s, 1H), 6.36 (d, J = 16.1 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.14 (s, 3H), 3.00 (s, 3H), 2.23 (s, 3H), 2.22 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.1 (C_q), 154.6 (C_q), 148.1 (C_q), 140.5 (C_q), 138.4 (CH), 134.1 (C_q), 128.0 (CH), 124.4 (C_q), 124.2 (CH), 118.4 (CH), 60.3 (CH_2), 36.8 (CH_3), 36.5 (CH_3), 19.9 (CH_3), 19.2 (CH_3), 14.3 (CH_3). IR (ATR): 2937, 1702, 1630, 1498, 1452, 1154, 1029, 991, 875 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 291 (5) [M^+], 203 (30), 174 (5), 146 (6), 72 (100). HR-MS (EI): *m*/*z* calcd for $C_{16}H_{21}NO_4$ 291.1471, found 291.1482. The analytical data are in accordance with those reported in the literature.[2]



3ab

(*E*)-Ethyl 3-{5-[(*N*,*N*-dimethylcarbamoyl)oxy]benzo[d][1,3]dioxol-4-yl}acrylate (3ab): The general procedure A was followed using **1ab** (105 mg, 0.50 mmol) and

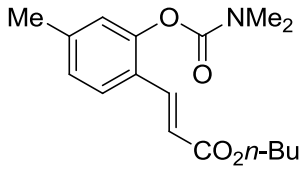
ethyl acrylate (**2a**) (100 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1→5/1) yielded **3ab** (100 mg, 66%) as a white solid (M.p.: 115–117 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 16.1 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 16.1 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 6.05 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.13 (s, 3H), 2.98 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.3 (C_q), 154.7 (C_q), 147.0 (C_q), 145.2 (C_q), 144.2 (C_q), 133.4 (CH), 122.7 (CH), 115.3 (CH), 112.3 (C_q), 108.9 (CH), 102.2 (CH_2), 60.4 (CH_2), 36.9 (CH_3), 36.5 (CH_3), 14.3 (CH_3). IR (ATR): 2909, 1714, 1633, 1457, 1304, 1201, 1162, 977, 862 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 307 (5) [M^+], 219 (5), 190 (8), 72 (100), 43 (7). HR-MS (EI): *m*/*z* calcd for $C_{15}H_{17}NO_6$ 307.1056, found 307.1059.



3ac

(*E*)-Methyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-4-methylphenyl}acrylate (3ac): The general procedure A was followed using **1a** (90 mg, 0.50 mmol) and methyl acrylate (**2b**) (86 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 4/1) yielded **3ac** (114 mg, 87%) as a white solid (M.p.: 77–80 °C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 16.1 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.97 (d, *J* = 1.6 Hz, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 3.77 (s, 3H), 3.15 (s, 3H), 3.01 (s, 3H), 2.34 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.4 (C_q), 154.3 (C_q), 150.0 (C_q), 141.9 (C_q), 138.6 (CH), 127.1 (CH), 126.6 (CH), 124.3

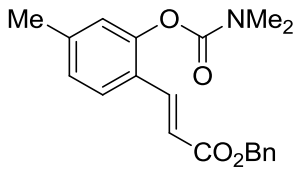
(C_q), 123.8 (CH), 118.1 (CH), 51.5 (CH_3), 36.7 (CH_3), 36.4 (CH_3), 21.3 (CH_3). IR (ATR): 2949, 1737, 1715, 1631, 1383, 1321, 1276, 1161, 985, 807, 746 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 263 (5) [M^+], 175 (58), 160 (5), 132 (13), 72 (100). HR-MS (ESI): *m*/*z* calcd for $C_{14}H_{17}NO_4+H^+$ 264.1230, found 264.1230.



3ad

(*E*)-*n*-Butyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-4-methylphenyl}acrylate (3ad): The general procedure A was followed using **1a** (90 mg, 0.50 mmol) and *n*-butyl acrylate (**2c**) (128 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 4/1) yielded **3ad** (148 mg, 97%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 16.1 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.37 (d, *J* = 16.1 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.14 (s, 3H), 3.00 (s, 3H), 2.33 (s, 3H), 1.74–1.58 (m, 2H), 1.50–1.30 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.1 (C_q), 154.4 (C_q), 150.0 (C_q), 141.9 (C_q), 138.2 (CH), 127.0 (CH), 126.7 (CH), 124.5 (C_q), 123.9 (CH), 118.6 (CH), 64.3 (CH_2), 36.8 (CH_3), 36.5 (CH_3), 30.7 (CH_2), 21.4 (CH_3), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2958, 1709, 1633, 1381, 1269, 1244, 1150, 813, 732 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 305 (4) [M^+], 217 (58), 161 (32), 132 (21), 103 (8), 72 (100), 56 (8), 41 (18). HR-MS (ESI): *m*/*z* calcd for $C_{17}H_{23}NO_4+H^+$ 306.1700,

found 306.1702. The analytical data are in accordance with those reported in the literature.[3]

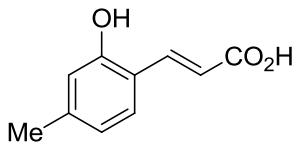


3ae

(*E*)-Benzyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-4-methylphenyl}acrylate (3ae): The general procedure A was followed using **1a** (90 mg, 0.50 mmol) and benzyl acrylate (**2d**) (162 mg, 1.00 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 4/1) yielded **3ae** (161 mg, 95%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, J = 16.1 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.43–7.27 (m, 5H), 7.01 (d, J = 8.0 Hz, 1H), 6.98 (s, 1H), 6.43 (d, J = 16.1 Hz, 1H), 5.22 (s, 2H), 3.11 (s, 3H), 2.99 (s, 3H), 2.34 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.7 (C_q), 154.3 (C_q), 150.0 (C_q), 142.0 (C_q), 138.8 (CH), 136.0 (C_q), 128.5 (CH), 128.1 (CH), 128.1 (CH), 127.0 (CH), 126.7 (CH), 124.3 (C_q), 123.8 (CH), 118.1 (CH), 66.2 (CH_2), 36.7 (CH_3), 36.4 (CH_3), 21.3 (CH_3). IR (ATR): 2937, 1710, 1631, 1380, 1245, 1147, 982, 813, 734, 696 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 339 (1) [M^+], 248 (5), 160 (36), 132 (23), 91 (38), 72 (100). HR-MS (ESI): *m*/*z* calcd for $C_{20}H_{21}NO_4$+H^+ 340.1543, found 340.1547.

Deprotection of Carbamate 3a [4]

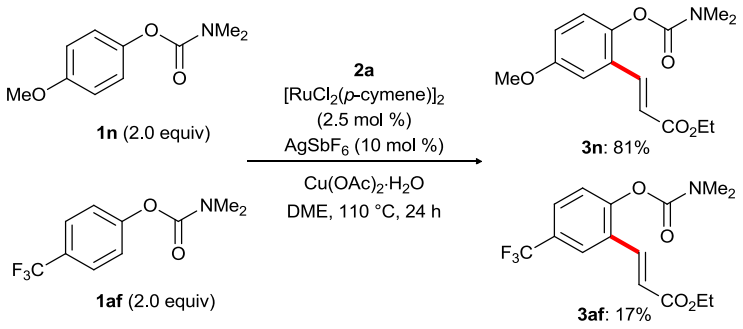
To a solution of the carbamate **3a** (170 mg, 0.61 mmol) in EtOH (5 mL) was added NaOH (245 mg, 6.10 mmol). The reaction mixture was stirred at 80 °C for 15 h. At ambient temperature, EtOH was evaporated under reduced pressure, the residue was diluted with Et_2O (20 mL), and the excess of NaOH was neutralized at 0 °C using a solution of 2 M HCl (5 mL). The aqueous solution was extracted with Et_2O (3×20 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was washed with CH_2Cl_2 to afford **4a** (80 mg, 73%) as a yellow solid (M.p.: 191–193 °C).



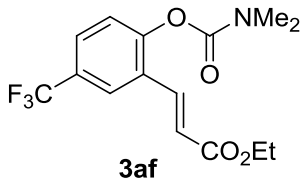
4a

(*E*)-3-(2-Hydroxy-4-methylphenyl)acrylic acid (4a): ^{1}H-NMR (300 MHz, d^6-DMSO): δ = 12.04 (s_{br}, 1H), 10.00 (s, 1H), 7.78 (d, J = 16.1 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 6.71 (s, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.43 (d, J = 16.1 Hz, 1H), 2.23 (s, 3H). ^{13}C-NMR (75 MHz, DMSO): δ = 168.0 (C_q), 156.4 (C_q), 141.4 (C_q), 139.5 (CH), 128.5 (CH), 120.3 (CH), 118.2 (C_q), 117.0 (CH), 116.4 (CH), 21.0 (CH_3). IR (ATR): 2925, 1660, 1601, 1421, 1298, 1259, 1205, 986, 854 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 178 (35) [M^+], 160 (47), 132 (100), 104 (32), 77 (30), 43 (18). HR-MS (EI): *m*/*z* calcd for $C_{10}H_{10}O_3$ 178.0630, found 178.0634.

Intermolecular Competition Experiment with Carbamates 1n and 1af (Scheme 6)



A suspension of **1n** (195 mg, 1.00 mmol), **1af** (233mg, 1.00 mmol), ethyl acrylate (**2a**) (50 mg, 0.50 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.00 mmol) in DME (3.0 mL) was stirred at 110 °C for 24 h under an atmosphere of N_2. At ambient temperature, EtOAc (15 mL) was added and the mixture was filtered through silica. The solvents were removed *in vacuo*. Purification of the remaining residue by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **3n** (119 mg, 81%) as a white solid and **3af** (28 mg, 17%) as a white solid (M.p.: 107–109 °C).



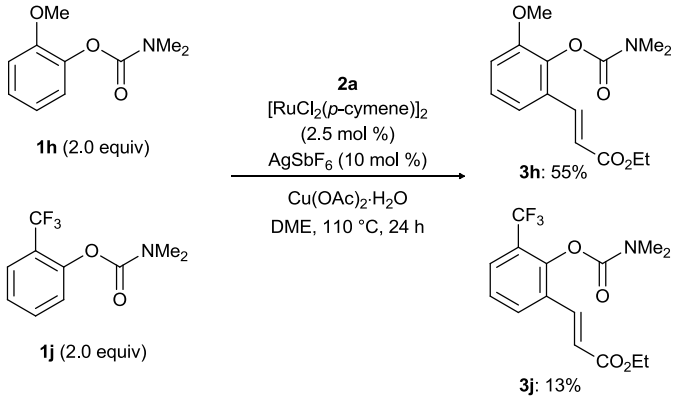
3af

(*E*)-Ethyl 3-{2-[(*N*,*N*-dimethylcarbamoyl)oxy]-5-(trifluoromethyl)phenyl}

acrylate (3af): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, J = 1.9 Hz, 1H), 7.80 (d, J = 16.3 Hz, 1H), 7.59 (dd, J = 8.6 Hz, 1.9 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 6.48 (d, J = 16.3 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.15 (s, 3H), 3.01 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.3 (C_q), 153.5 (C_q), 152.3 (C_q), 136.8 (CH),

127.9 (q, $^{2}J_{C\text{-}F}$ = 33 Hz, C_q), 127.9 (C_q), 127.5 (q, $^{3}J_{C\text{-}F}$ = 4 Hz, CH), 124.5 (q, $^{3}J_{C\text{-}F}$ = 4 Hz, CH), 124.0 (CH), 123.6 (q, $^{1}J_{C\text{-}F}$ = 272 Hz, C_q), 121.6 (CH), 60.8 (CH_2), 36.9 (CH_3), 36.5 (CH_3), 14.2 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): -62.5 (s). IR (ATR): 2943, 1702, 1486, 1334, 1110, 1008, 858, 858 cm^{-1}. MS (EI) *m*/*z* (relative intensity) 331 (5) [M^+], 243 (18), 186 (8), 72 (100). HR-MS (ESI): *m*/*z* calcd for $C_{15}H_{16}F_3NO_4$+Na^+ 354.0929, found 354.0924.

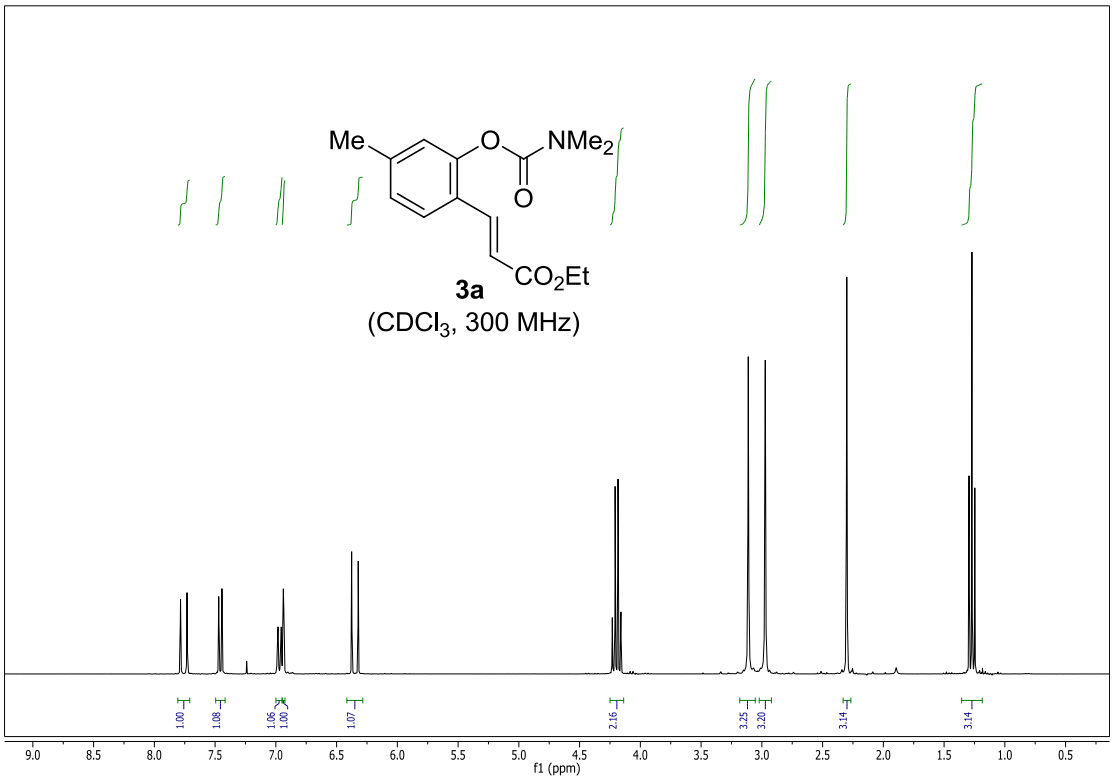
Scheme S-1 Competition Experiment with Carbamates 1h and 1j

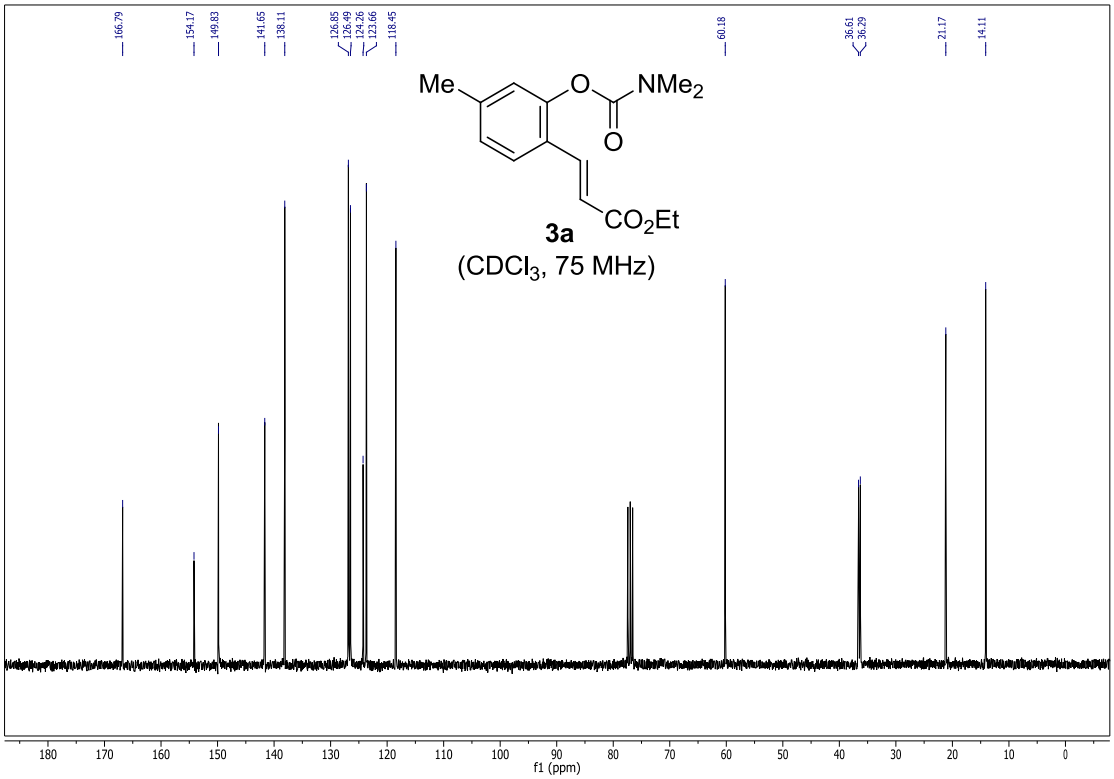


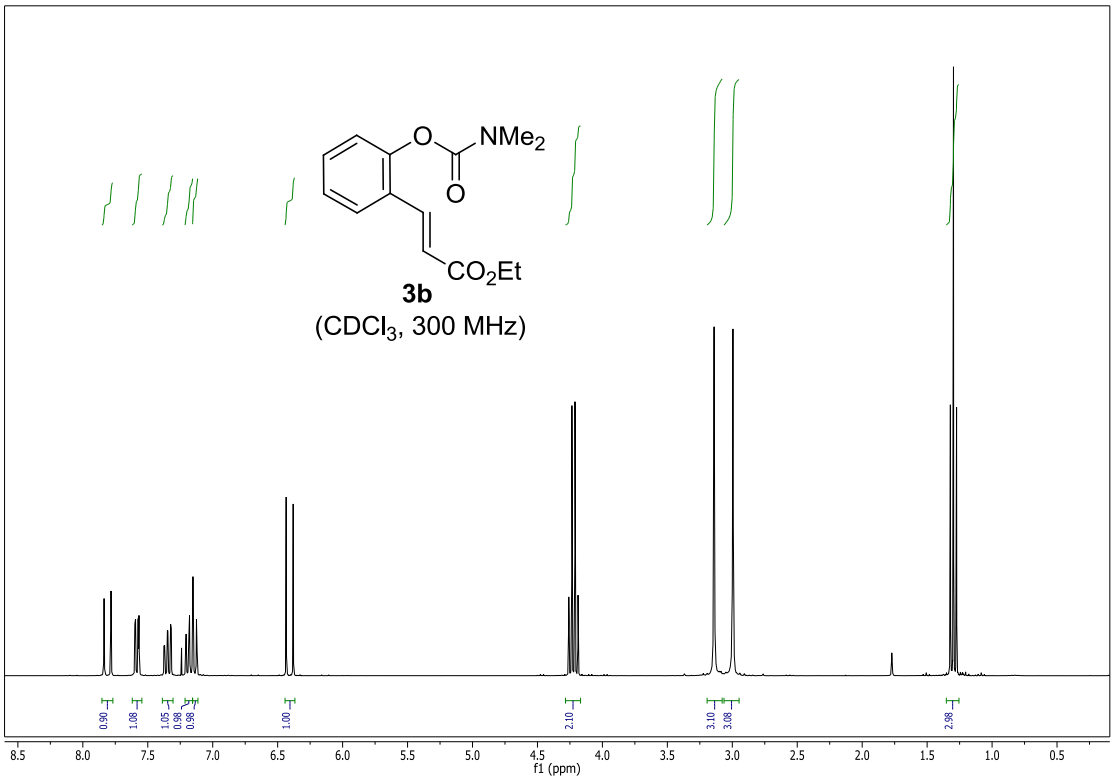
A suspension of **1h** (195 mg, 1.00 mmol), **1j** (233mg, 1.00 mmol), ethyl acrylate (**2a**) (50 mg, 0.50 mmol), $[RuCl_2(p\text{-cymene})]_2$ (7.7 mg, 2.5 mol %), $AgSbF_6$ (17.2 mg, 10 mol %) and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.00 mmol) in DME (3.0 mL) was stirred at 110 °C for 24 h under an atmosphere of N_2. At ambient temperature, EtOAc (15 mL) was added and the mixture was filtered through silica. The solvents were removed *in vacuo*. Purification of the remaining residue by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **3h** (81 mg, 55%) as a white solid and **3j** (21 mg, 13%) as a colorless oil.

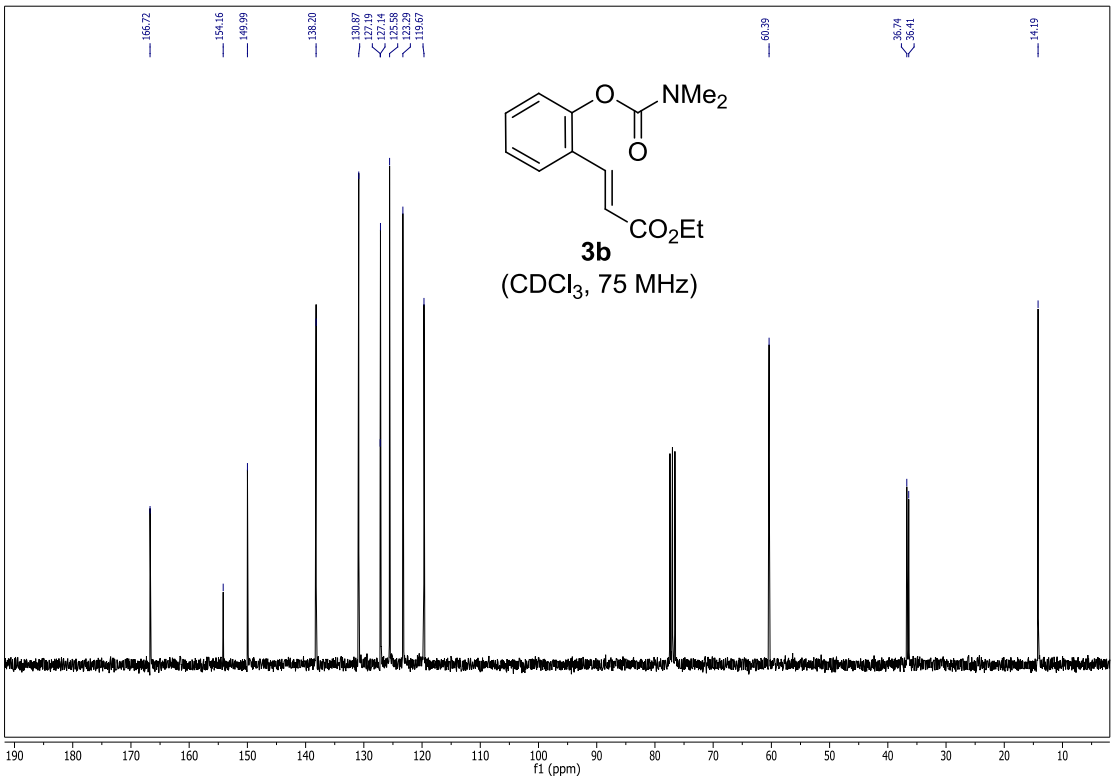
Reference

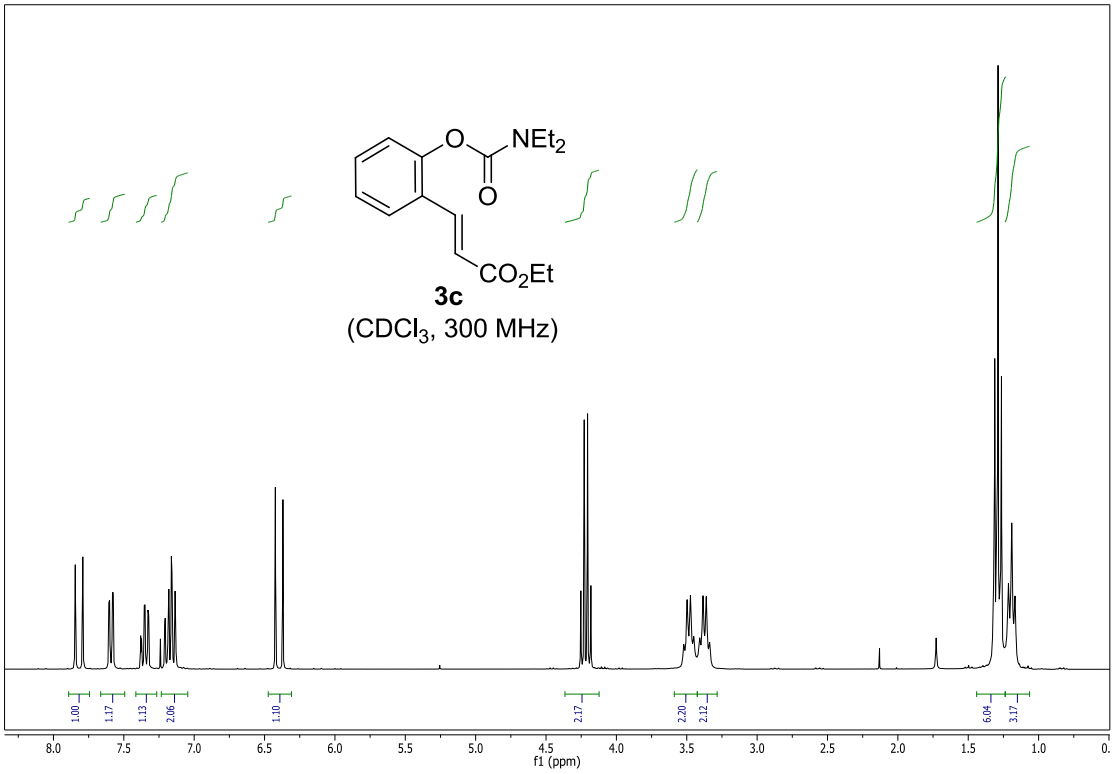
1. F. Garcia, M. MacPartlin, J. V. Morey, D. Nobuto, Y. Kondo, H. Naka, M. Uchiyama and A. E. H. Wheatley, *Eur. J. Org. Chem.*, 2008, 644.
2. C. Feng and T.-P. Loh, *Chem. Comm.*, 2011, **47**, 10458.
3. T.-J. Gong, B. Xiao, Z.-J. Liu, J. Wan, J. Xu, D.-F. Luo, Y. Fu and L. Liu, *Org. Lett.*, 2011, **13**, 3235.
4. R. Sanz, M. P. Castroviejo, Y. Fernandez and F. J. Fananas, *J. Org. Chem.*, 2005, **70**, 6548.

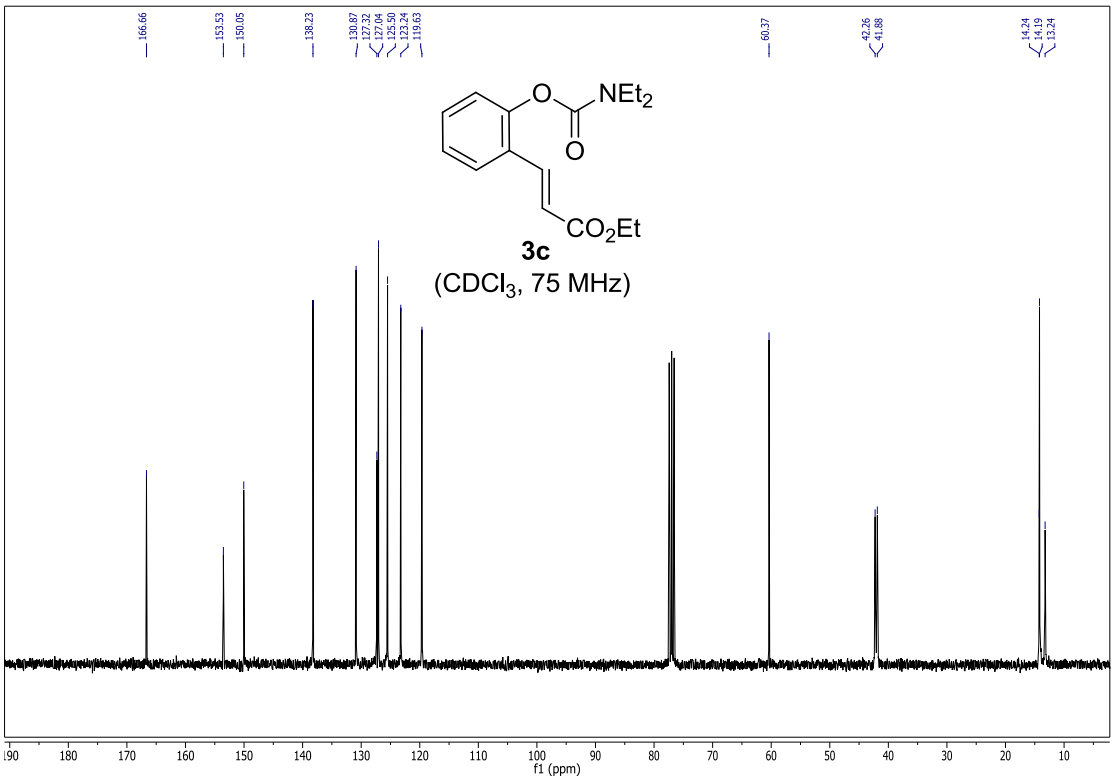

Me
O
NMe2
O
CO2Et
3a
(CDCl3, 300 MHz)
f1 (ppm)

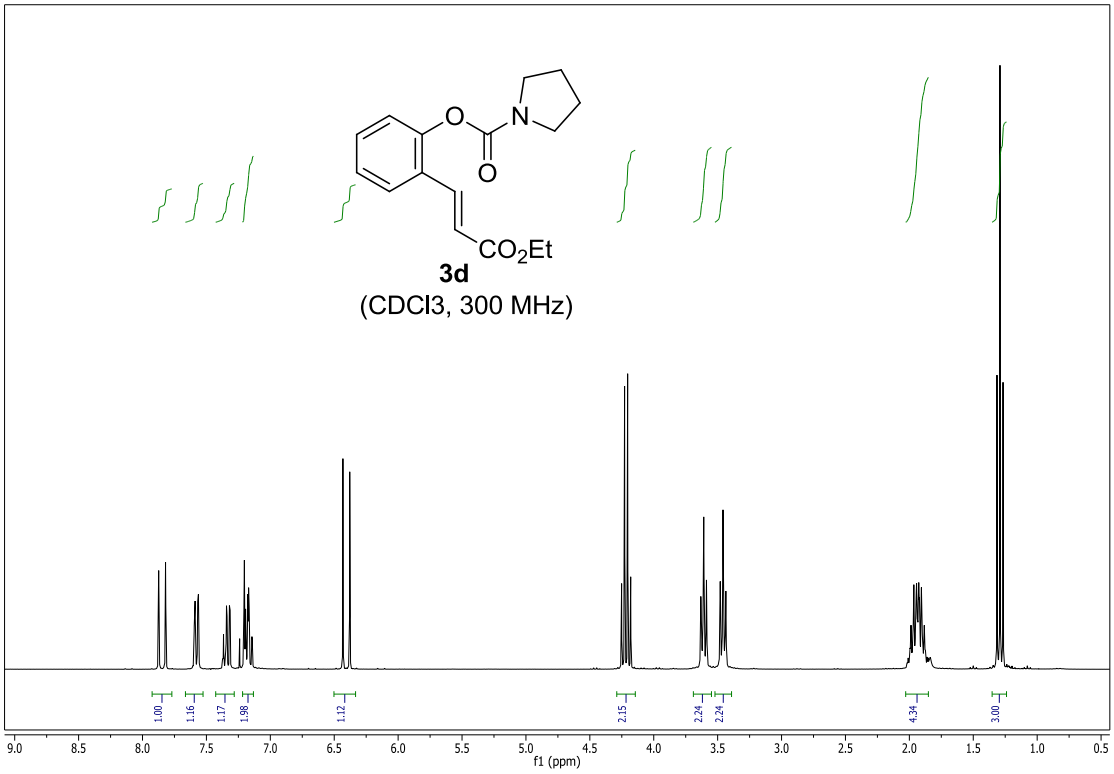

166.79
154.17
149.83
141.65
138.11
126.85
126.49
124.26
123.66
118.45
60.18
36.61
36.29
21.17
14.11
Me
O
NMe2
O
CO2Et
3a
(CDCl3, 75 MHz)
f1 (ppm)

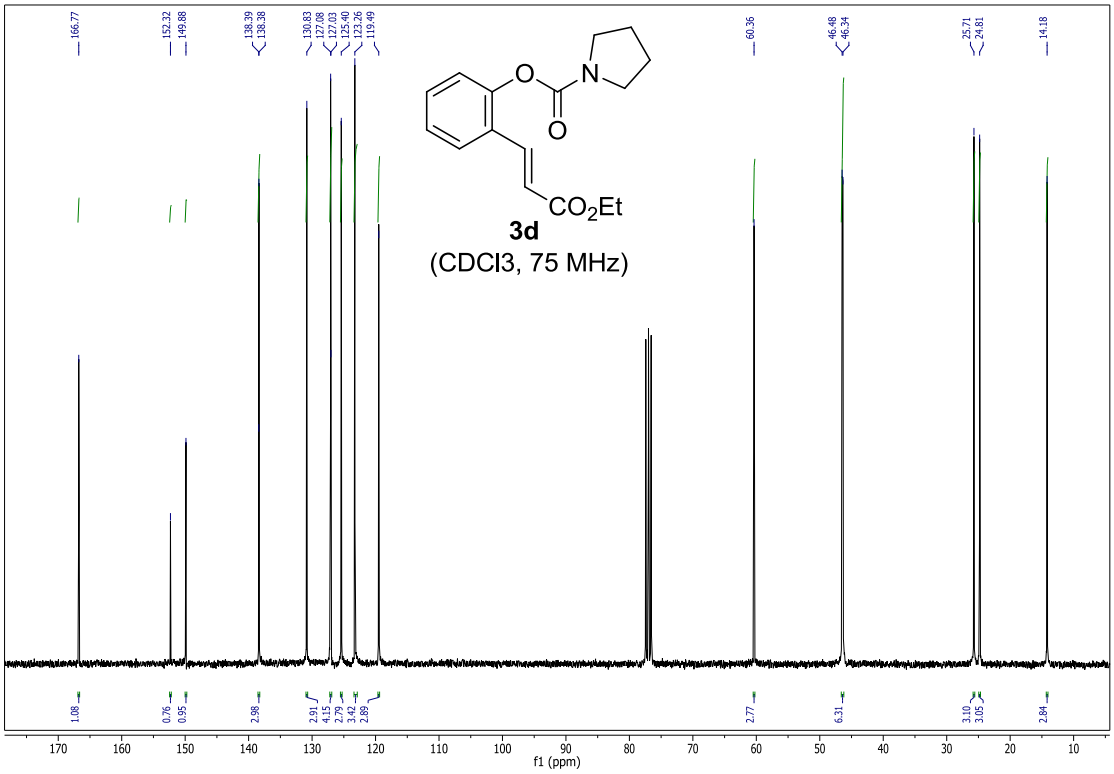

O
NMe2
O
CO2Et
3b
(CDCl3, 300 MHz)
f1 (ppm)

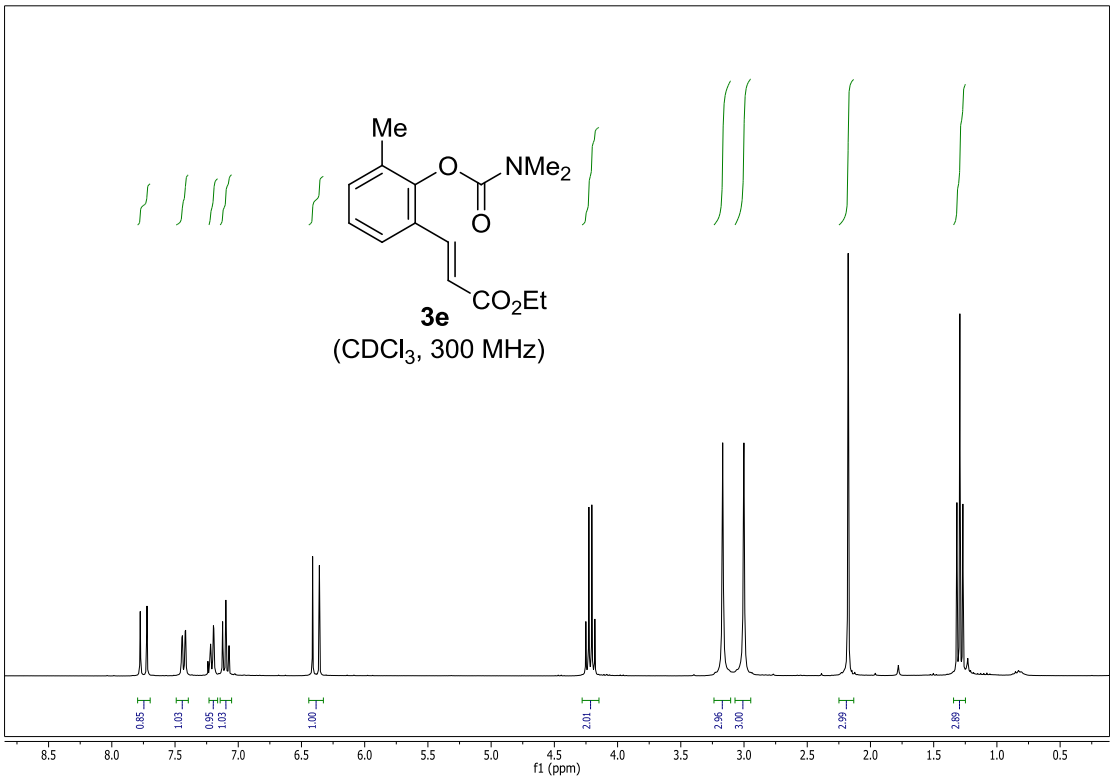

166.72
154.16
149.99
138.20
130.87
127.19
127.14
125.58
123.29
119.67
60.39
36.74
36.41
14.19
O
NMe2
O
CO2Et
3b
(CDCl3, 75 MHz)
f1 (ppm)

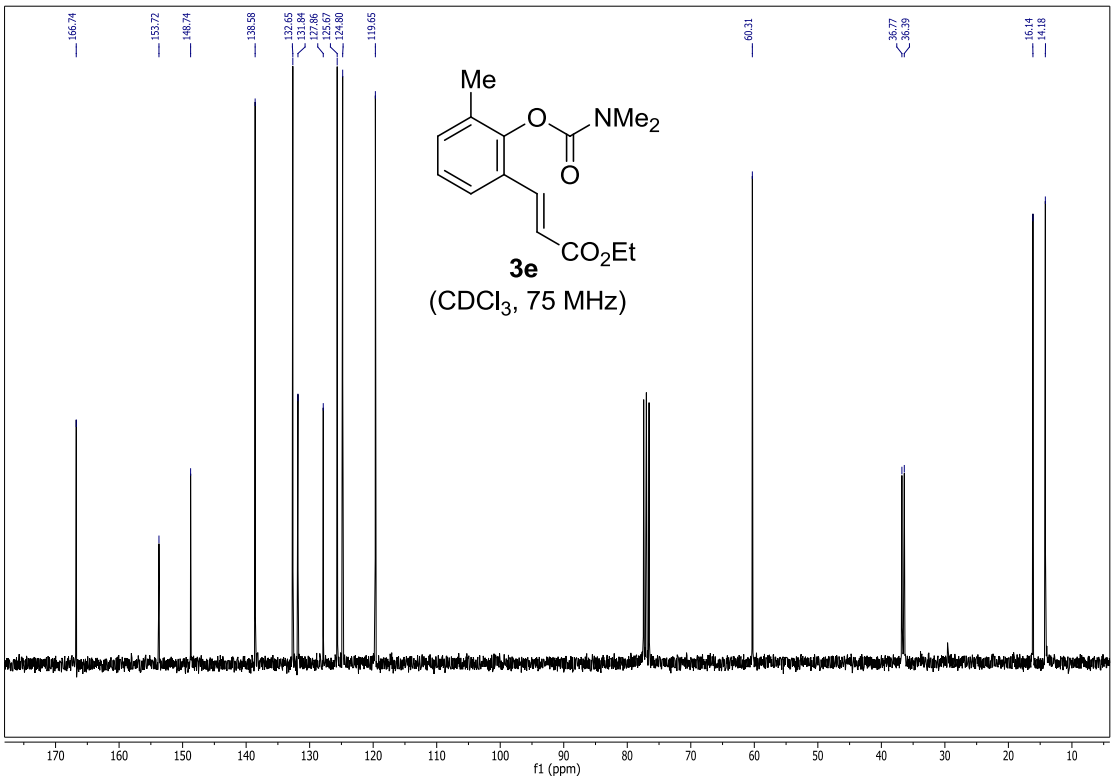

O
NEt2
O
CO2Et
3c
(CDCl3, 300 MHz)
1.00
1.17
1.13
2.06
1.10
2.17
2.20
2.12
6.04
3.17
f1 (ppm)

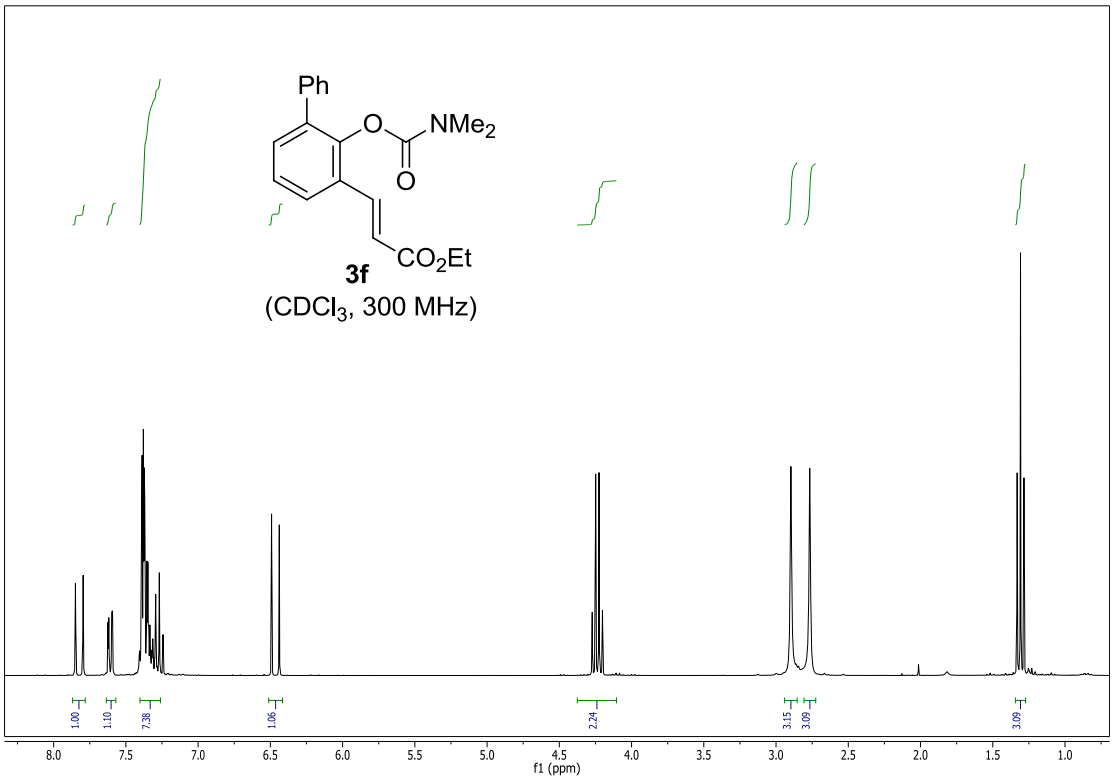

166.66
153.53
150.05
138.23
130.87
127.23
127.04
125.50
123.24
119.63
60.37
42.26
41.88
14.24
14.19
13.24
O
NEt2
O
CO2Et
3c
(CDCl3, 75 MHz)
f1 (ppm)

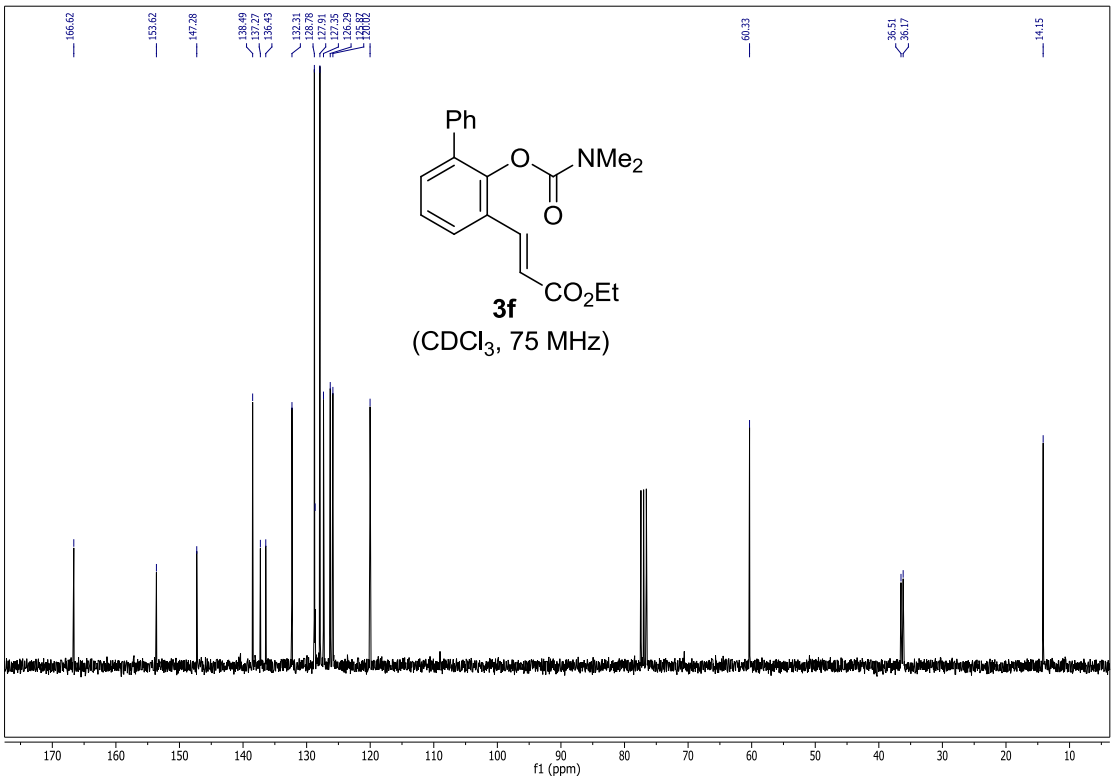

O
N
O
CO2Et
3d
(CDCl3, 300 MHz)
f1 (ppm)

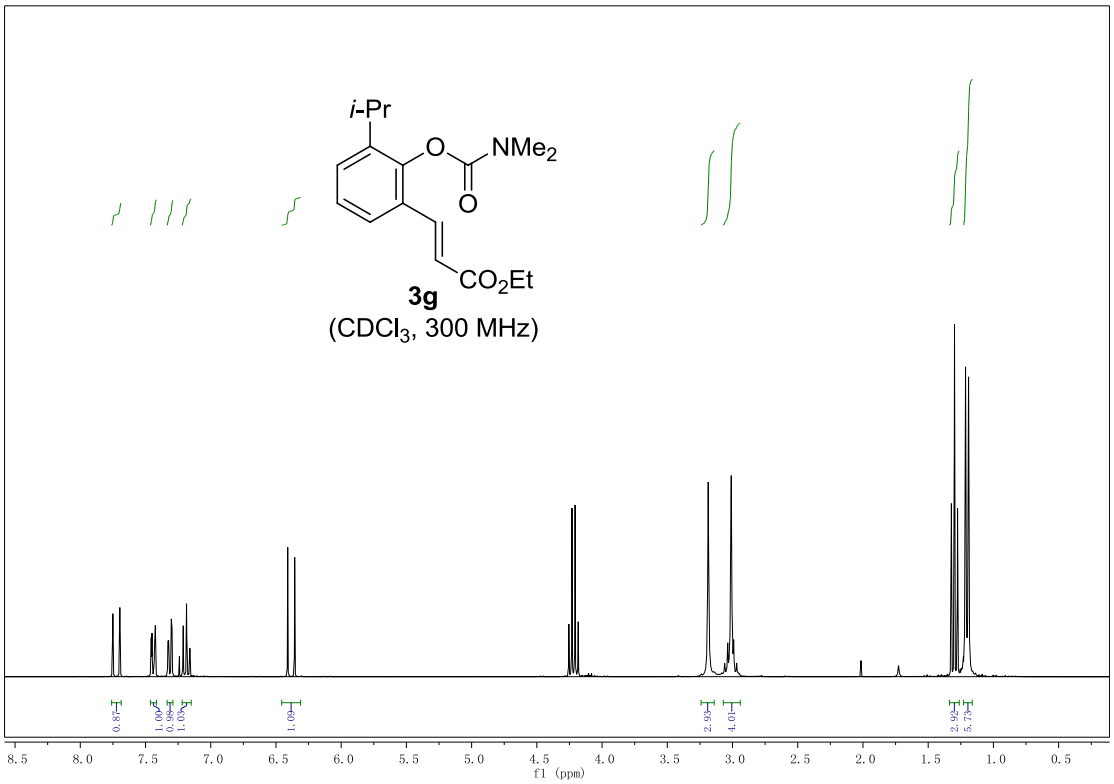

O
N
O
CO2Et
3d
(CDCl3, 75 MHz)
f1 (ppm)

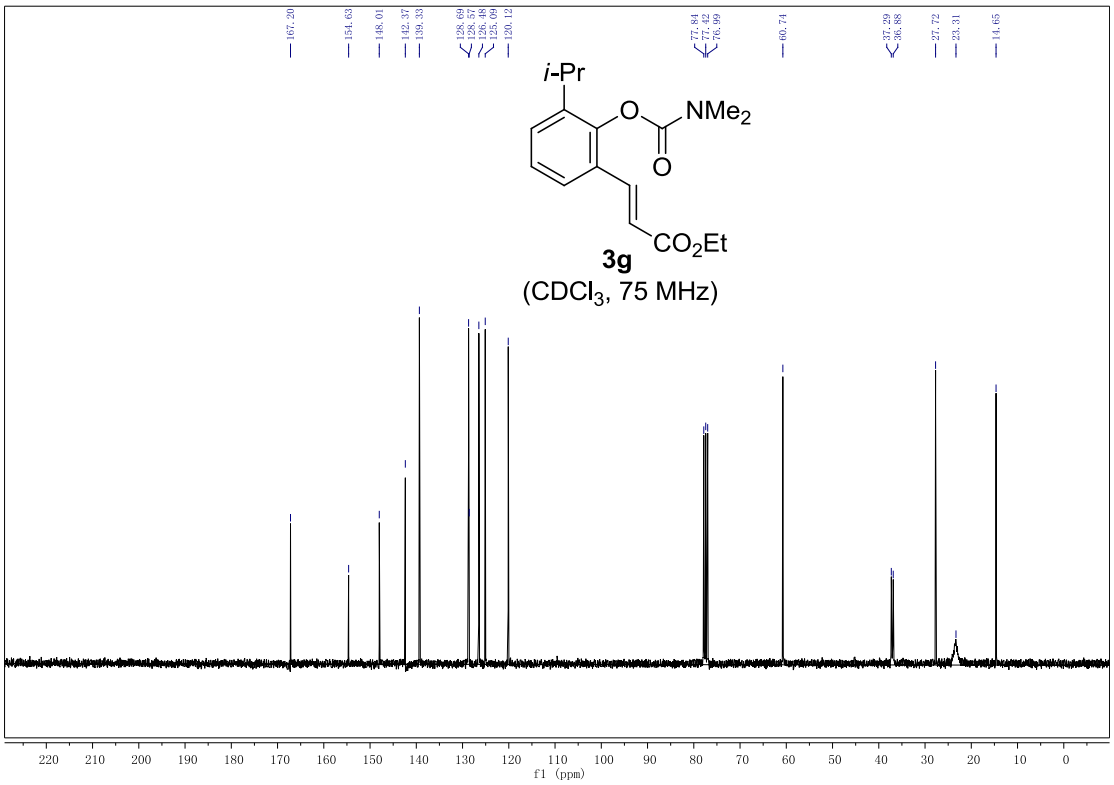


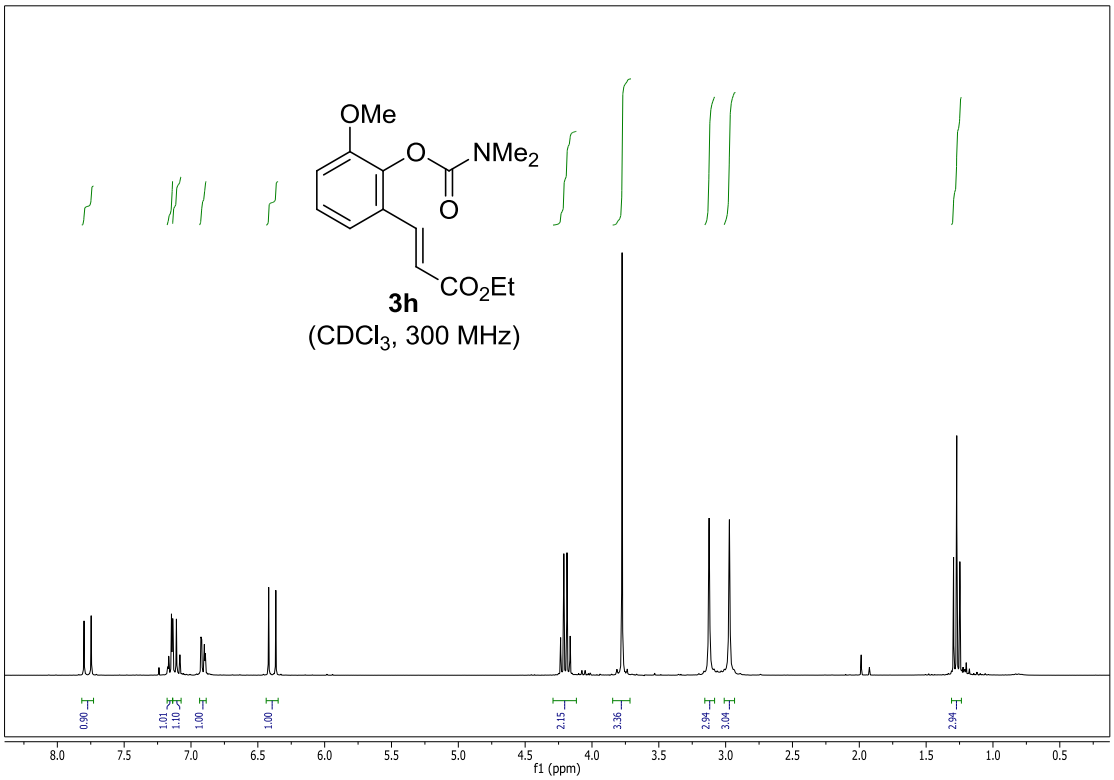


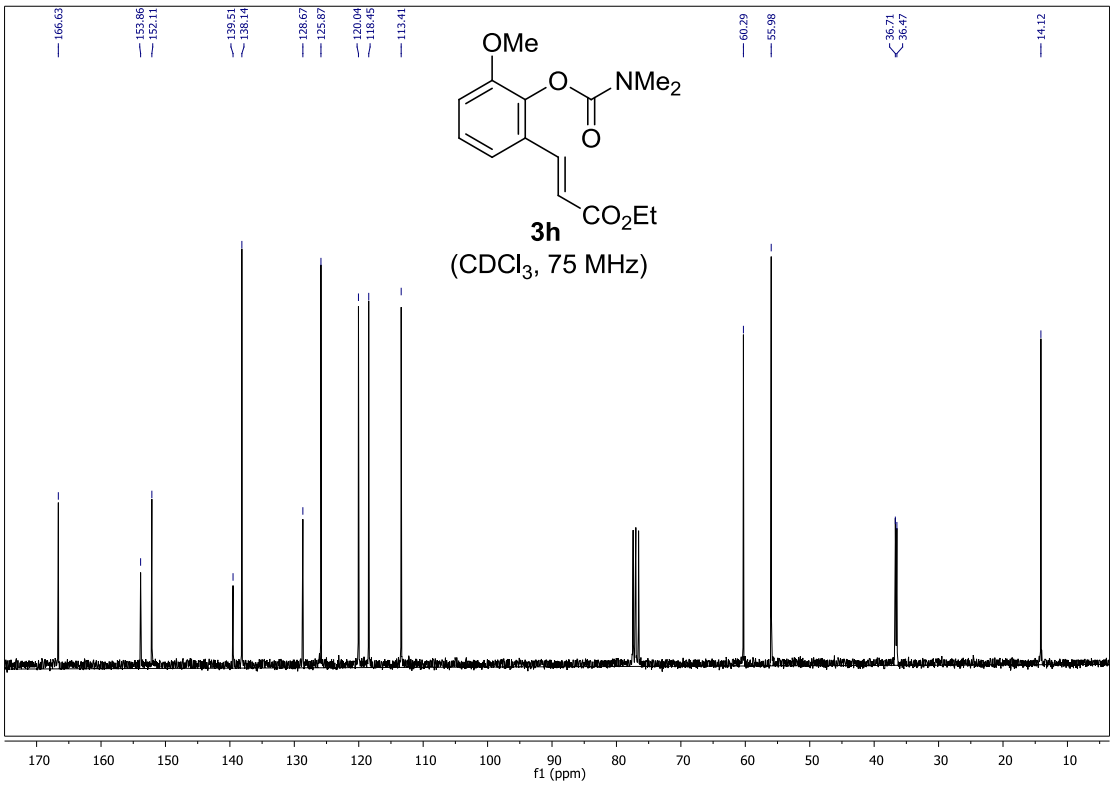


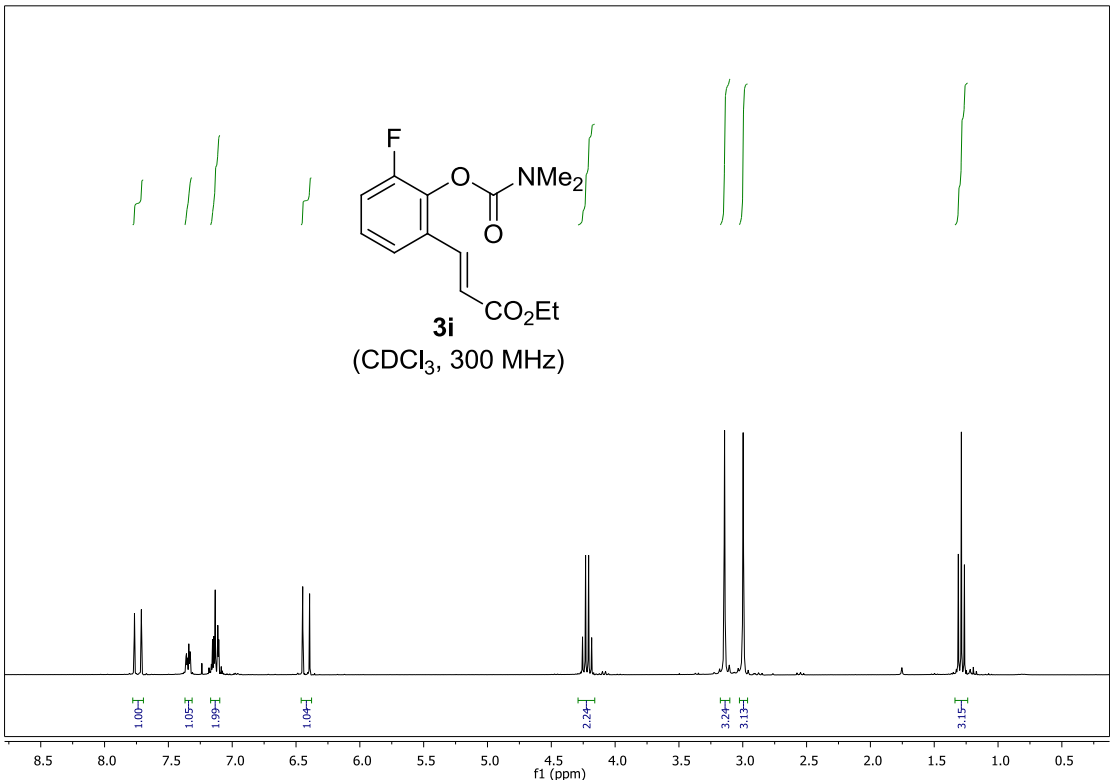


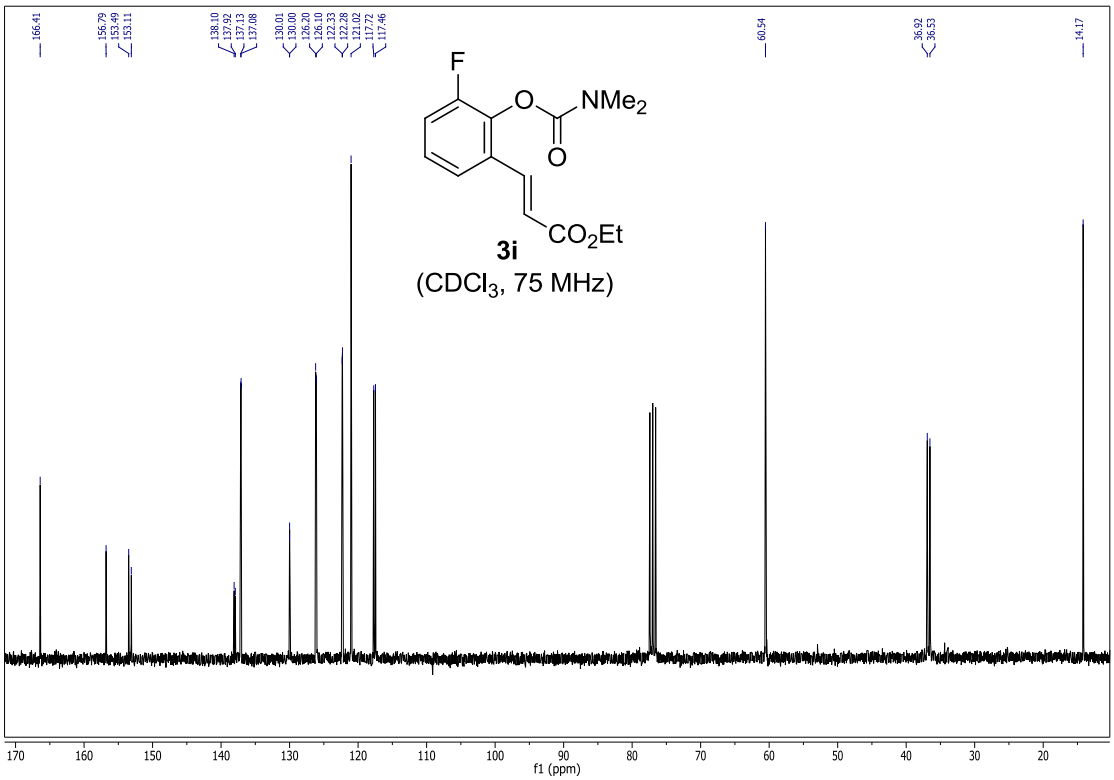

i-Pr
O
NMe2
O
CO2Et
3g
(CDCl3, 300 MHz)
f1 (ppm)

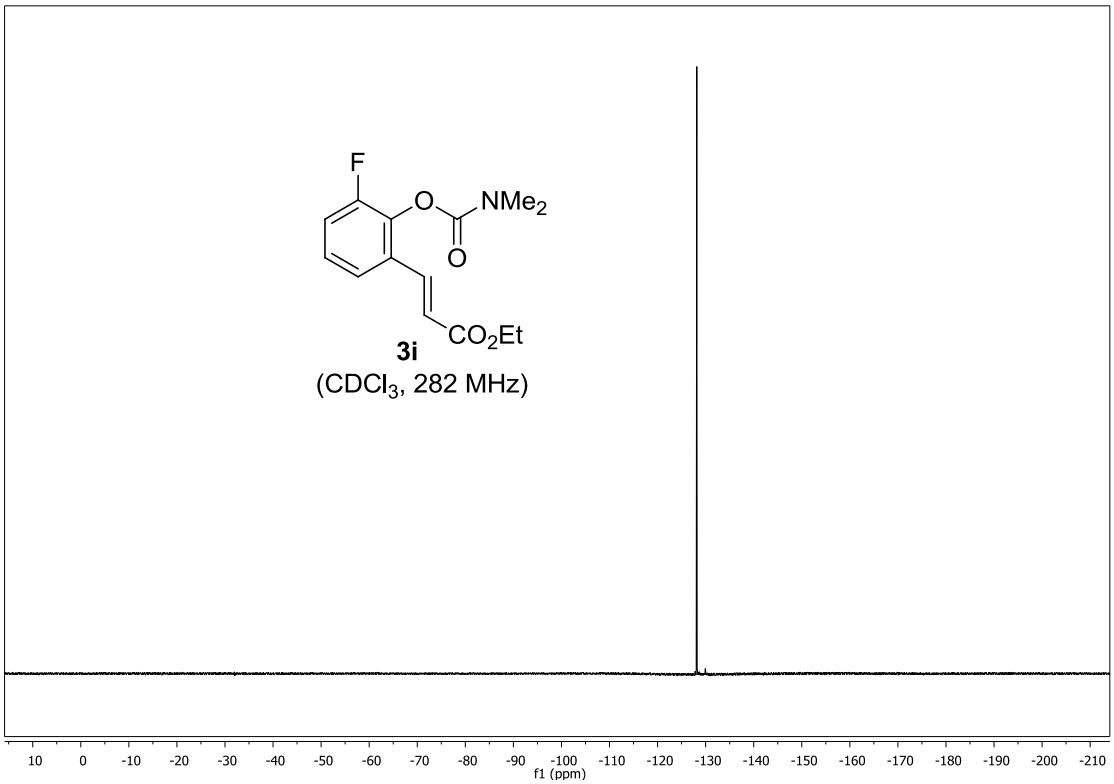

i-Pr
O
NMe2
O
CO2Et
3g
(CDCl3, 75 MHz)
f1 (ppm)


OMe
O
NMe2
O
CO2Et
3h
(CDCl3, 300 MHz)
f1 (ppm)


166.63
153.86
152.11
139.51
138.14
128.67
125.87
120.04
118.45
113.41
60.29
55.98
36.71
36.47
14.12
OMe
O
NMe2
O
CO2Et
3h
(CDCl3, 75 MHz)
f1 (ppm)

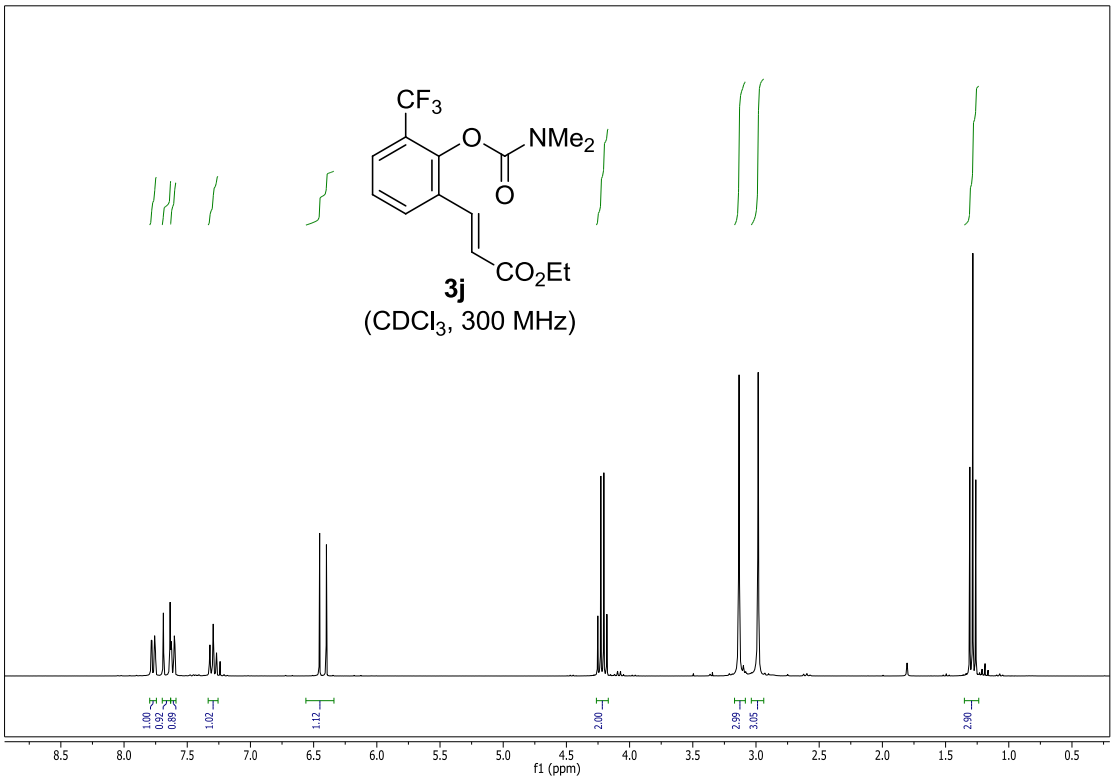

F
O
NMe2
O
CO2Et
3i
(CDCl3, 300 MHz)
1.00
1.05
1.99
1.04
2.24
3.24
3.13
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

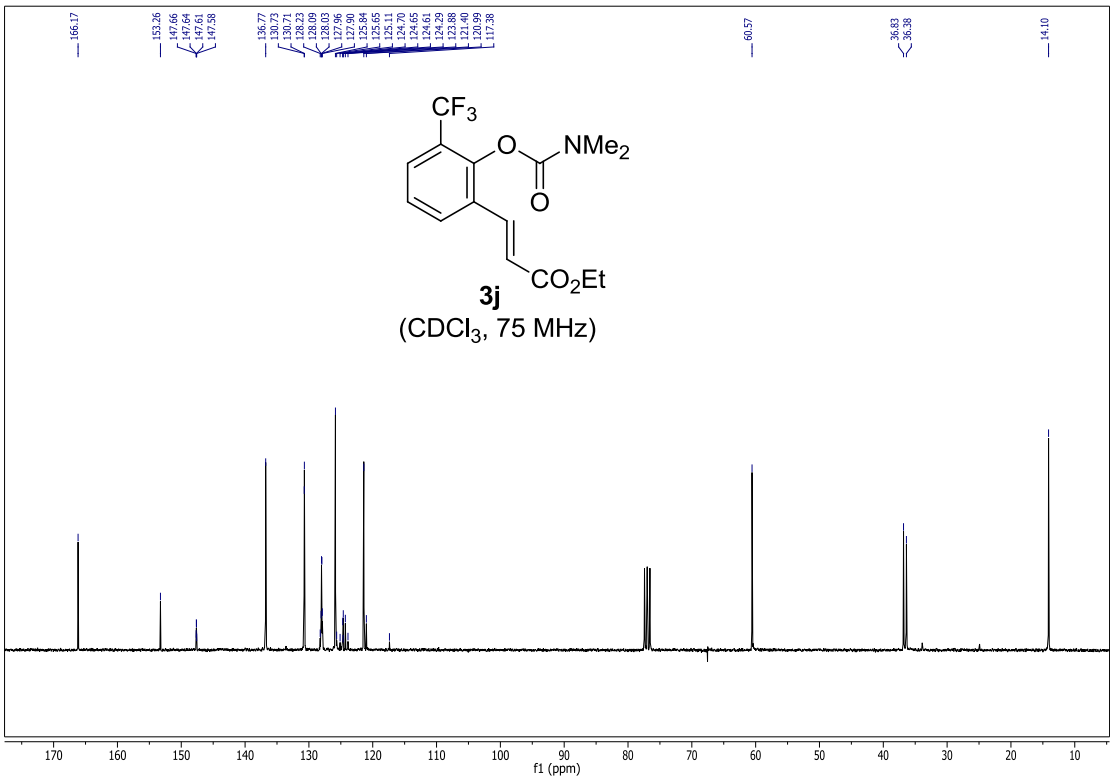

166.41
156.79
153.49
153.11
138.10
137.92
137.73
137.08
130.01
130.00
126.20
126.10
122.33
122.28
121.02
117.72
117.46
60.94
36.92
36.53
14.17
F
O
NMe2
O
CO2Et
3i
(CDCl3, 75 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

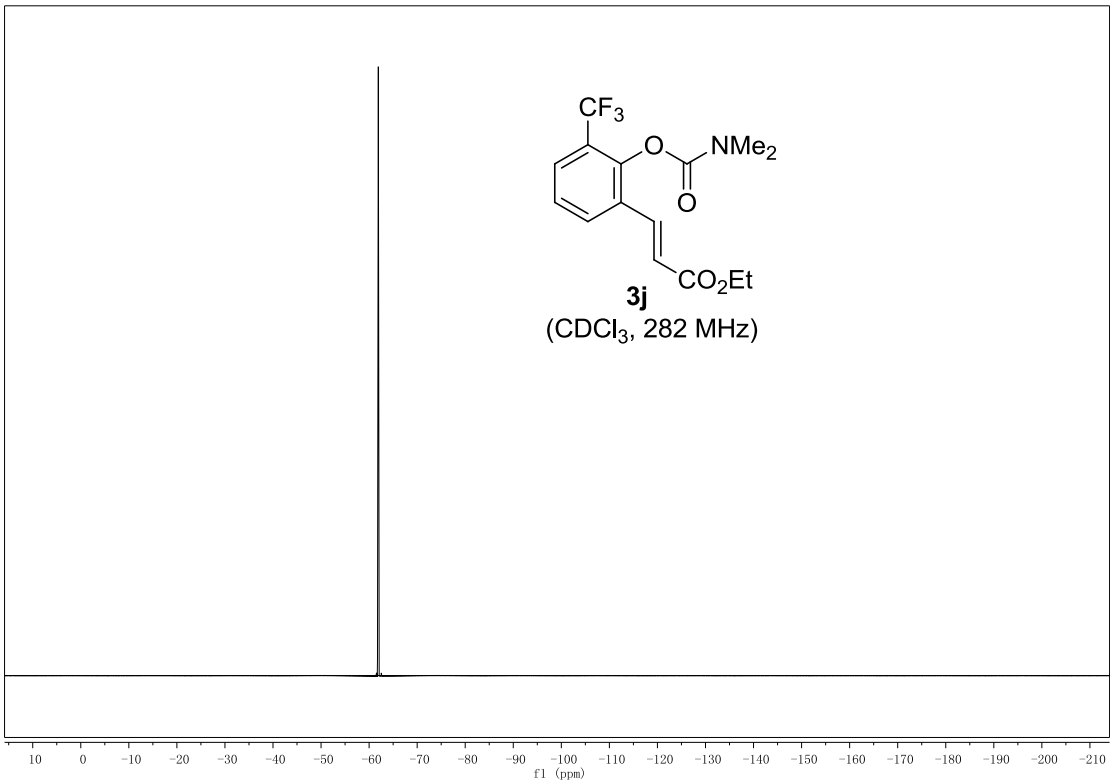


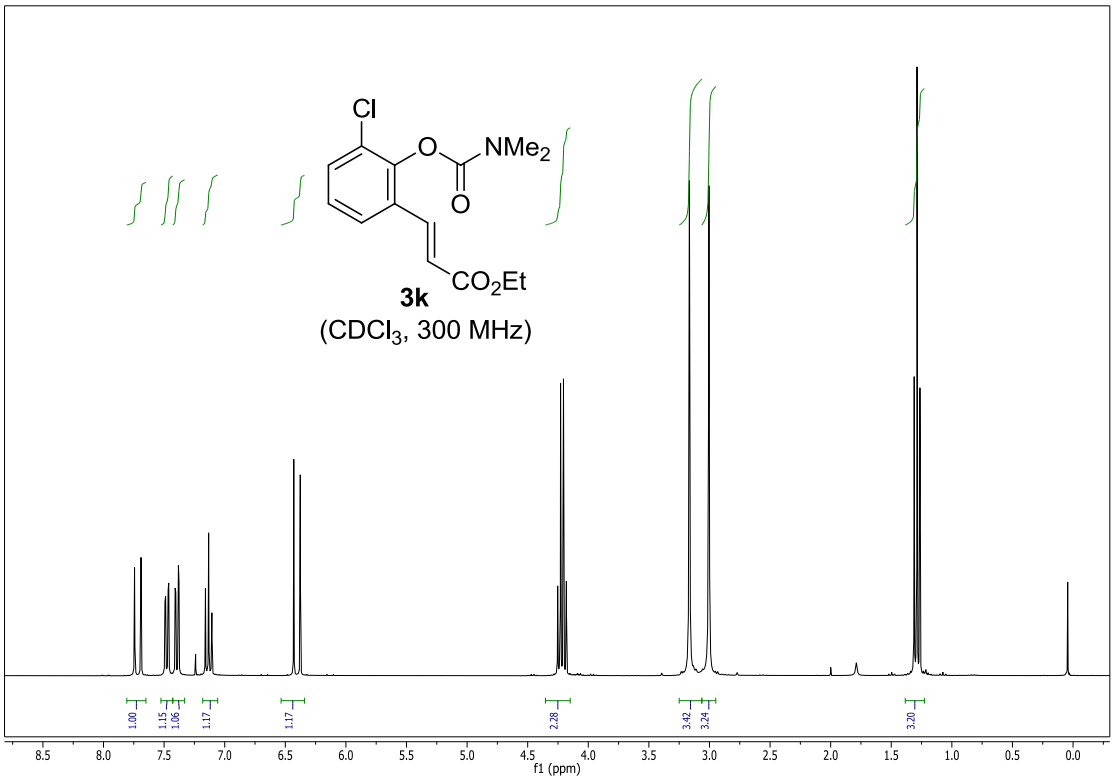
3i

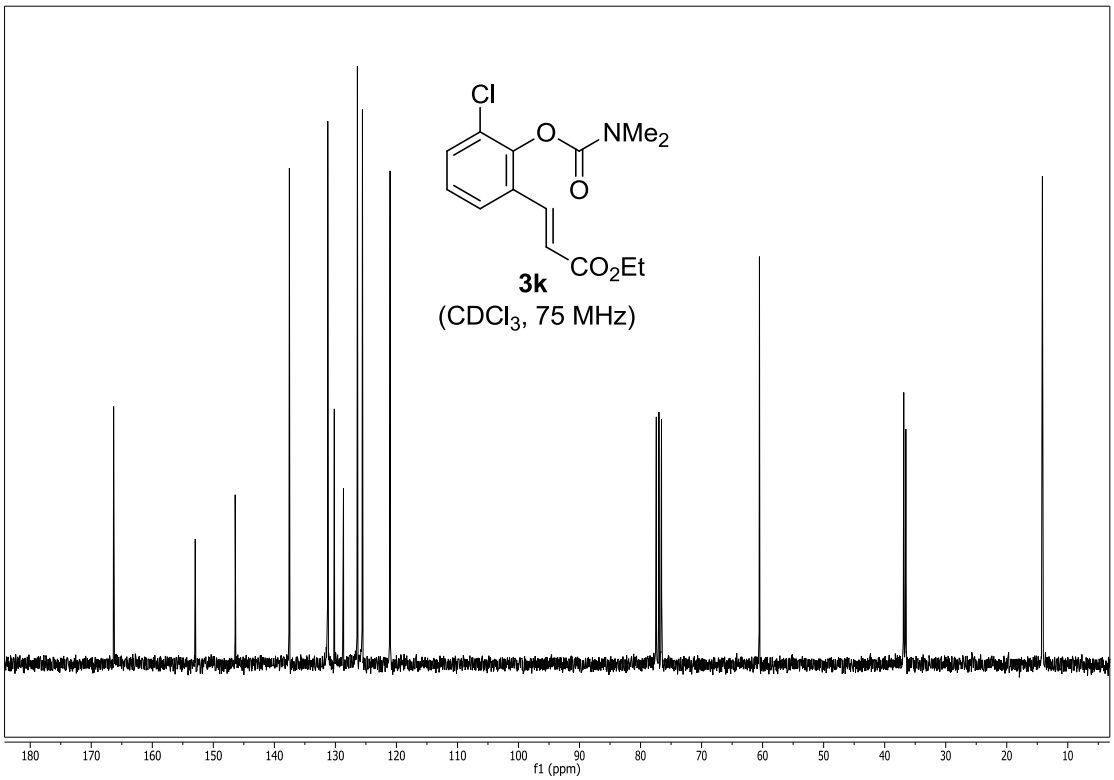
($CDCl_3$, 282 MHz)

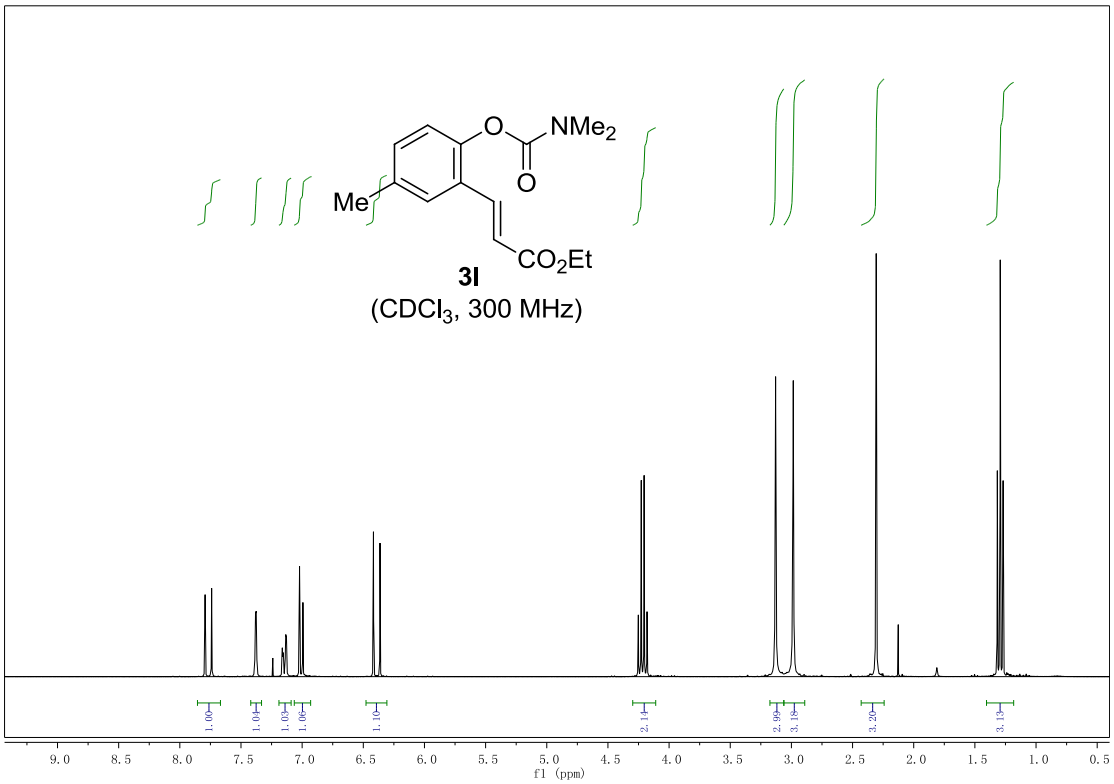

CF3
O
NMe2
O
CO2Et
3j
(CDCl3, 300 MHz)
f1 (ppm)

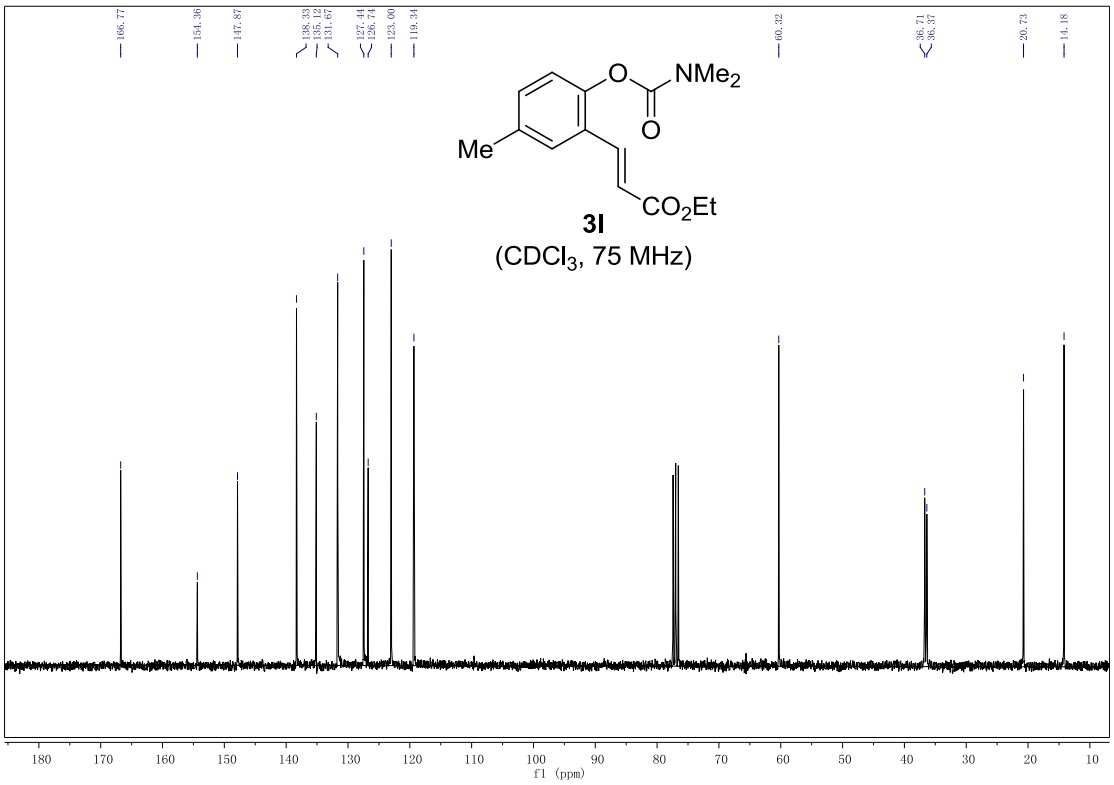

166.17
153.26
147.66
147.64
147.61
147.58
136.77
130.73
130.71
128.23
128.09
128.03
127.96
127.90
125.84
125.65
125.11
124.70
124.65
124.61
124.29
123.88
121.40
120.98
117.38
60.57
36.83
36.38
14.10
CF3
O
NMe2
O
CO2Et
3j
(CDCl3, 75 MHz)
f1 (ppm)

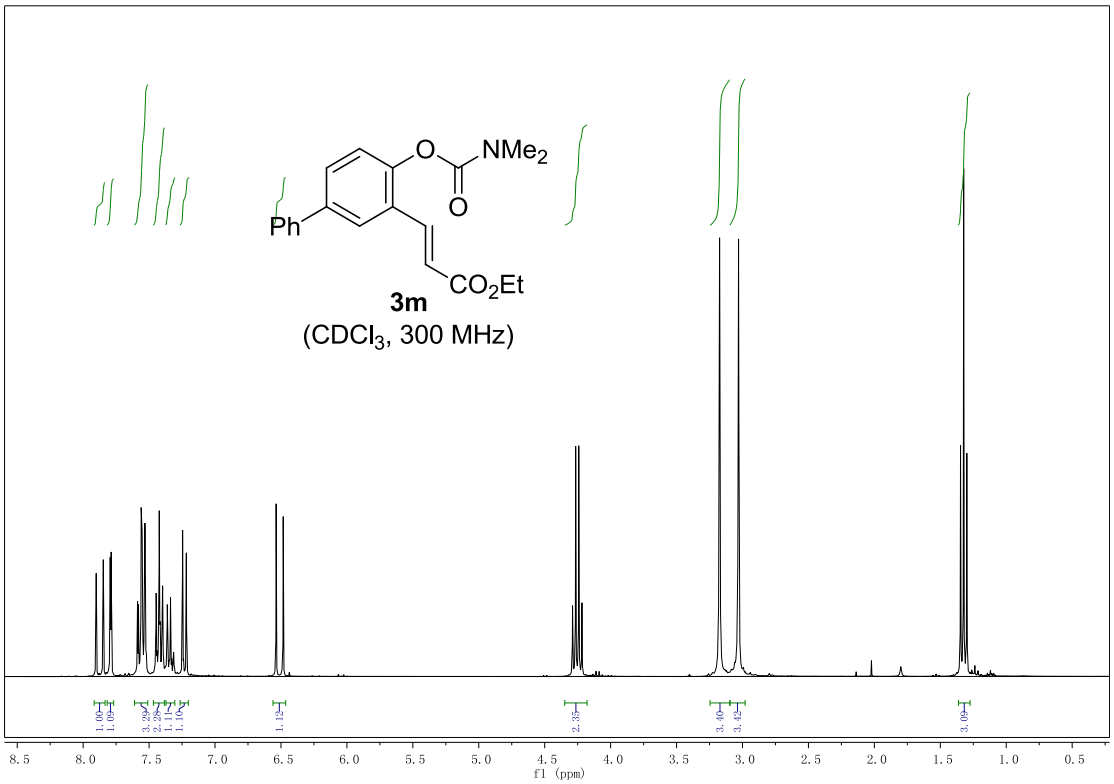

CF3
O
NMe2
O
CO2Et
3j
(CDCl3, 282 MHz)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

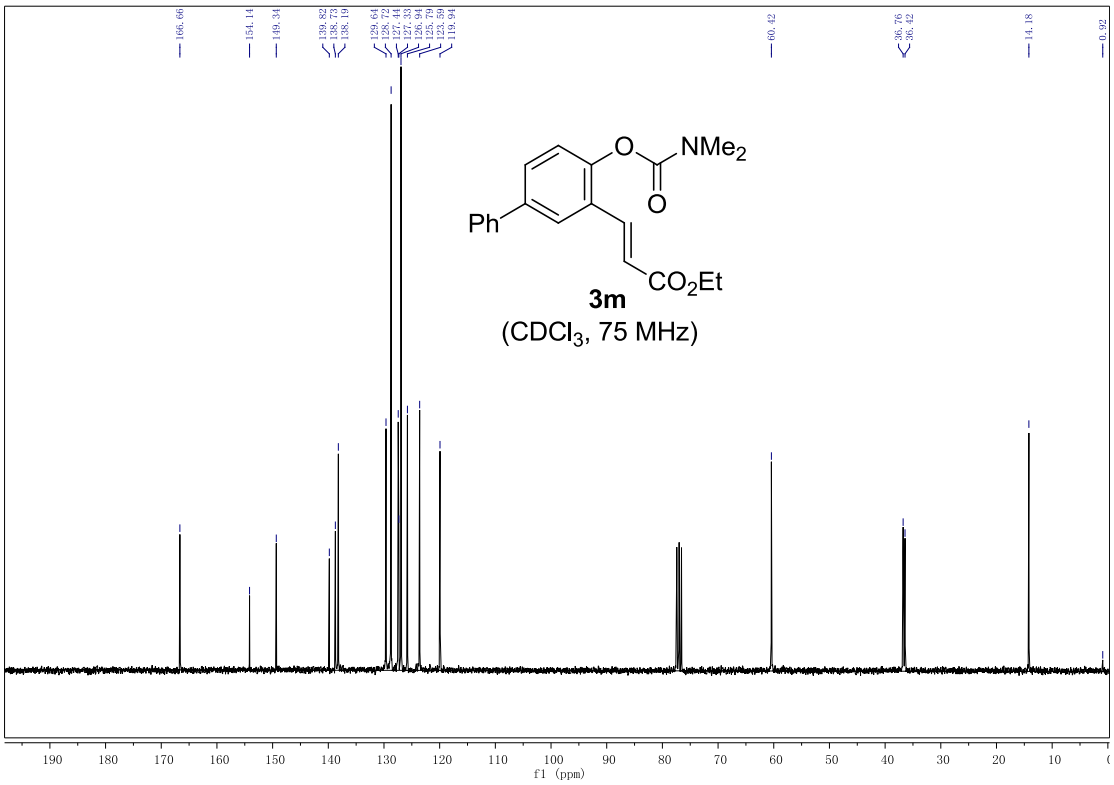

Cl
O
NMe2
O
CO2Et
3k
(CDCl3, 300 MHz)
1.00
1.15
1.06
1.17
1.17
2.28
3.42
3.24
3.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

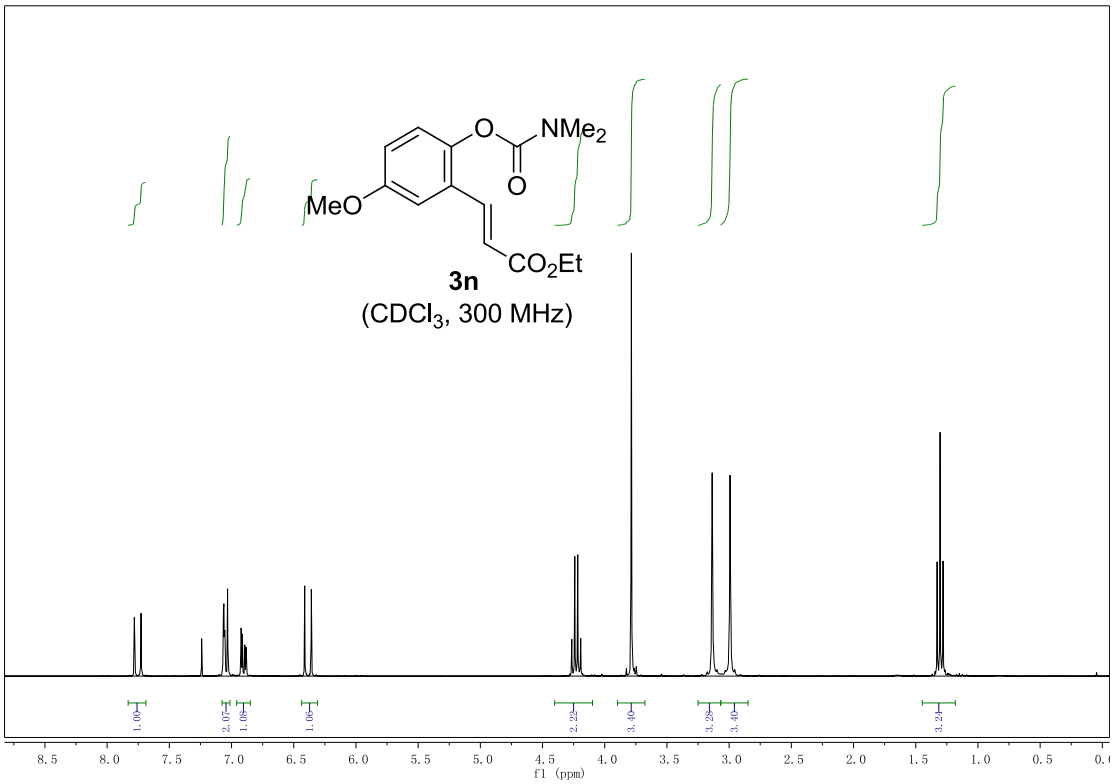

Cl
O
NMe2
O
CO2Et
3k
(CDCl3, 75 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

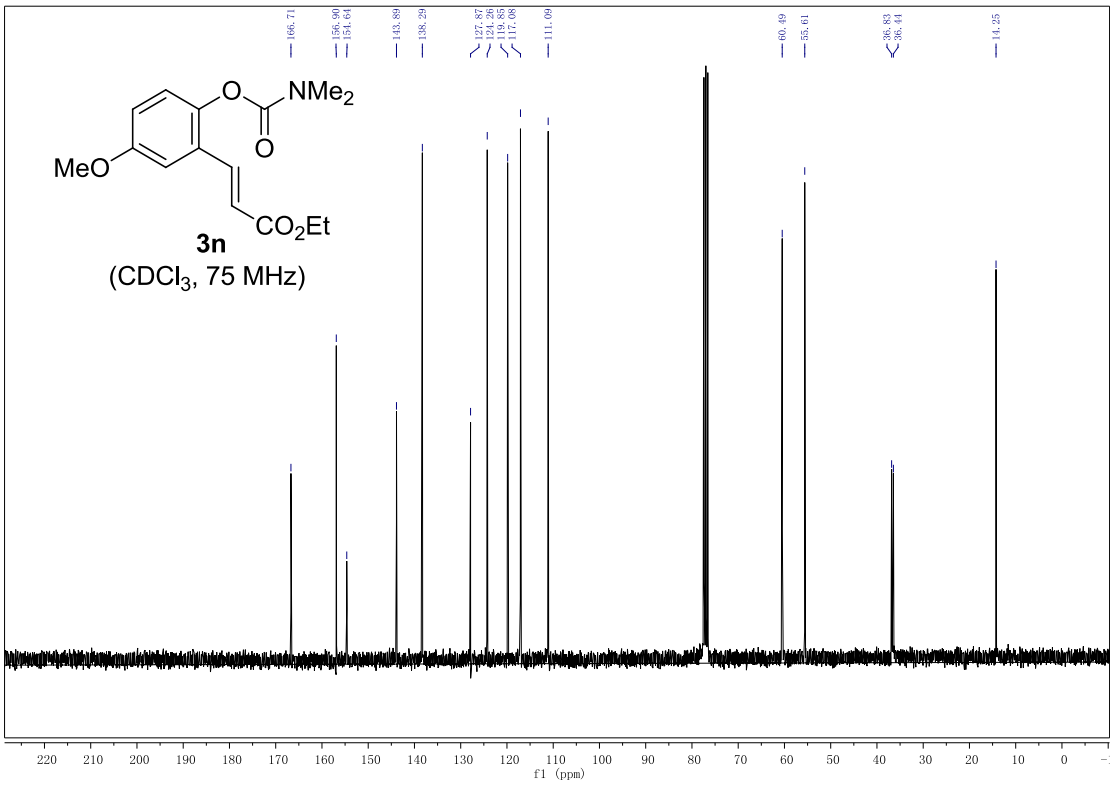

O
NMe2
O
Me
CO2Et
3l
(CDCl3, 300 MHz)
f1 (ppm)

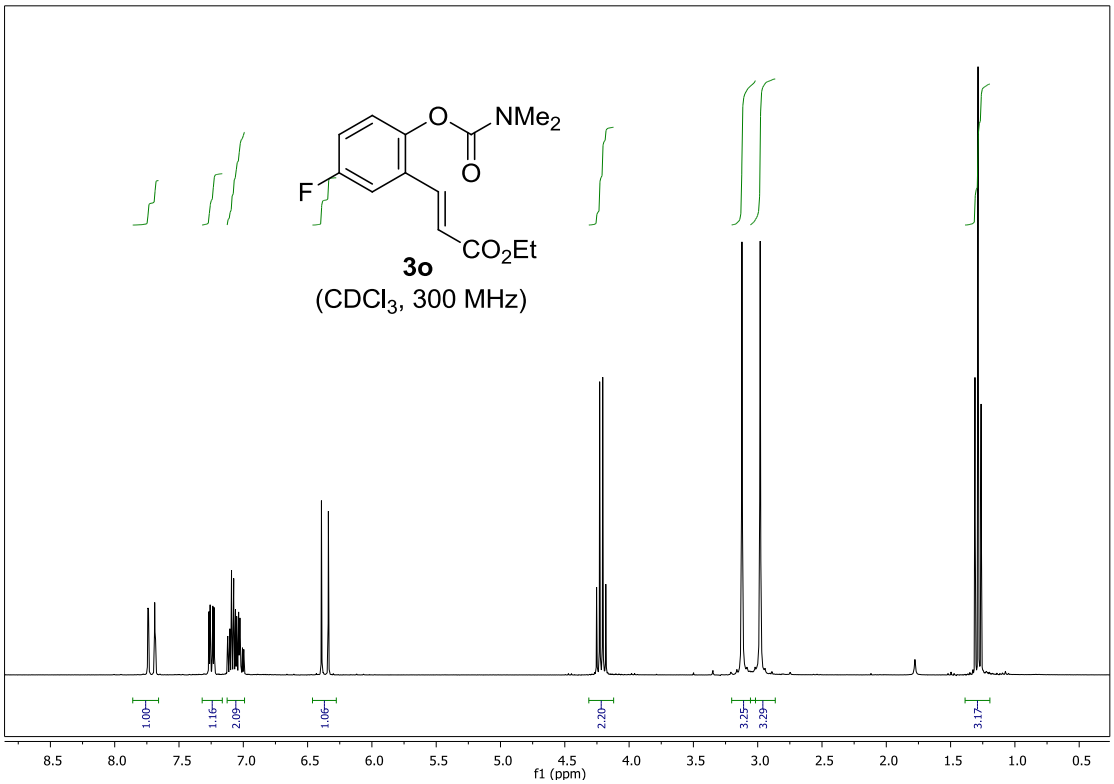

O
NMe2
O
Me
CO2Et
3l
(CDCl3, 75 MHz)
f1 (ppm)

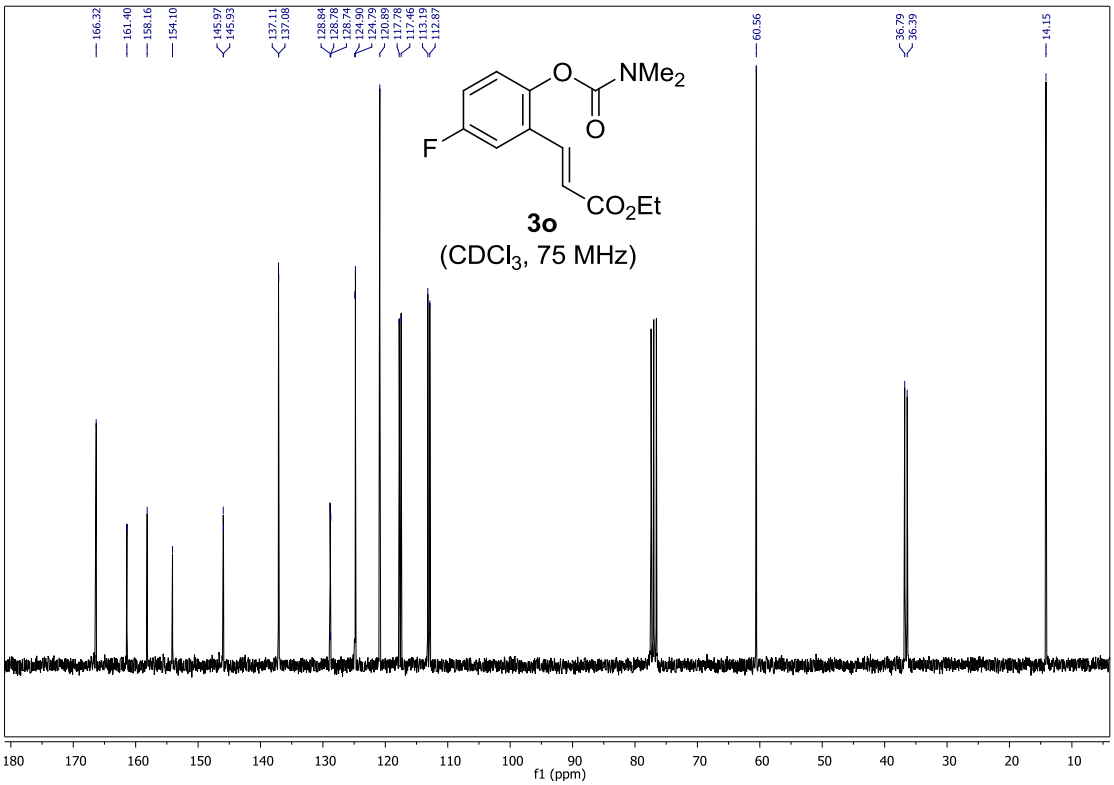

O
NMe2
O
Ph
CO2Et
3m
(CDCl3, 300 MHz)
f1 (ppm)

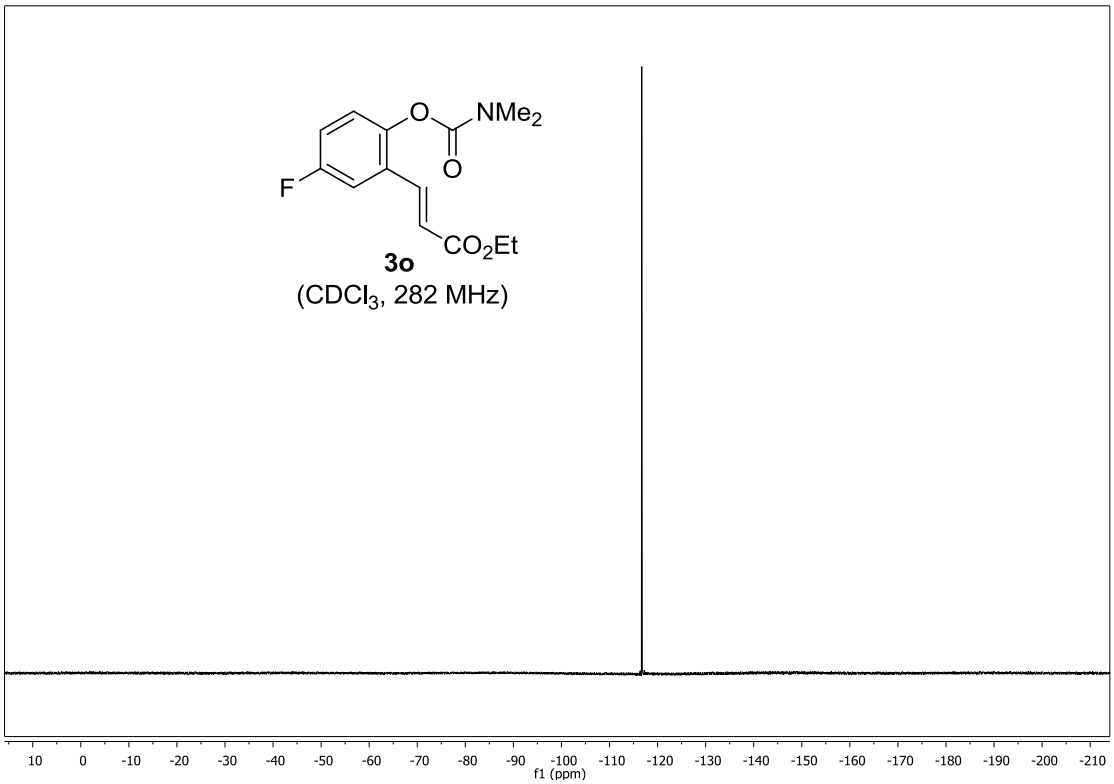

166.66
154.14
149.34
139.82
138.73
138.19
129.64
128.72
127.44
127.33
126.94
125.79
123.59
119.94
60.42
36.76
36.42
14.18
0.92
O
NMe2
O
Ph
CO2Et
3m
(CDCl3, 75 MHz)
f1 (ppm)

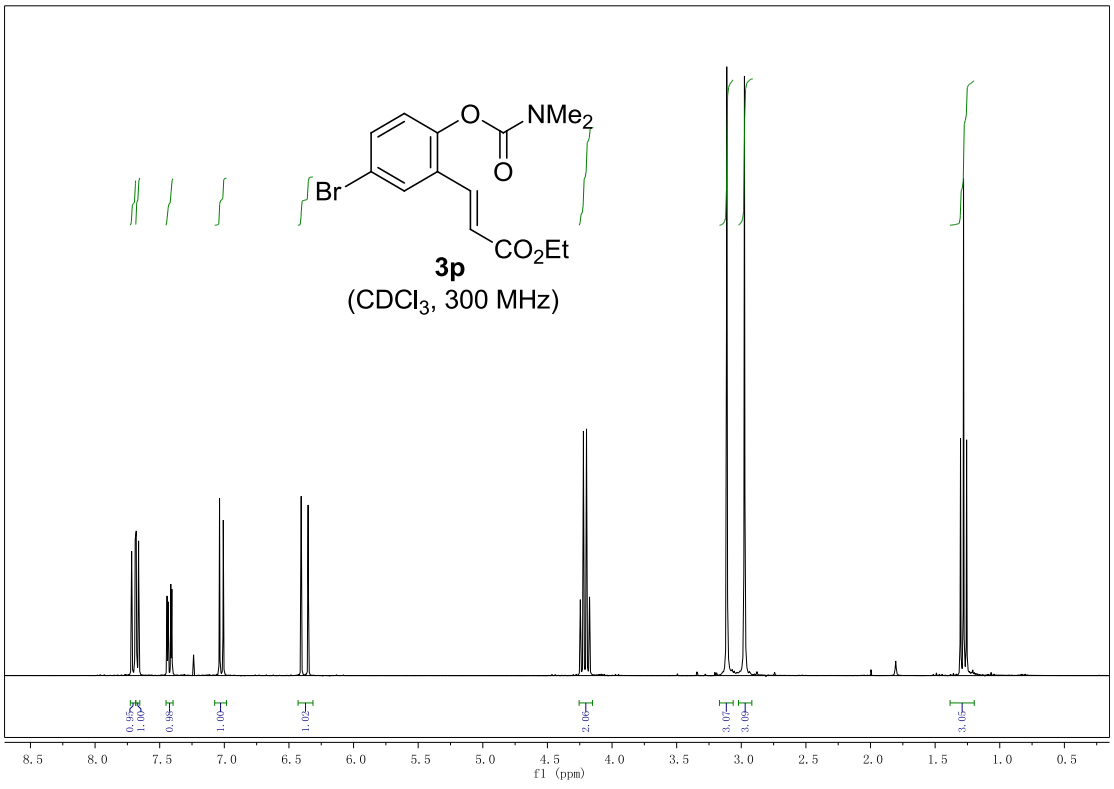

O
NMe2
O
MeO
CO2Et
3n
(CDCl3, 300 MHz)
f1 (ppm)

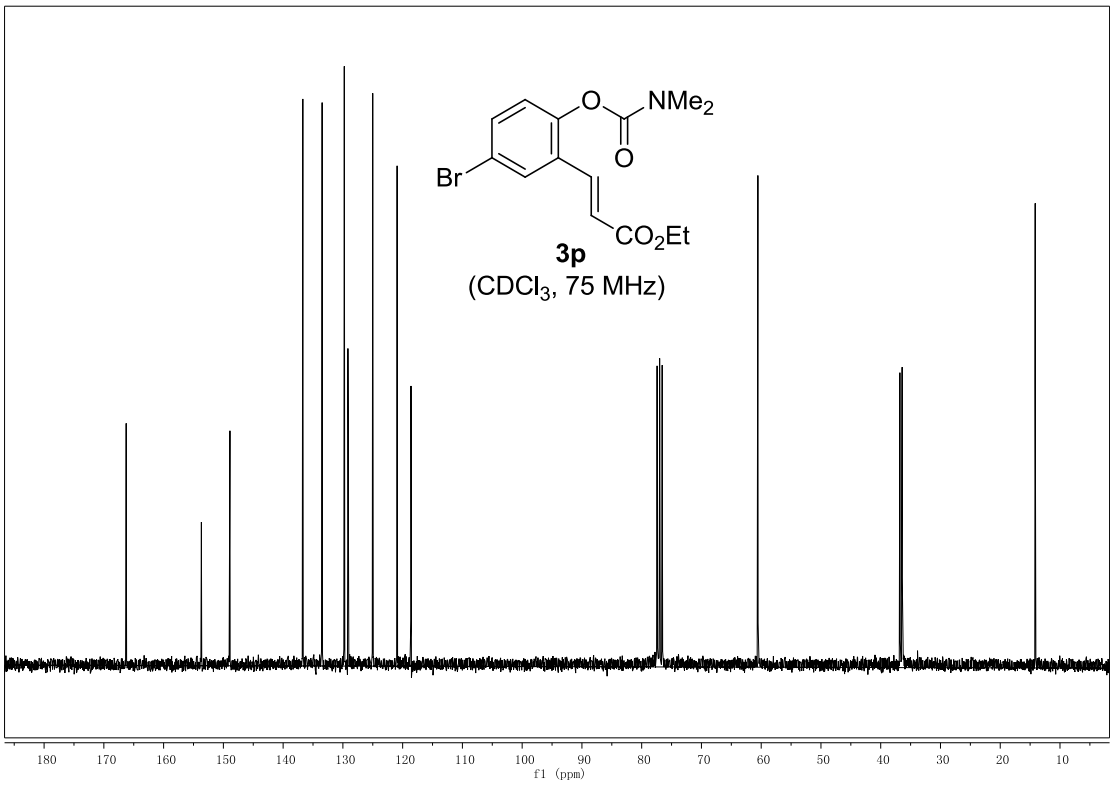

166.71
156.90
154.64
143.89
138.29
127.87
124.36
119.85
117.08
111.09
60.49
55.61
36.83
36.44
14.25
O
NMe2
O
MeO
CO2Et
3n
(CDCl3, 75 MHz)
f1 (ppm)

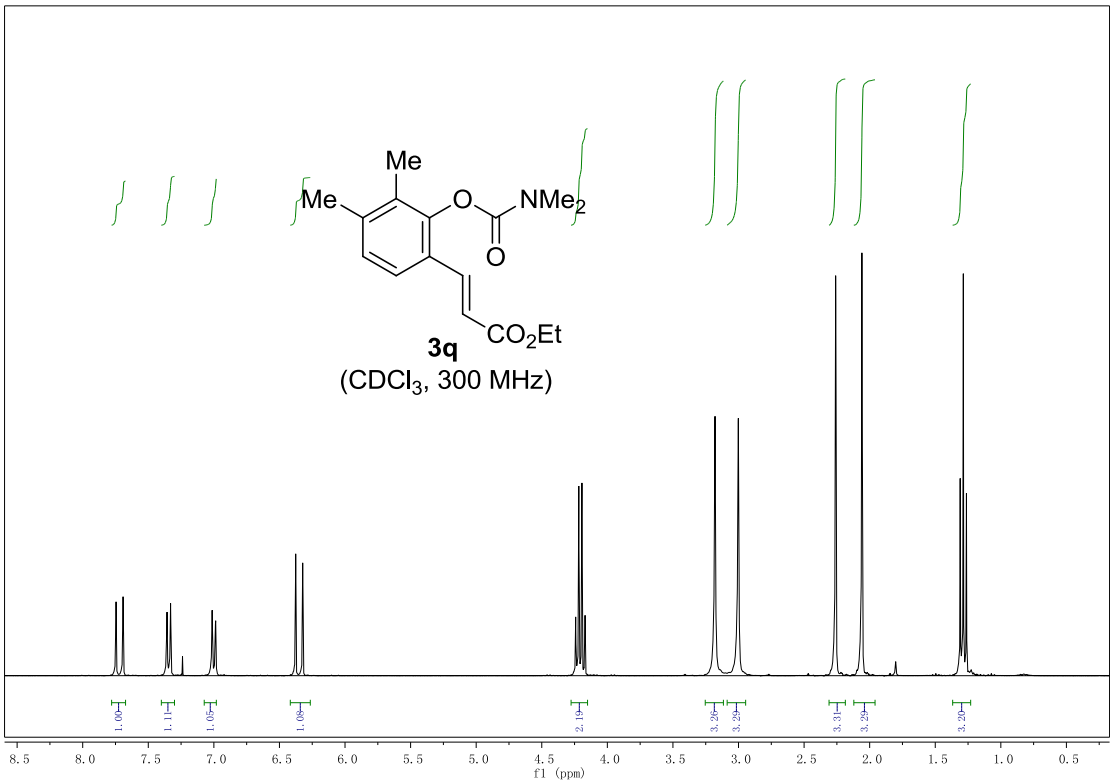

O
NMe2
O
F
CO2Et
3o
(CDCl3, 300 MHz)
1.00
1.16
2.09
1.06
2.20
3.25
3.29
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

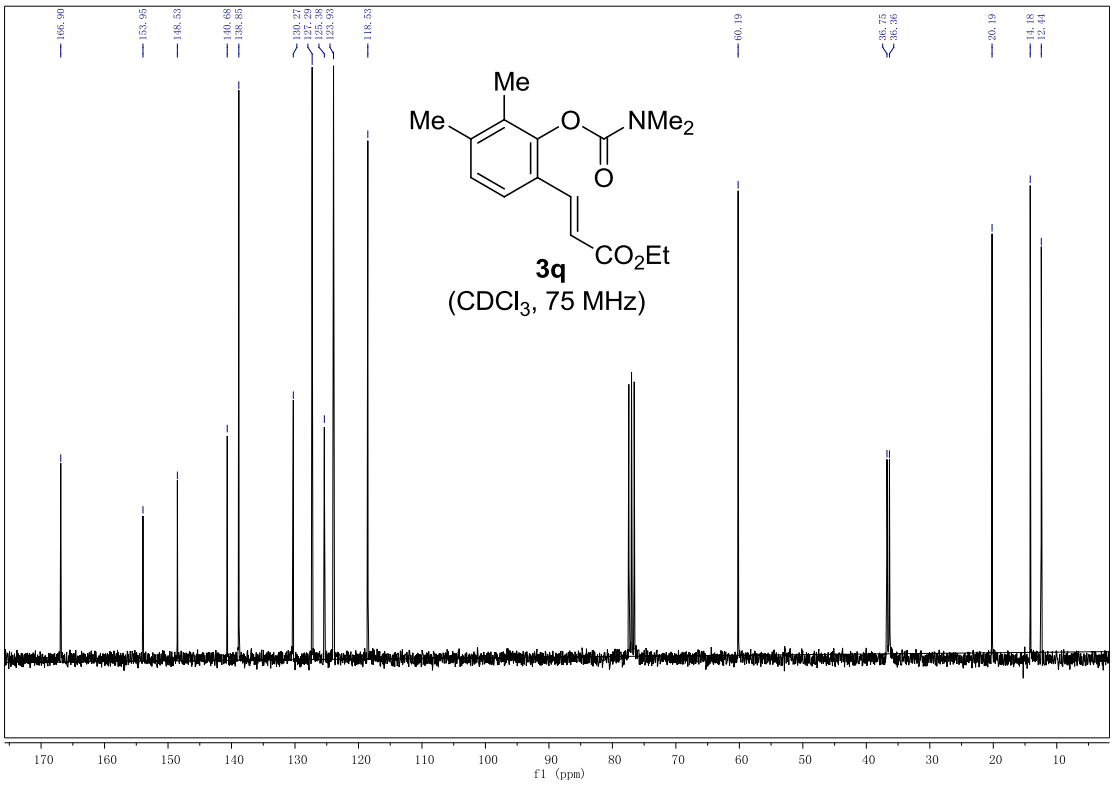

166.32
161.40
158.16
154.10
145.97
145.93
137.11
137.08
128.84
128.78
128.74
124.90
124.79
120.89
117.78
117.46
113.19
112.87
60.56
36.79
36.39
14.15
O
NMe2
O
F
CO2Et
3o
(CDCl3, 75 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

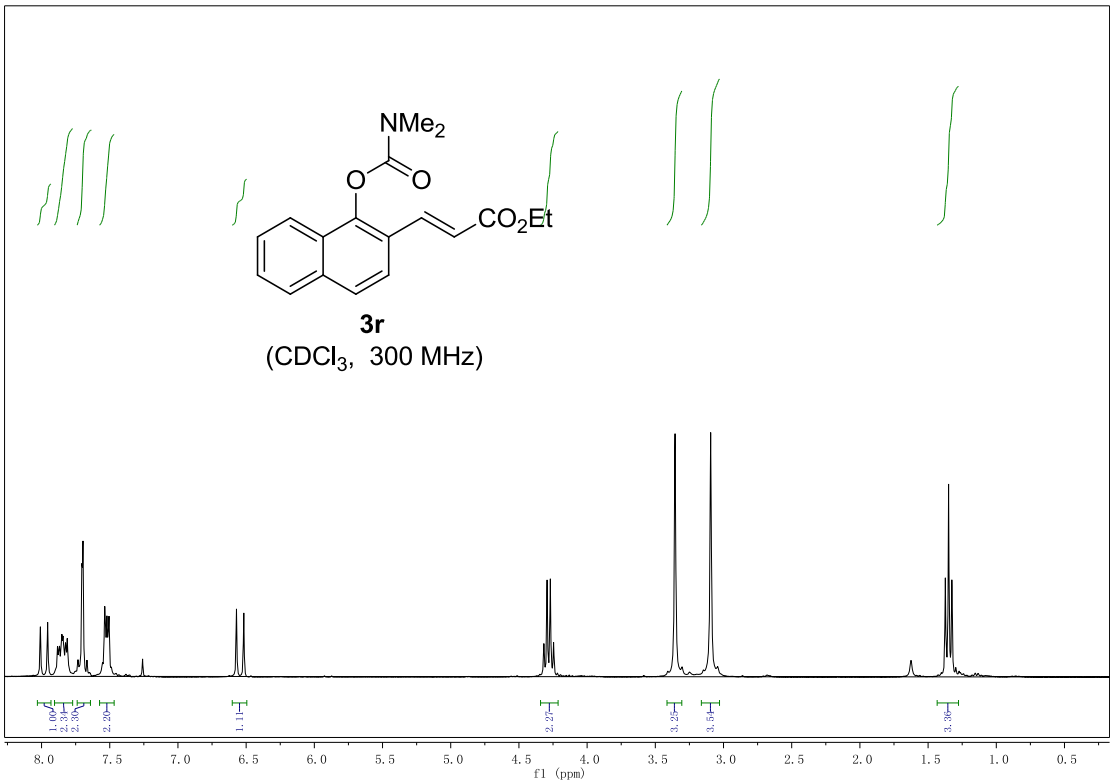

O
NMe2
O
F
CO2Et
3o
(CDCl3, 282 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

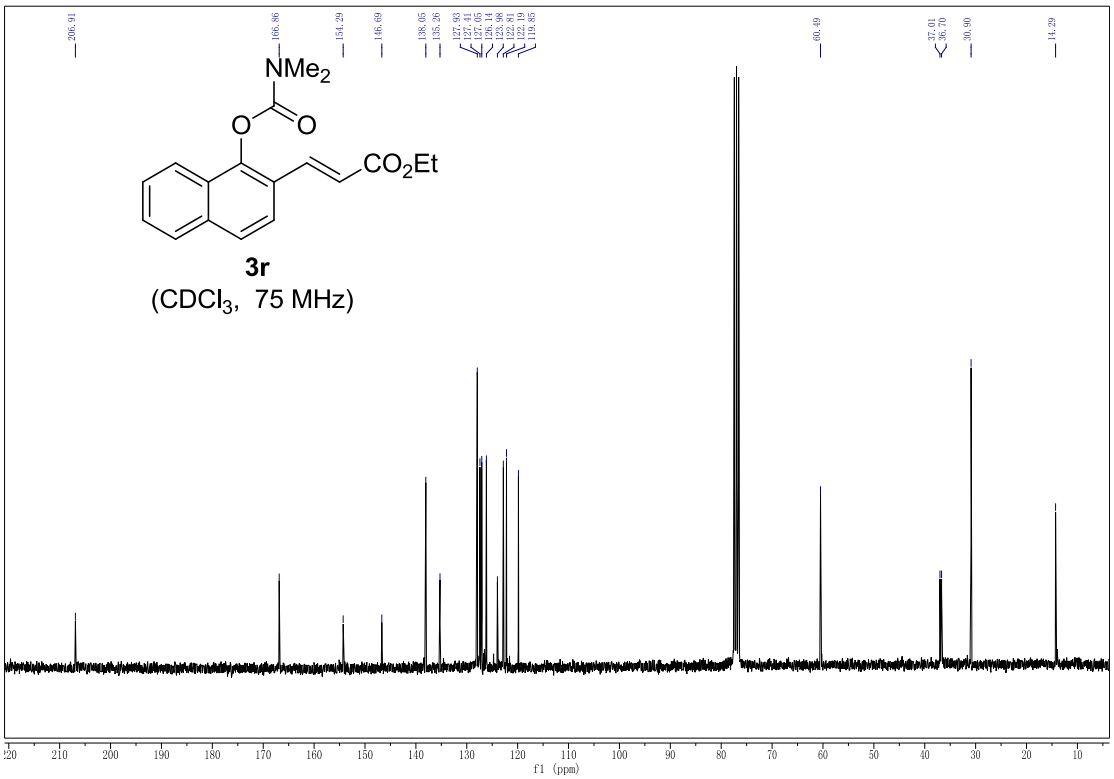


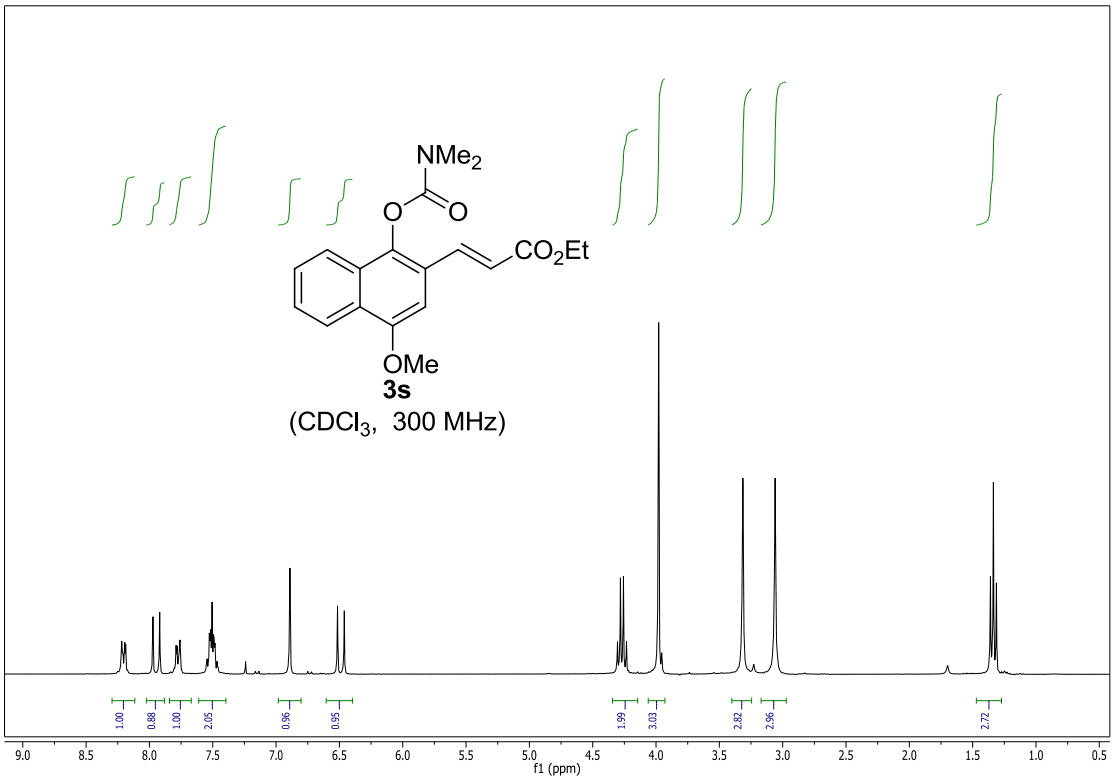


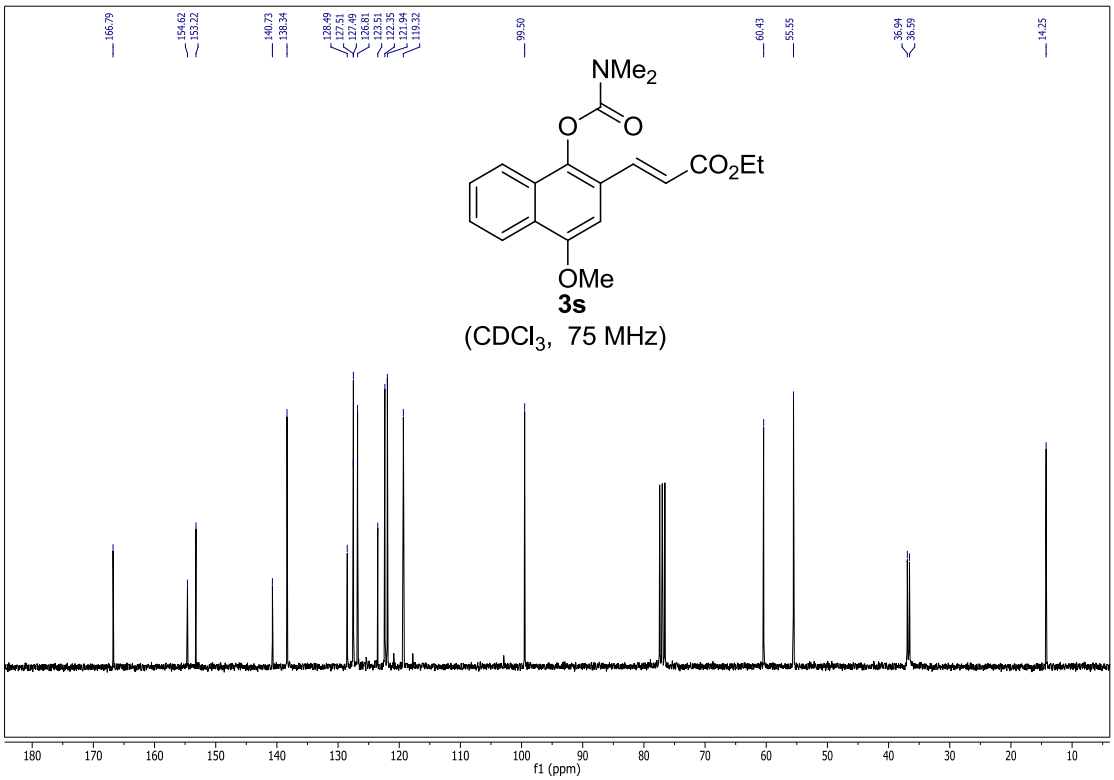

Me
Me
O
NMe2
O
CO2Et
3q
(CDCl3, 300 MHz)
f1 (ppm)

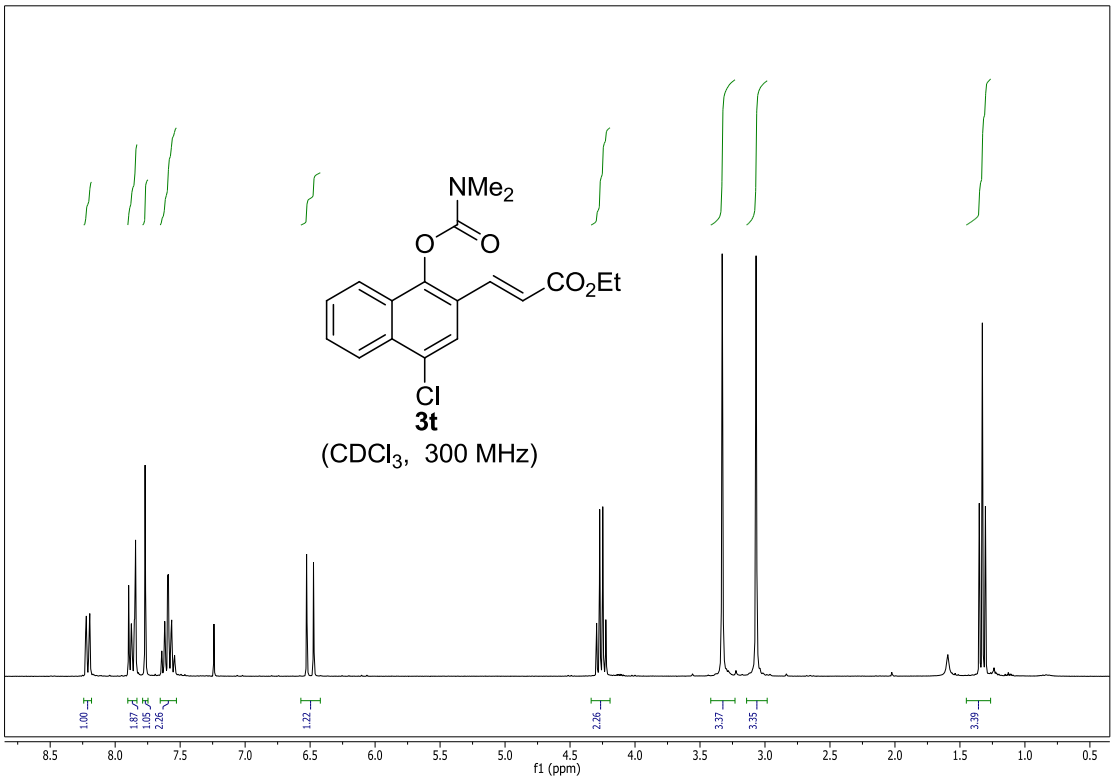

166.90
153.95
148.53
140.68
138.86
130.27
127.29
125.38
123.93
118.53
60.19
36.75
36.36
20.19
14.18
12.44
Me
Me
O
NMe2
O
CO2Et
3q
(CDCl3, 75 MHz)
f1 (ppm)

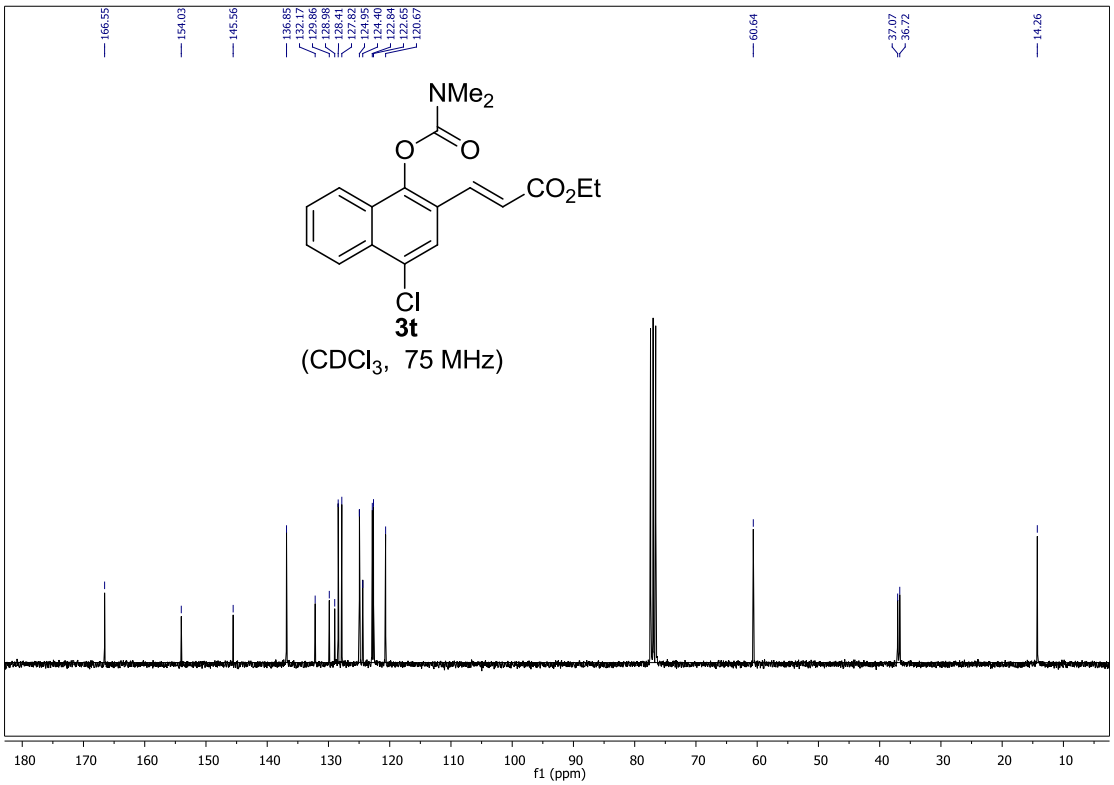

NMe2
O
O
CO2Et
3r
(CDCl3, 300 MHz)
f1 (ppm)

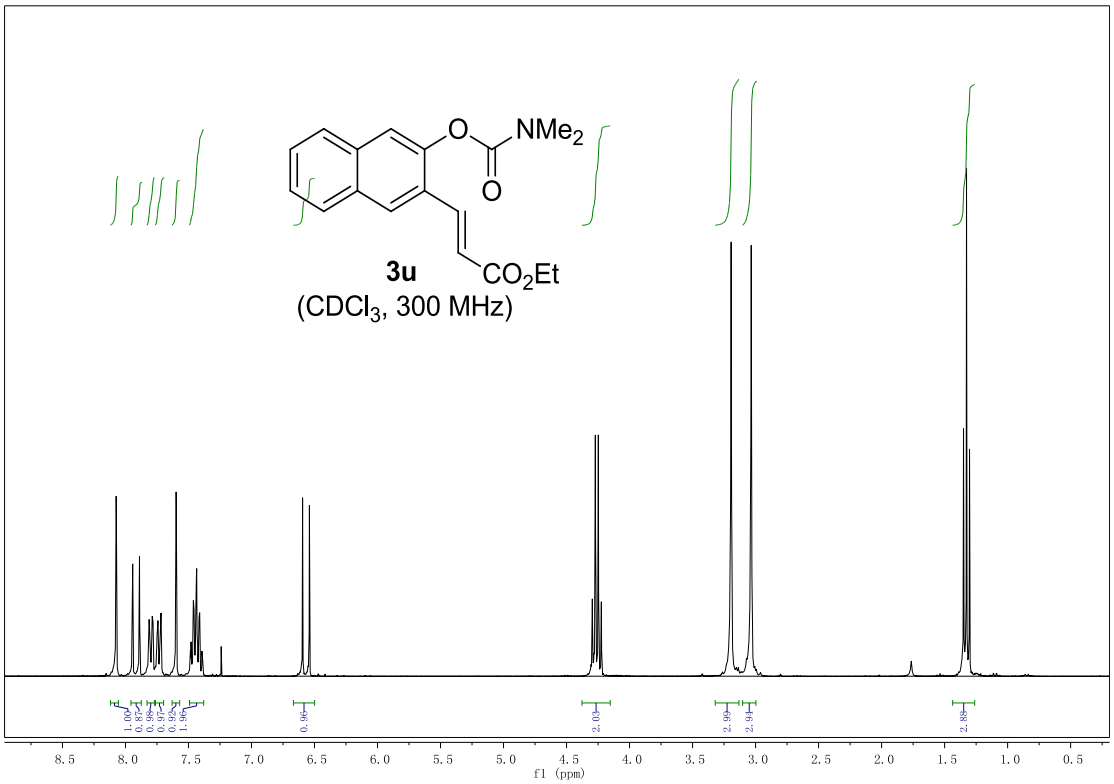

NMe2
O
O
CO2Et
3r
(CDCl3, 75 MHz)
f1 (ppm)

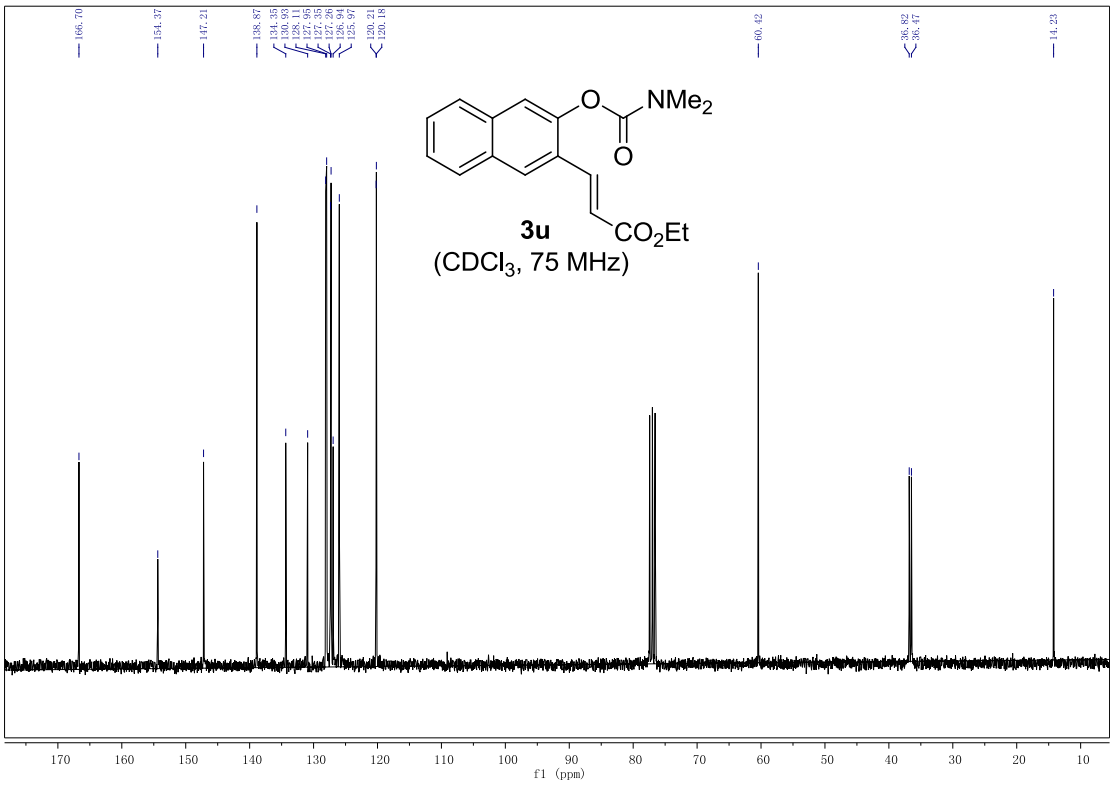

NMe2
O
O
CO2Et
OMe
3s
(CDCl3, 300 MHz)
f1 (ppm)

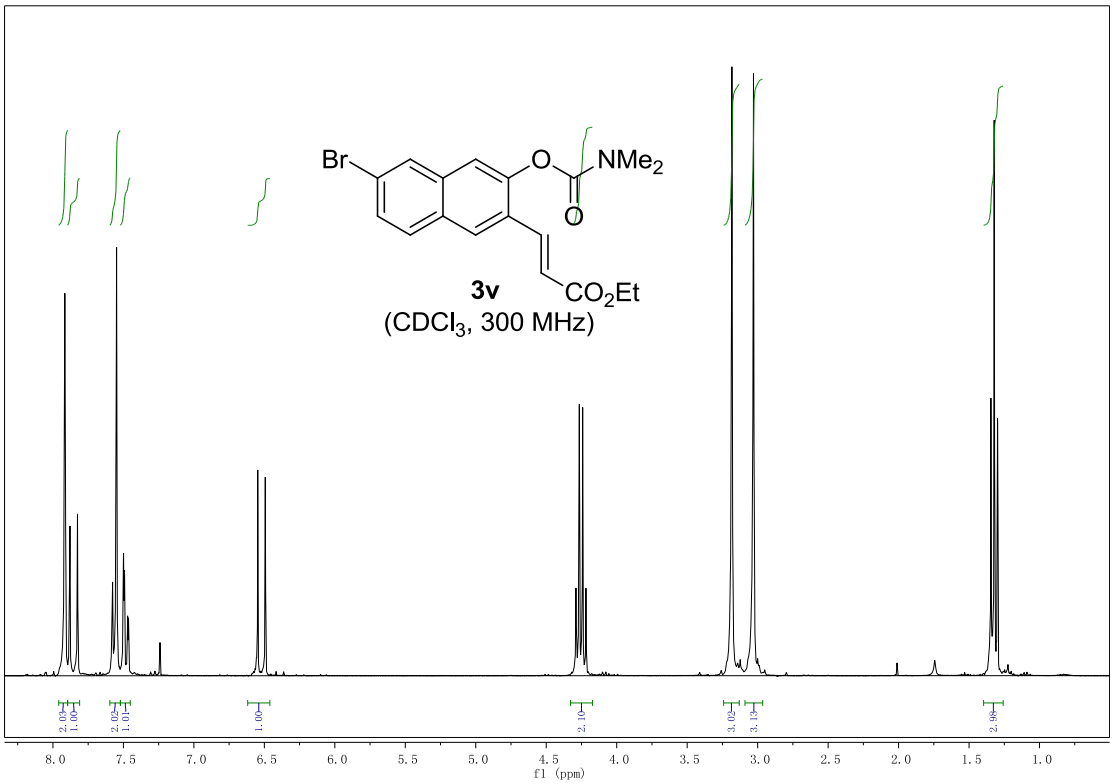

166.79
154.62
153.22
140.73
138.34
128.49
127.51
127.40
126.81
123.51
122.35
121.94
119.32
99.50
60.43
55.55
36.94
36.99
14.25
NMe2
O
O
CO2Et
OMe
3s
(CDCl3, 75 MHz)
f1 (ppm)

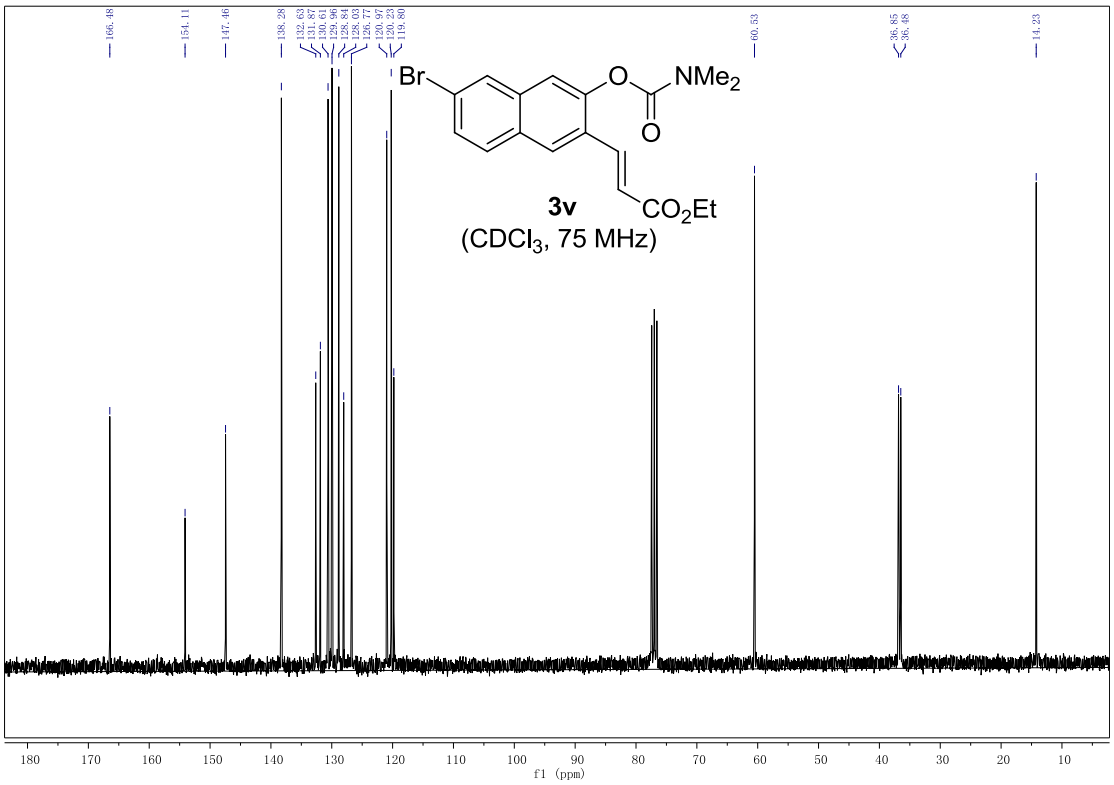


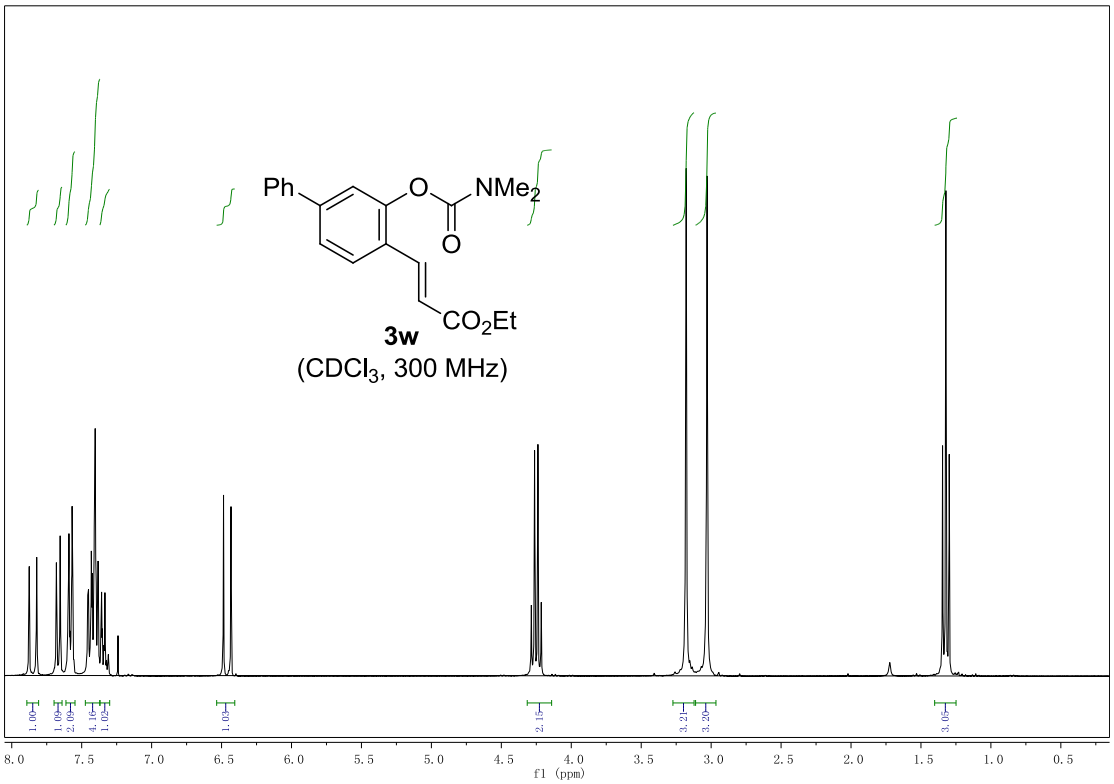


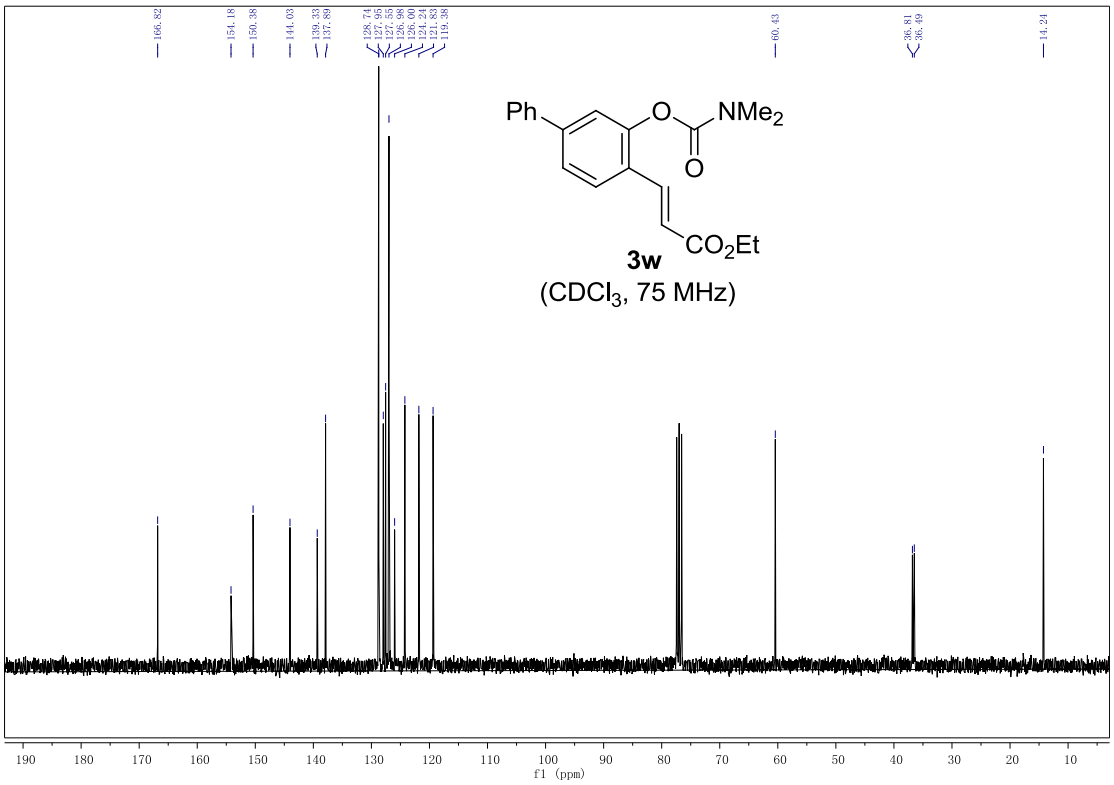

O
NMe2
O
3u
CO2Et
(CDCl3, 300 MHz)
f1 (ppm)

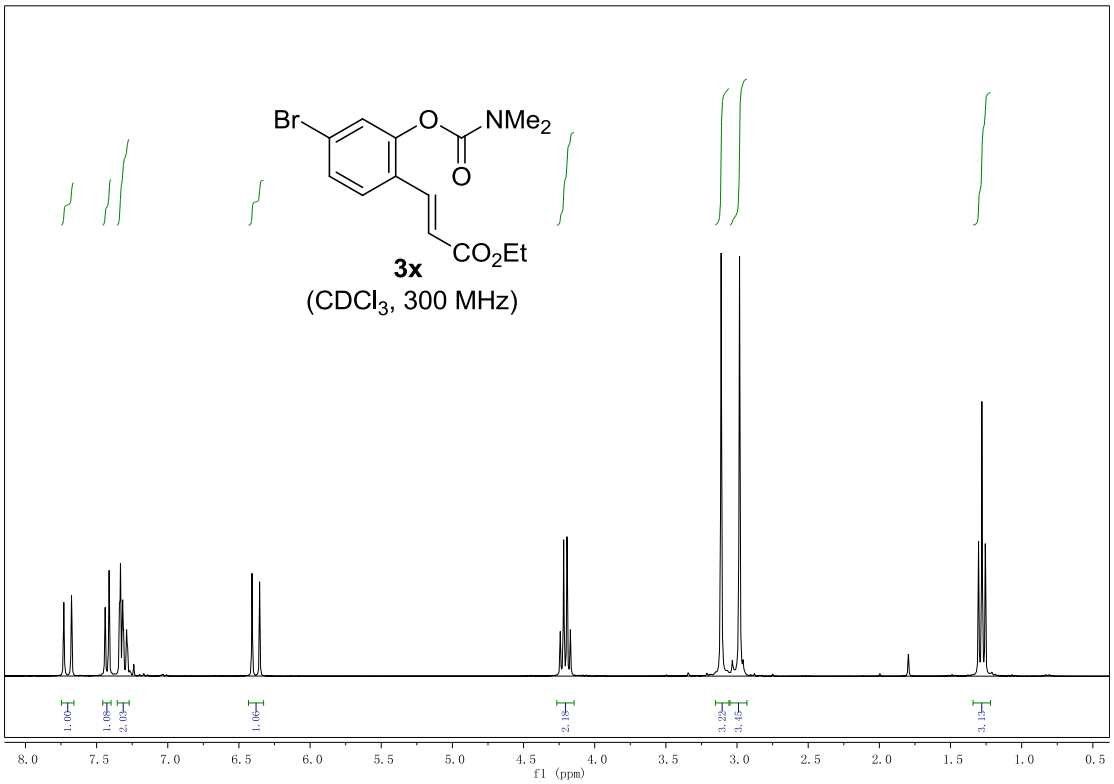

O
NMe2
O
3u
CO2Et
(CDCl3, 75 MHz)
f1 (ppm)

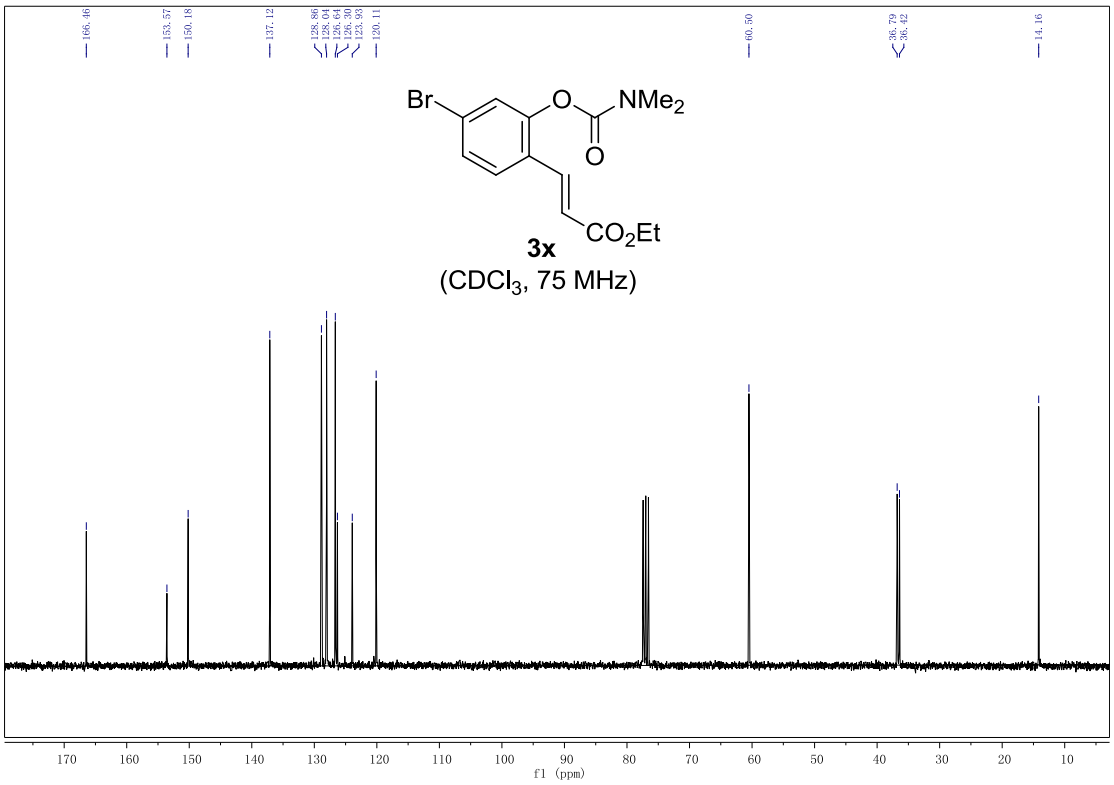

Br
O
NMe2
O
3v
CO2Et
(CDCl3, 300 MHz)
f1 (ppm)

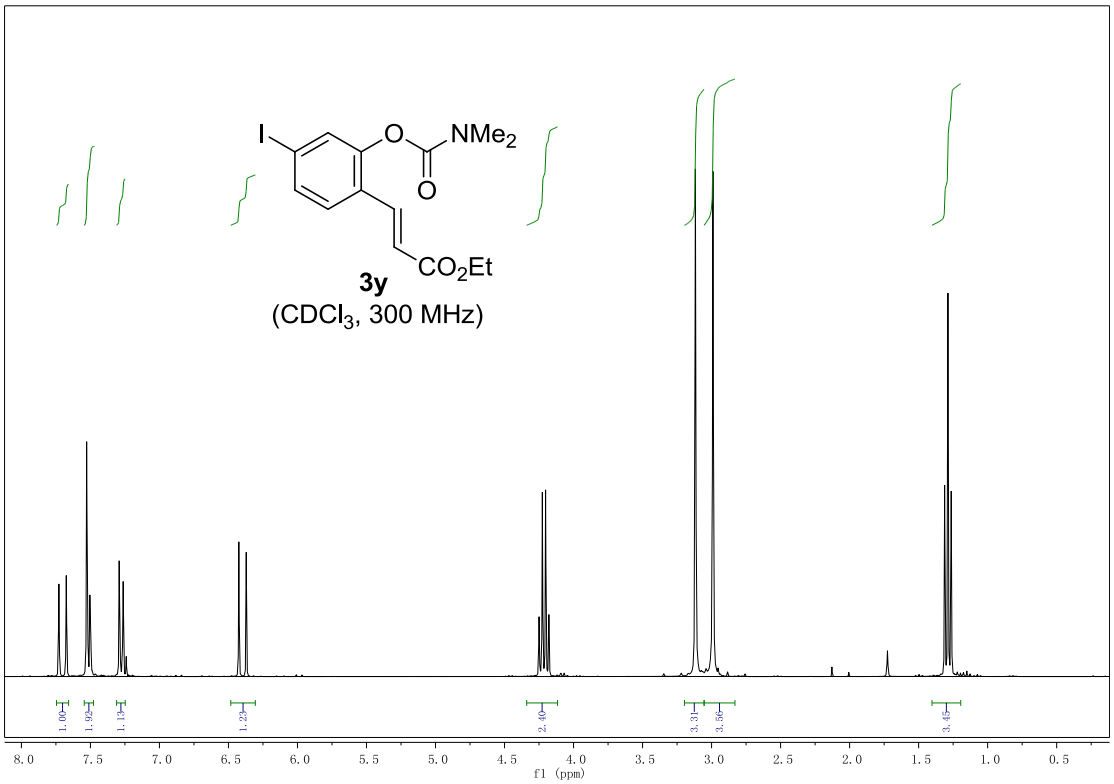

166.48
154.11
147.46
138.28
132.63
131.87
130.61
129.96
128.84
128.03
126.77
120.97
120.23
119.80
60.53
36.85
36.48
14.23
Br
O
NMe2
O
3v
CO2Et
(CDCl3, 75 MHz)
f1 (ppm)

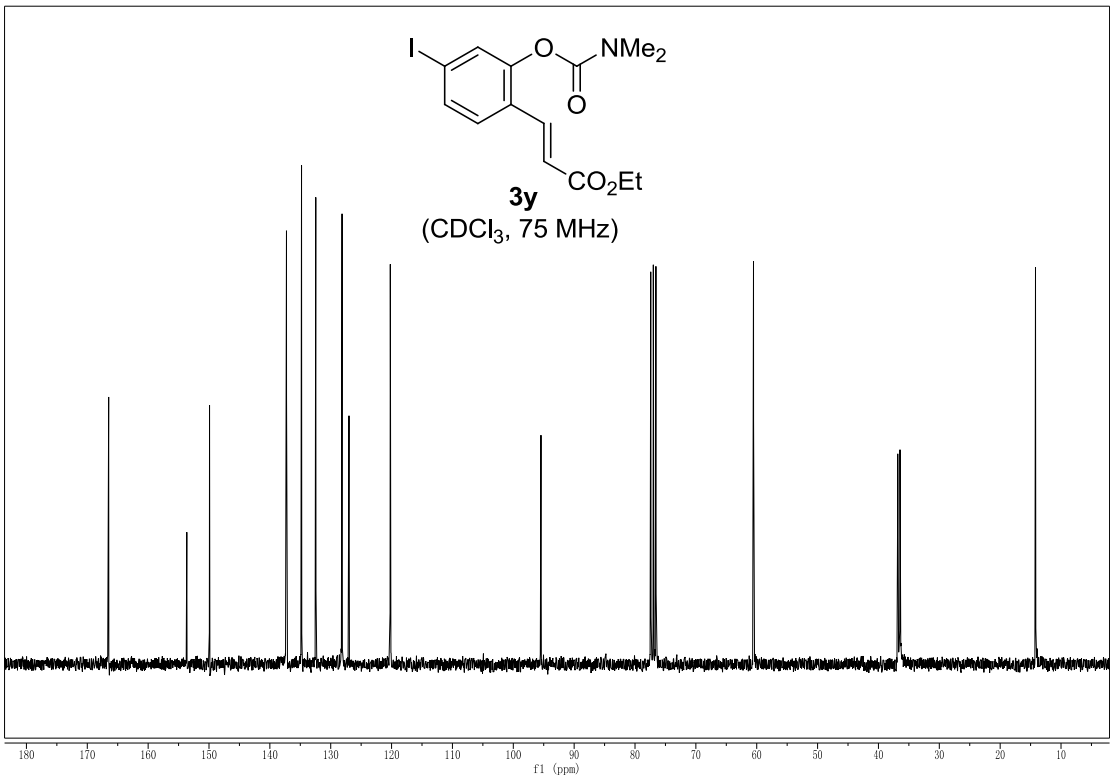

Ph
O
NMe2
O
CO2Et
3w
(CDCl3, 300 MHz)
f1 (ppm)

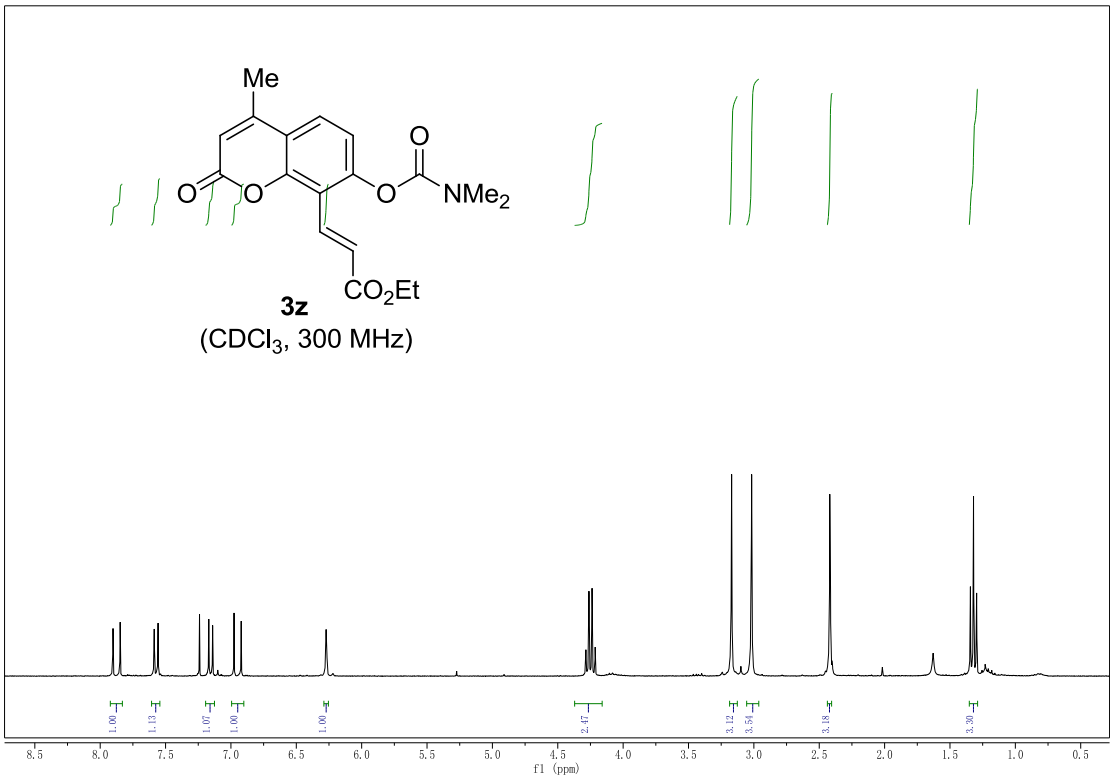

166.82
154.18
150.38
144.03
139.33
137.89
128.74
127.95
127.55
126.98
126.00
124.24
121.85
119.38
60.43
36.81
36.49
14.24
Ph
O
NMe2
O
CO2Et
3w
(CDCl3, 75 MHz)
f1 (ppm)

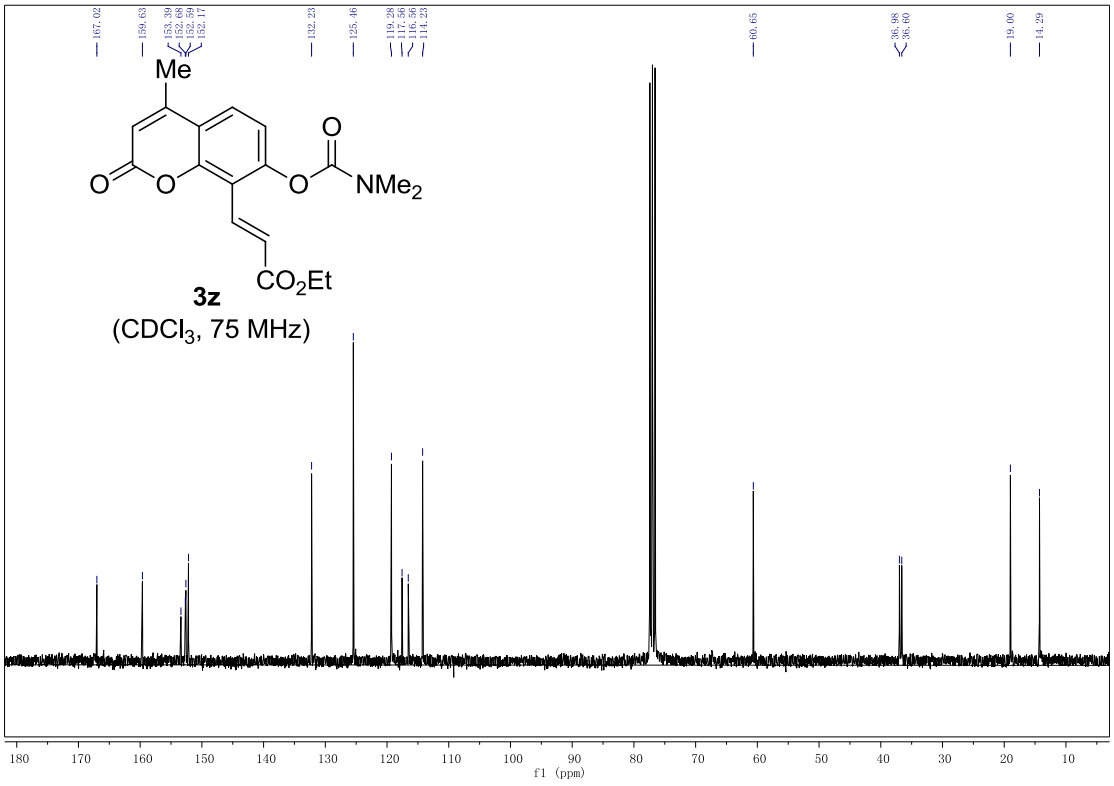

Br
O
NMe2
O
CO2Et
3x
(CDCl3, 300 MHz)
f1 (ppm)

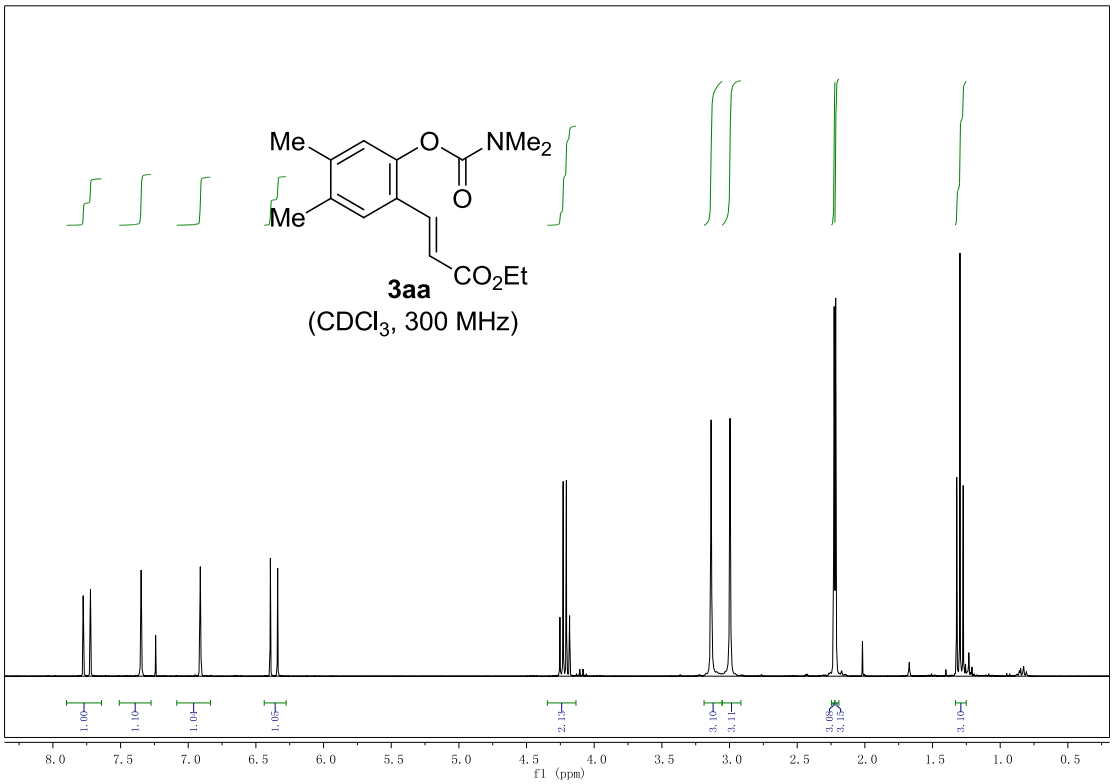

166.46
153.57
150.18
137.12
128.86
128.04
126.64
126.30
123.93
120.11
60.50
36.79
36.42
14.16
Br
O
NMe2
O
CO2Et
3x
(CDCl3, 75 MHz)
f1 (ppm)

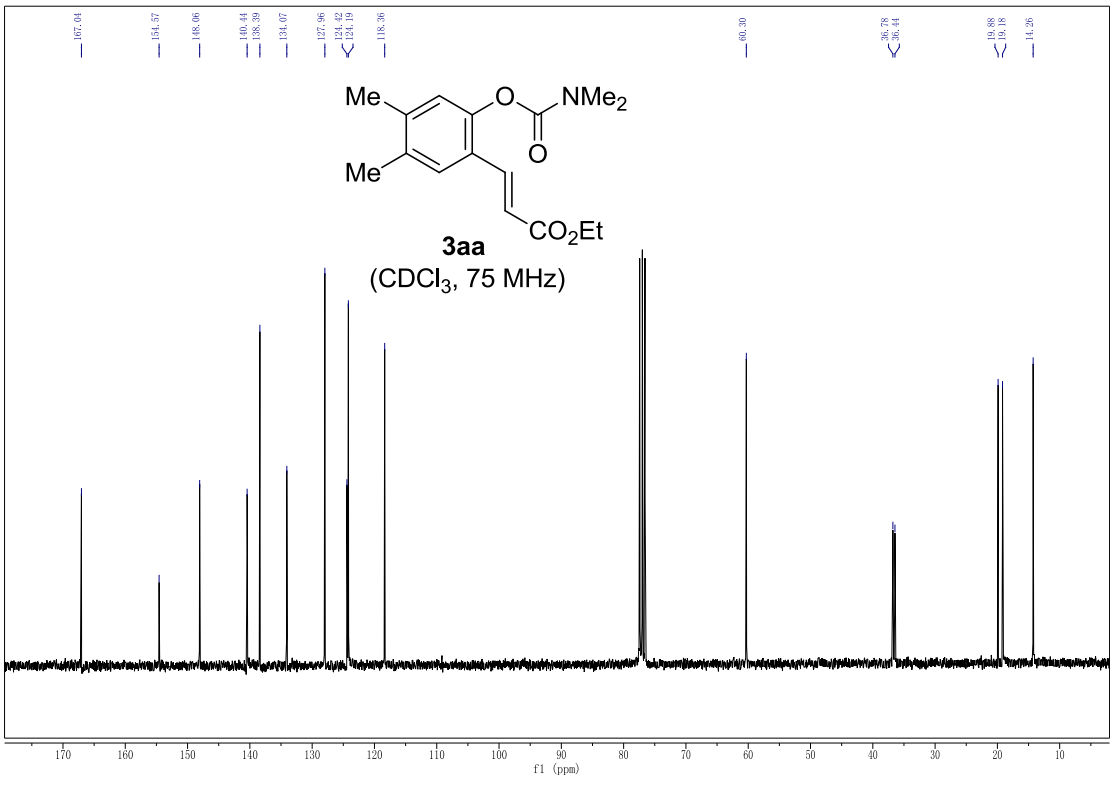

I
O
NMe2
O
CO2Et
3y
(CDCl3, 300 MHz)
f1 (ppm)

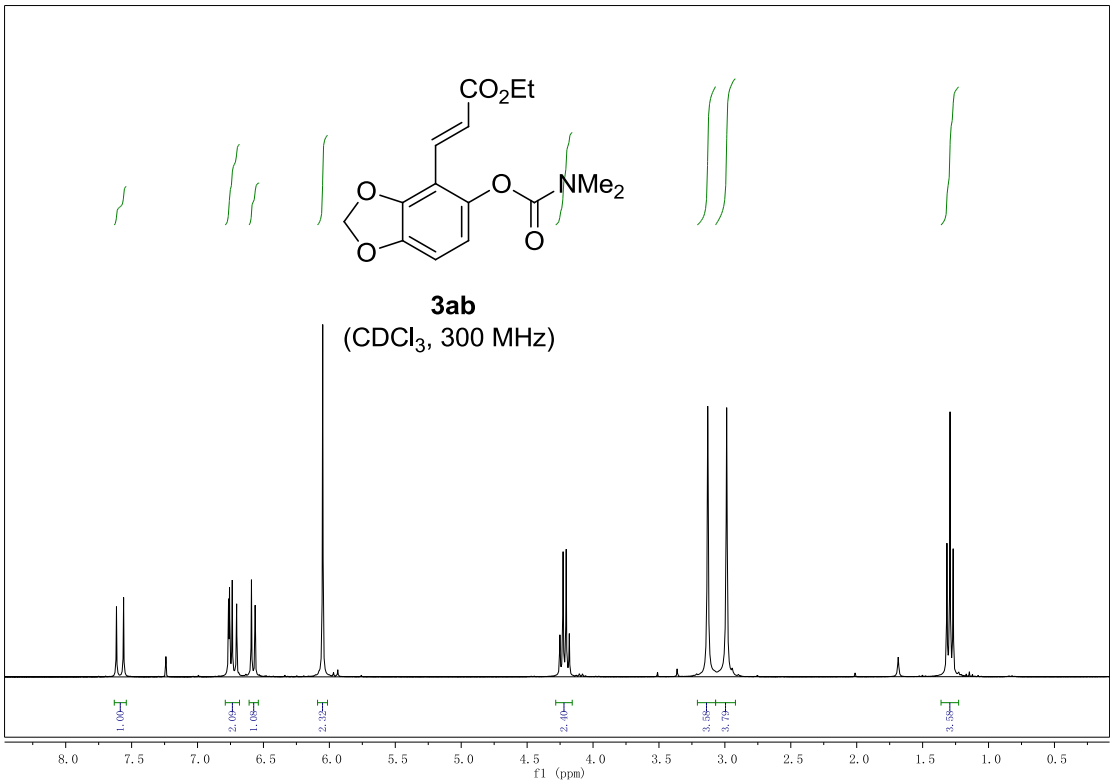

I
O
NMe2
O
CO2Et
3y
(CDCl3, 75 MHz)
f1 (ppm)

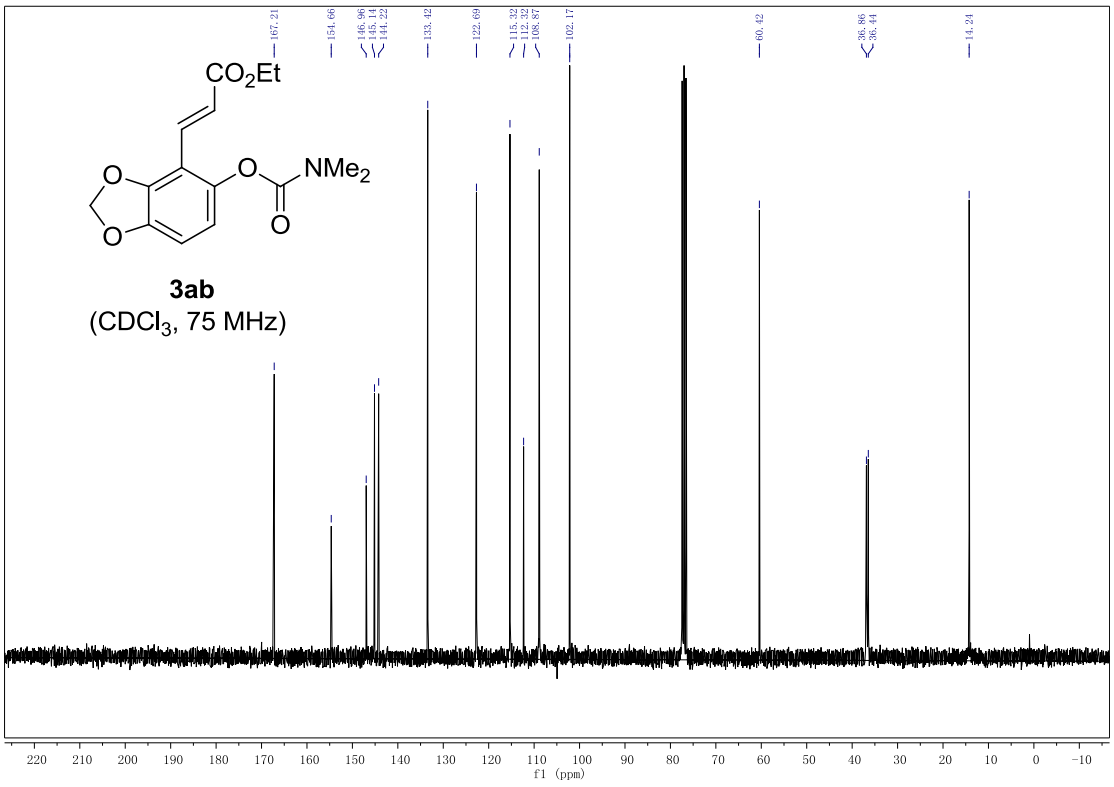

Me
O
O
O
O
NMe2
CO2Et
3z
(CDCl3, 300 MHz)
f1 (ppm)

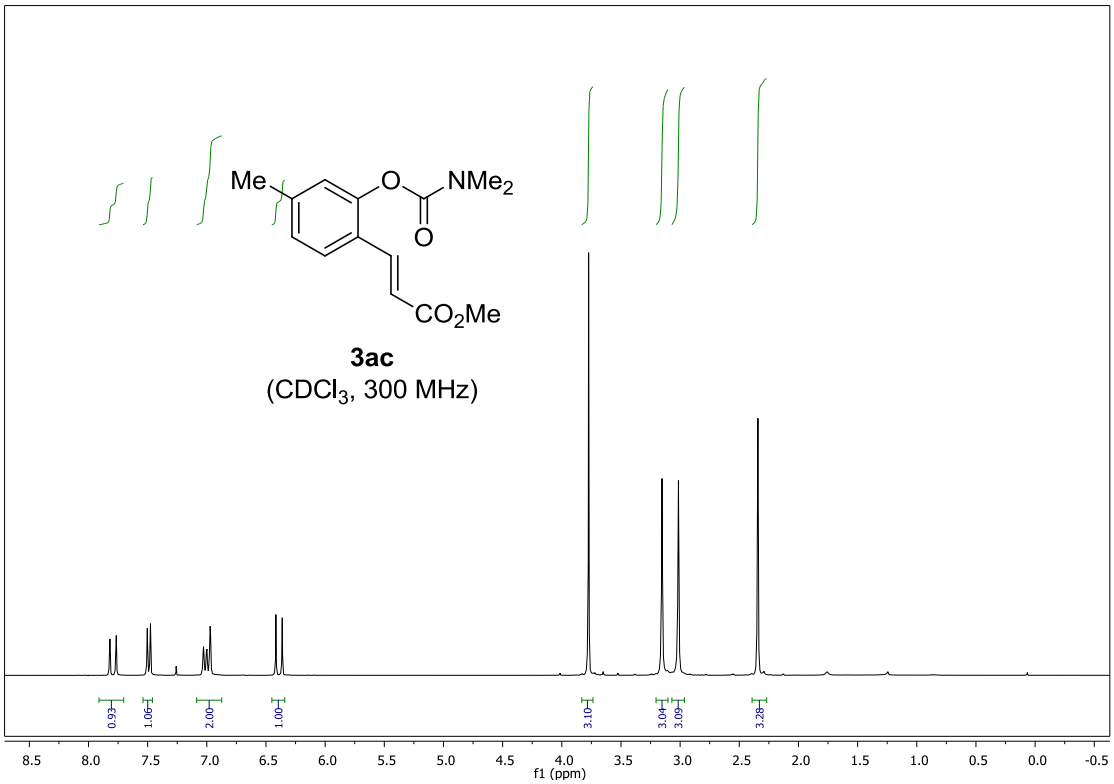

167.02
159.63
153.39
152.68
152.59
152.17
132.23
125.46
119.28
117.56
116.56
114.23
60.65
36.98
36.60
19.00
14.29
Me
O
O
O
O
NMe2
CO2Et
3z
(CDCl3, 75 MHz)
f1 (ppm)

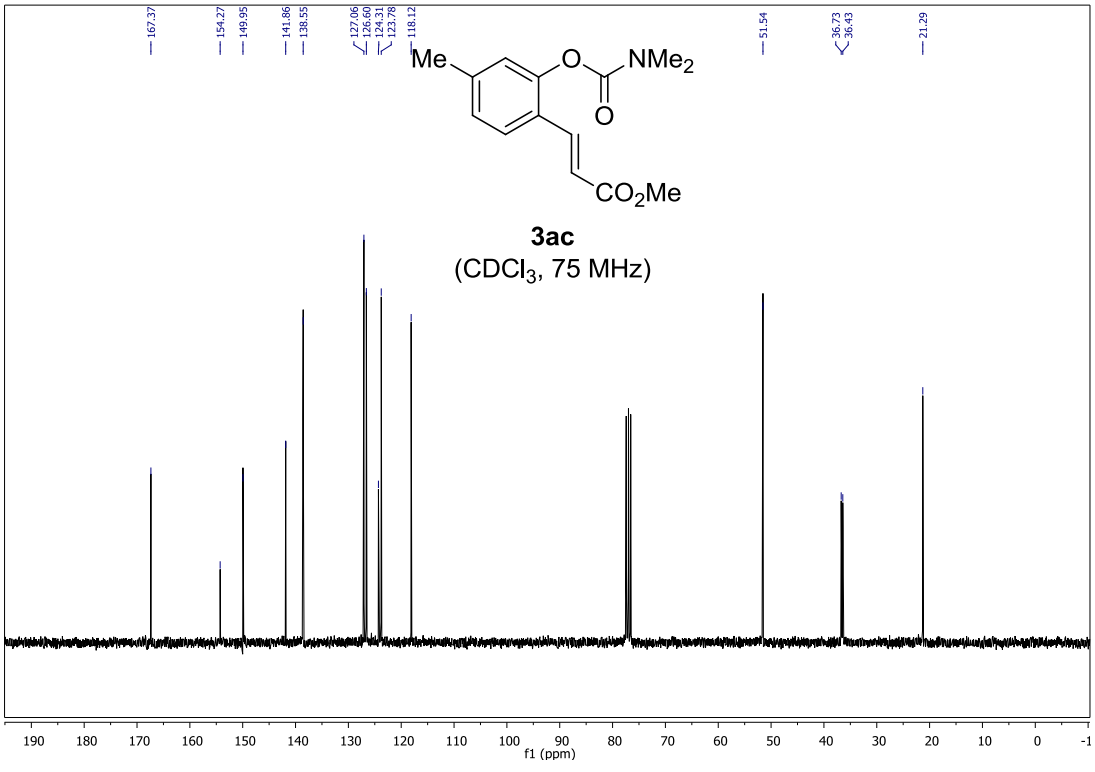

Me
O
NMe2
O
Me
CO2Et
3aa
(CDCl3, 300 MHz)
f1 (ppm)

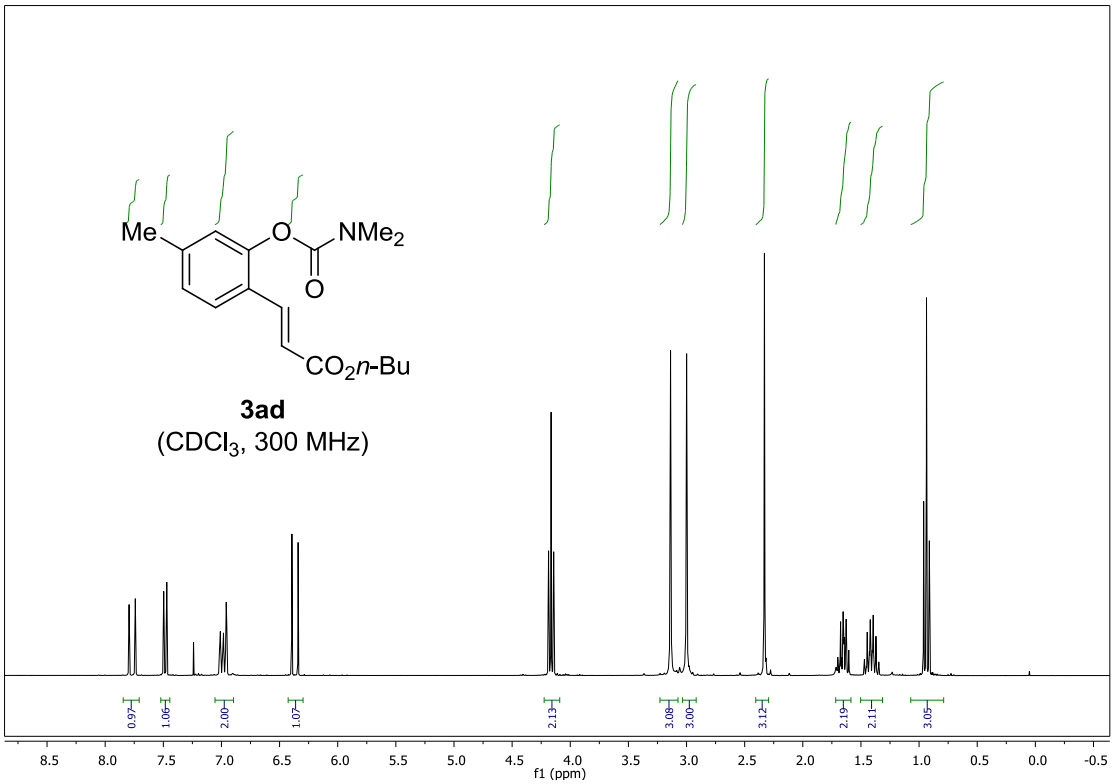

Me
O
NMe2
O
Me
CO2Et
3aa
(CDCl3, 75 MHz)
f1 (ppm)

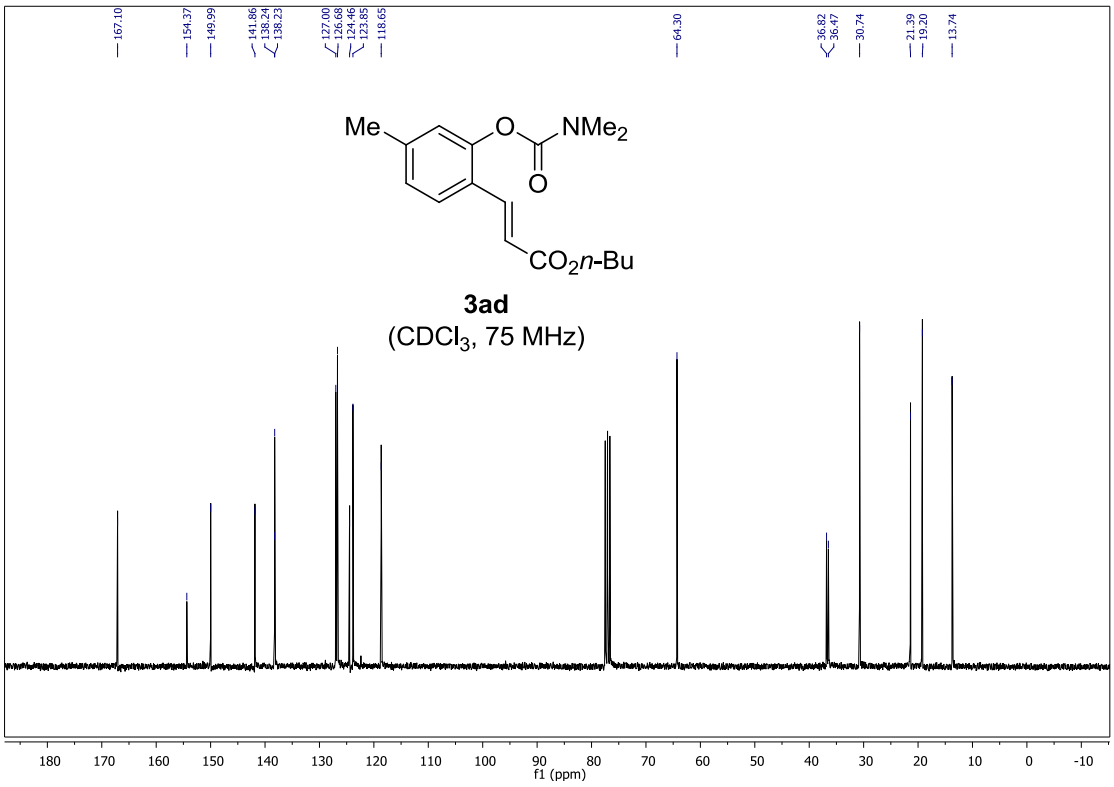


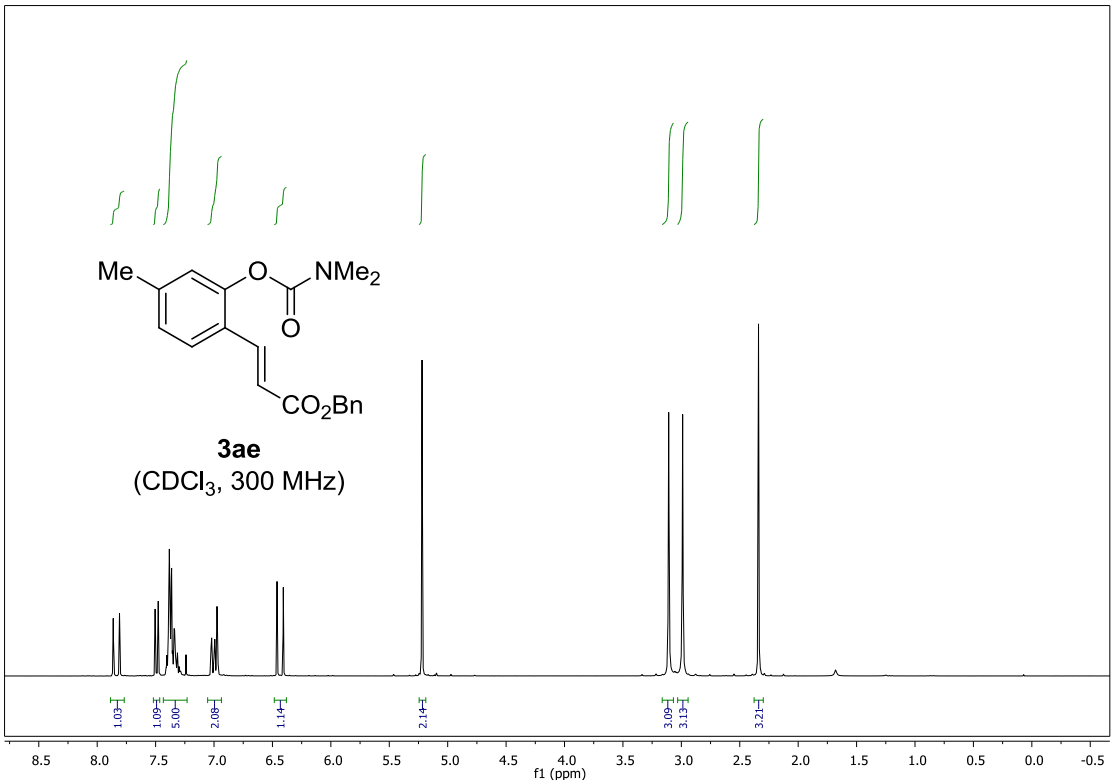



Me
O
NMe2
O
CO2Me
3ac
(CDCl3, 300 MHz)
0.93
1.06
2.00
1.00
3.10
3.04
3.09
3.28
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

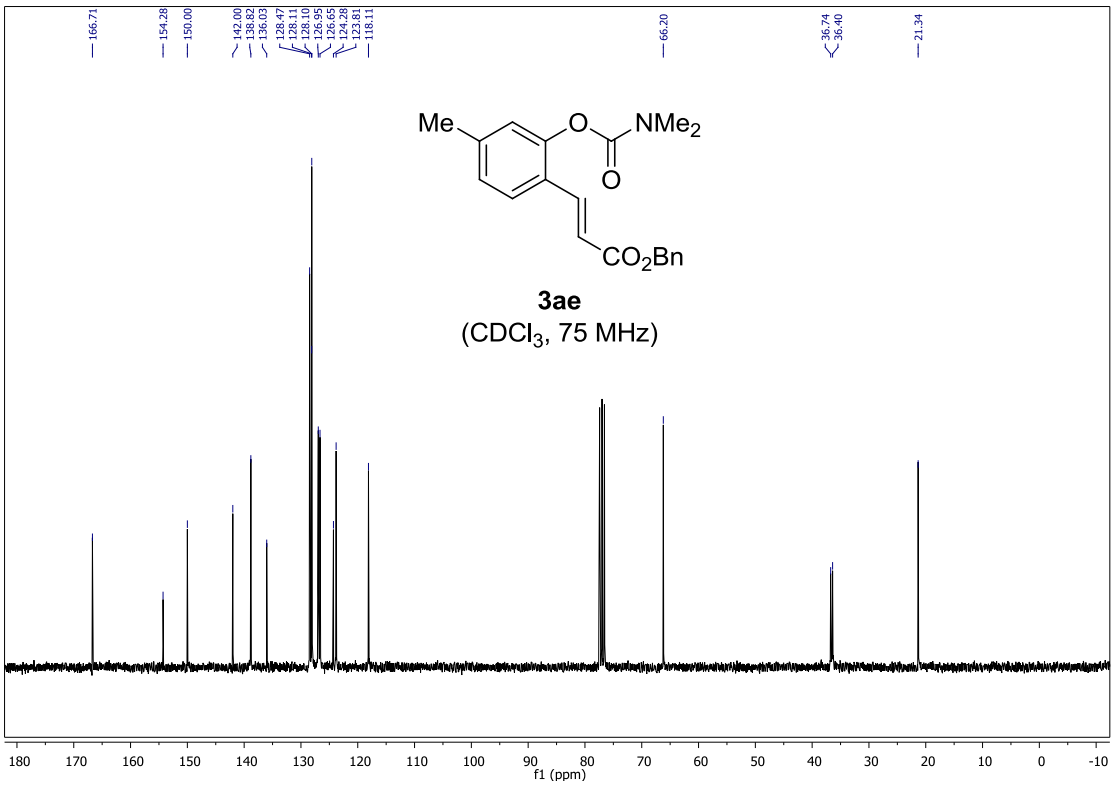

167.37
154.27
149.95
141.86
138.55
127.06
126.60
124.11
123.78
118.12
51.54
36.73
36.43
21.29
Me
O
NMe2
O
CO2Me
3ac
(CDCl3, 75 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Me
O
NMe2
O
CO2n-Bu
3ad
(CDCl3, 300 MHz)
0.97
1.06
2.00
1.07
2.13
3.08
3.00
3.12
2.19
2.11
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

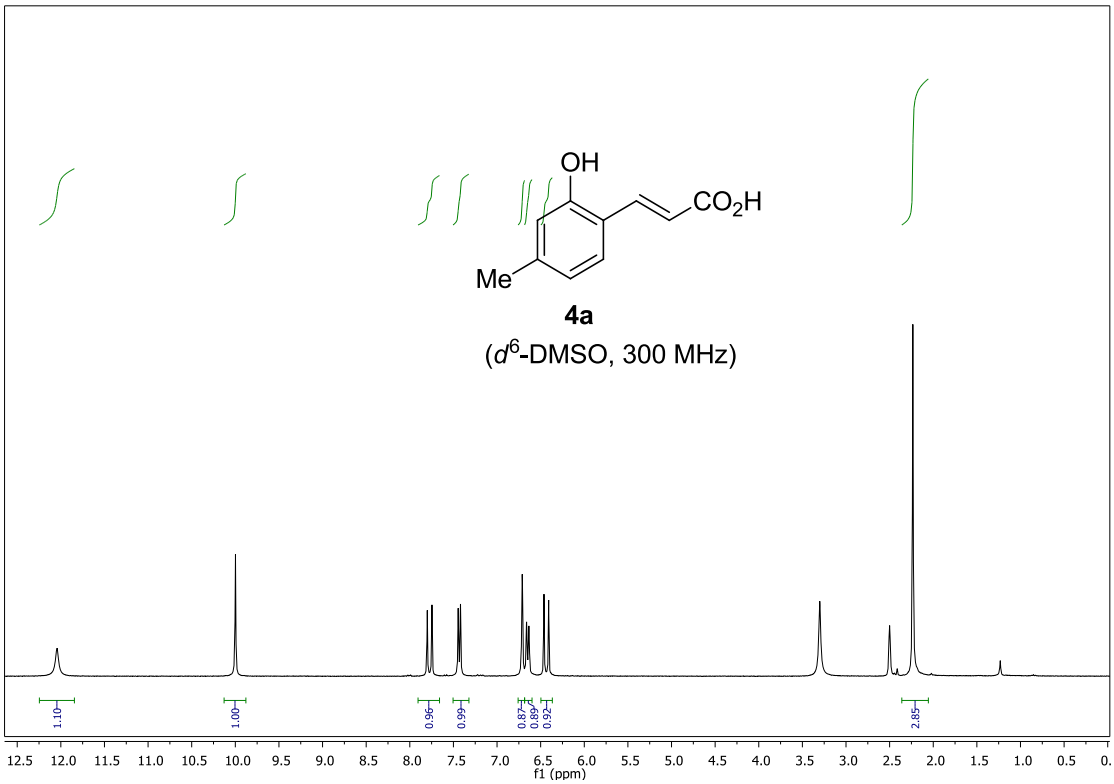

167.10
154.37
149.99
141.86
138.24
138.23
127.00
126.68
124.46
123.85
118.65
64.30
36.82
36.47
30.74
21.39
19.20
13.74
Me
O
NMe2
O
CO2n-Bu
3ad
(CDCl3, 75 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

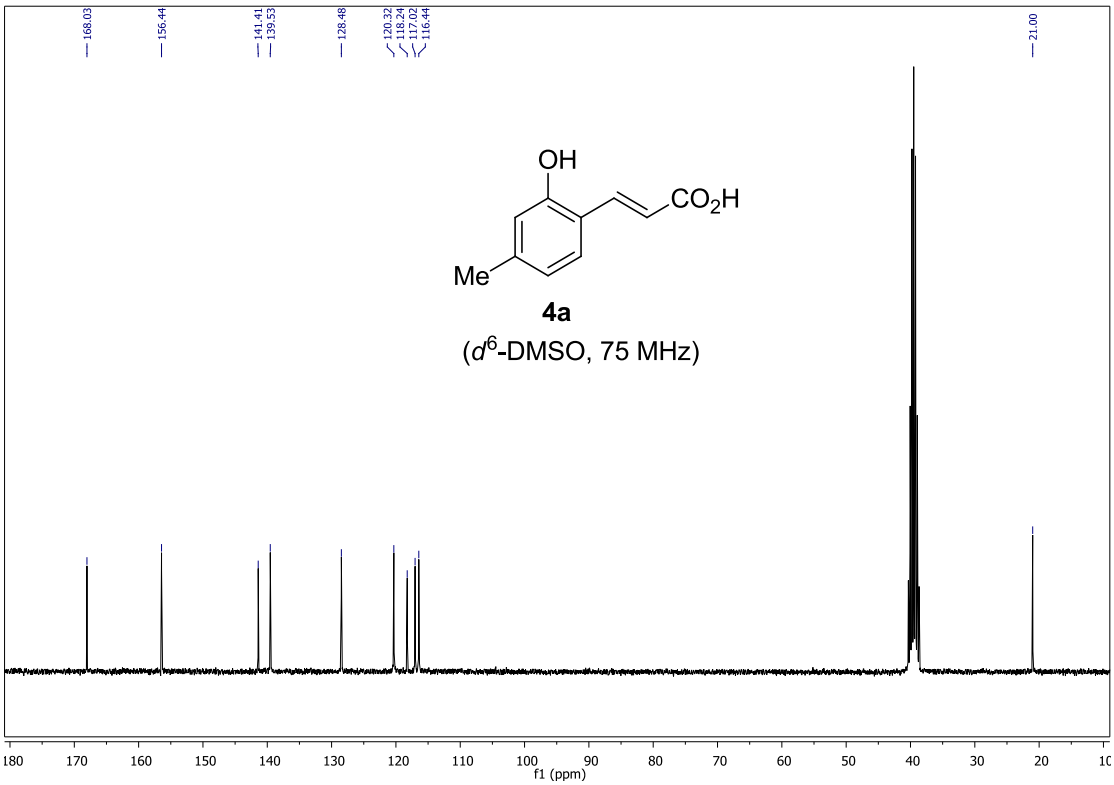


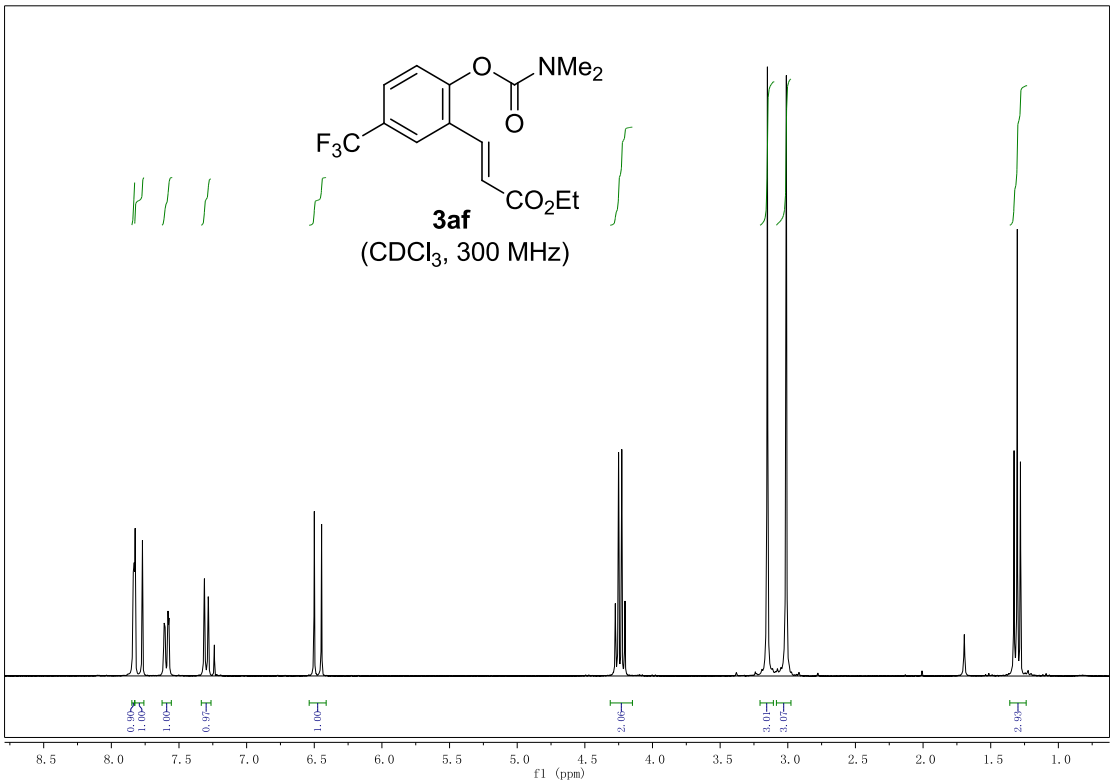
3ae
($CDCl_3$, 300 MHz)

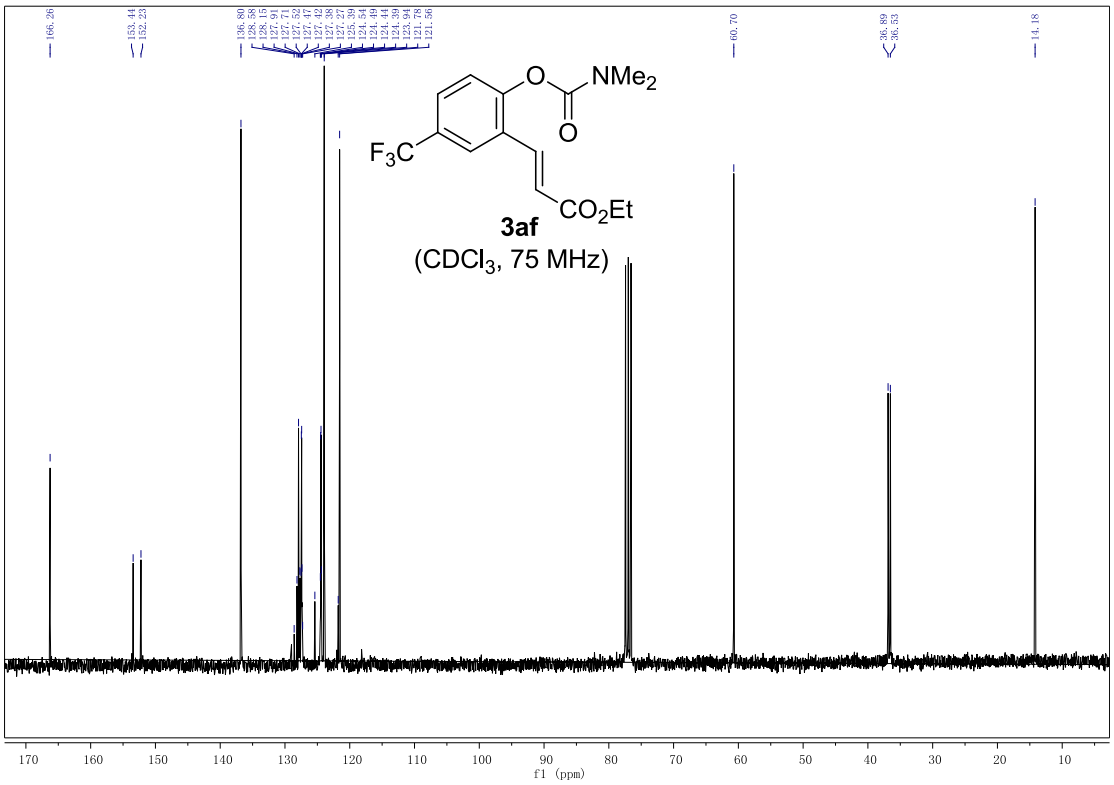


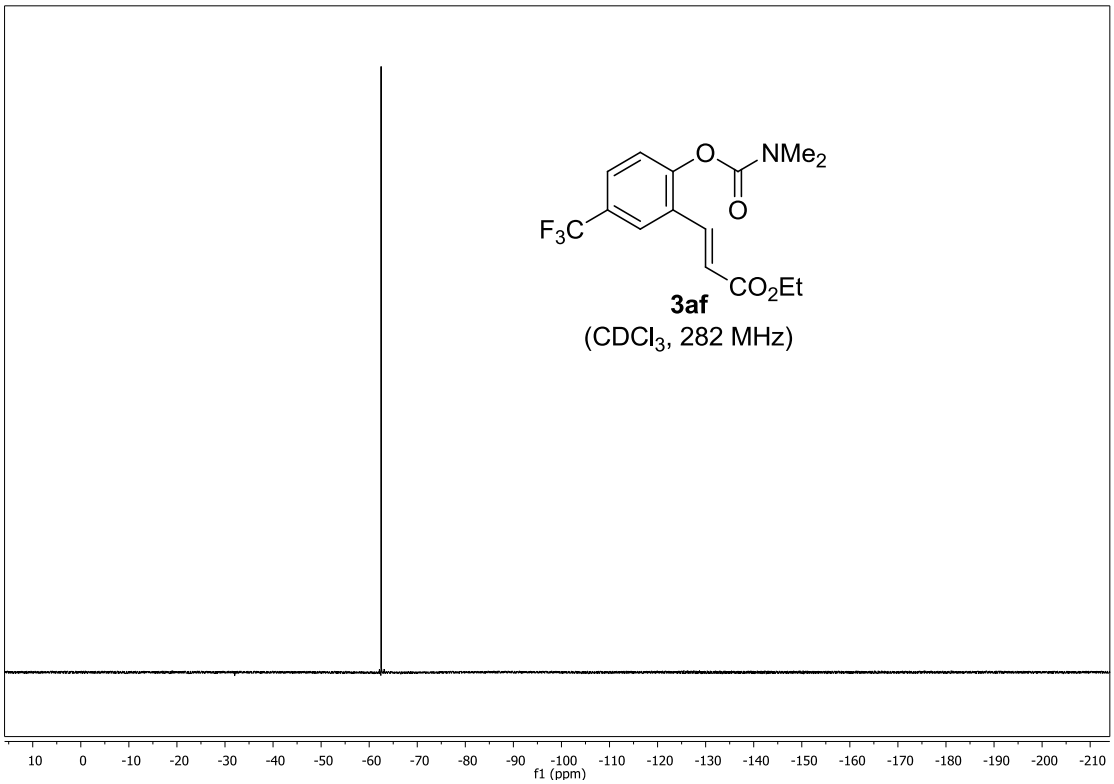
3ae
($CDCl_3$, 75 MHz)


OH
CO2H
Me
4a
(d6-DMSO, 300 MHz)
1.10
1.00
0.96
0.99
0.87
0.89
0.92
2.85
f1 (ppm)


168.03
156.44
141.41
139.53
128.48
120.32
118.24
117.02
116.44
21.00
OH
CO2H
Me
4a
(d6-DMSO, 75 MHz)
f1 (ppm)


O
NMe2
O
F3C
CO2Et
3af
(CDCl3, 300 MHz)
f1 (ppm)


O
NMe2
O
F3C
CO2Et
3af
(CDCl3, 75 MHz)
f1 (ppm)



3af

($CDCl_3$, 282 MHz)