Supporting Information

Palladium-Catalyzed Decarboxylative *Ortho*-Ethoxycarbonylation of *O*-Methyl Ketoximes and 2-Arylpyridines with Potassium Oxalate Monoester

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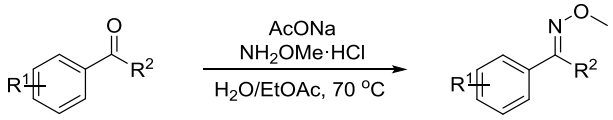
1. General

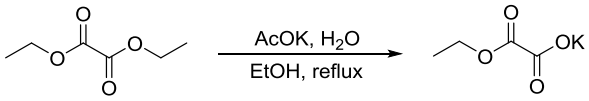
NMR spectra were recorded on a Brucker-400 MHz spectrometer. High-resolution mass spectra (HRMS) were measured with APCI-Orbitrap, or EI-TOF in the positive mode.

2. Substrates Preparation

Ketoxime compounds **1a-q** were synthesized according to the procedure reported in the literature.[1]



Potassium oxalate monoester **2** was synthesized according to the procedure reported in the literature.[2]



3. General Procedures for the Palladium-Catalyzed Decarboxylative *Ortho*-Ethoxycarbonylation of *O*-Methyl Ketoximes and 2-Arylpyridines with Potassium Oxalate Monoester

A mixture of *O*-methyl ketoximes or 2-arylpyridines **1** (0.5 mmol), potassium oxalate monoester **2** (1.0 mmol), $Pd(OAc)_2$ (0.05 mmol), $K_2S_2O_8$ (1.0 mmol), Ag_2CO_3 (1.0 mmol), and D-CSA (0.25 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) was stirred at 90 ℃ for a suitable time. The mixture was filtered by a silica gel plug with ethyl acetate as the eluent and evaporated in vacuum. Product **3** was purified by column chromatography over silica gel using petroleum ether and ethyl acetate (20:1 to 6:1) as the eluent.

4. Mechanistic Studies

4.1 Radical Scavenger 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) Experiment

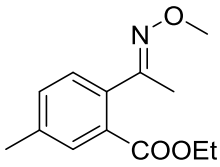
A mixture of **1e** (81.8 mg, 0.5 mmol), potassium oxalate monoester **2** (157.1 mg, 1.0 mmol), $Pd(OAc)_2$ (11.7 mg, 0.05 mmol), $K_2S_2O_8$ (271.0 mg, 1.0 mmol), Ag_2CO_3 (274.7 mg, 1.0 mmol), D-CSA (58.3 mg, 0.25 mmol), and 2,2,6,6-tetramethyl-1-piperidinyloxy (78.2 mg, 0.5 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) was stirred at 90 ℃ for 12 h. Upon completion, the resulting mixture was analyzed by TLC, and it was found that only trace amounts of the desired product **3e** could be identified.

4.2 Kinetic Isotope Experiment

A mixture of **1e** (37.0 mg, 0.25 mmol), **1e-*d*$_5$** (38.0 mg, 0.25 mmol), potassium oxalate monoester **2** (156.8 mg, 1.0 mmol), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol) , $K_2S_2O_8$ (271.2 mg, 1.0 mmol), Ag_2CO_3 (275.7 mg, 1.0 mmol), and D-CSA (58.2 mg, 0.25 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) was stirred at 90 ℃ for 12 h. The mixture was filtered by a silica gel plug with ethyl acetate as the eluent and evaporated in vacuum. The products were purified by column chromatography over silica gel using petroleum ether and ethyl acetate (20:1) as the eluent. The ratio of **3e** and **3e-*d*$_4$** was determined on the basis of ^{1}H NMR spectral analyses. Based on the integrations related to different hydrogen resonances, the kinetic isotope effect was calculated to be $k_H/k_D = 1.6$.

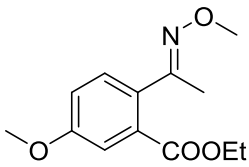
5. Characterization of Products

(*E*)-Ethyl 2-(1-(methoxyimino)ethyl)-5-methylbenzoate (3a)



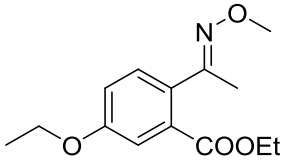
By following the general procedure, the reaction of **1a** (81.4 mg, 0.5 mmol) with **2** (156.4 mg, 1.0 mmol), $Pd(OAc)_2$ (11.5 mg, 0.05 mmol), Ag_2CO_3 (275.4 mg, 1.0 mmol), $K_2S_2O_8$ (270.4 mg, 1.0 mmol), and D-CSA (58.2 mg, 0.25 mmol) afforded **3a** (96.4 mg, 82% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 1.1 Hz, 1H), 7.31 (dd, J = 7.8, 1.1 Hz, 1H) 7.23 (d, J = 7.8 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 2.39 (s, 3H), 2.14 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 157.3, 138.7, 136.0, 132.5, 130.8, 130.1, 129.2, 61.8, 61.3, 21.2, 16.8, 14.2; HRMS (EI-TOF) m/z [M^+] calcd for $C_{13}H_{17}NO_3$ 235.1208; found 235.1219.

(*E*)-Ethyl 5-methoxy-2-(1-(methoxyimino)ethyl)benzoate (3b)



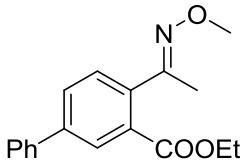
By following the general procedure, the reaction of **1b** (89.7 mg, 0.5 mmol) with **2** (157.1 mg, 1.0 mmol), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol), Ag_2CO_3 (275.6 mg, 1.0 mmol), $K_2S_2O_8$ (271.4 mg, 1.0 mmol), and D-CSA (58.1 mg, 0.25 mmol) afforded **3b** (106.7 mg, 85% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 2.7 Hz, 1H), 7.27 (d, J = 8.5 Hz, 1H), 7.03 (dd, J = 8.5, 2.7 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 3.85 (s, 3H), 2.13 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 159.7, 157.0, 131.6, 131.2, 130.5, 117.7, 115.2, 61.8, 61.5, 55.7, 16.8, 14.2; HRMS (EI-TOF) m/z [M^+] calcd for $C_{13}H_{17}NO_4$ 251.1158; found 251.1157.

(*E*)-Ethyl 5-ethoxy-2-(1-(methoxyimino)ethyl)benzoate (3c)



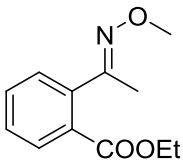
By following the general procedure, the reaction of **1c** (96.4 mg, 0.5 mmol) with **2** (157.1 mg, 1.0 mmol), $Pd(OAc)_2$ (11.5 mg, 0.05 mmol), Ag_2CO_3 (275.1 mg, 1.0 mmol), $K_2S_2O_8$ (270.9 mg, 1.0 mmol), and D-CSA (58.6 mg, 0.25 mmol) afforded **3c** (118.1 mg, 89% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 2.6 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.01 (dd, J = 8.5, 2.6 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.07 (q, J = 7.0 Hz, 2H), 3.93 (s, 3H), 2.13 (s, 3H), 1.42 (t, J = 7.0 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 159.0, 157.1, 131.6, 131.1, 130.5, 118.1, 115.8, 64.0, 61.8, 61.4, 16.8, 14.8, 14.2; HRMS (EI-TOF) m/z [M^+] calcd for $C_{14}H_{19}NO_4$ 265.1314; found 265.1313.

(*E*)-Ethyl 4-(1-(methoxyimino)ethyl)-[1,1'-biphenyl]-3-carboxylate (3d)



By following the general procedure, the reaction of **1d** (112.9 mg, 0.5 mmol) with **2** (157.4 mg, 1.0 mmol), $Pd(OAc)_2$ (11.7 mg, 0.05 mmol), Ag_2CO_3 (276.4 mg, 1.0 mmol), $K_2S_2O_8$ (270.7 mg, 1.0 mmol), and D-CSA (57.6 mg, 0.25 mmol) afforded **3d** (125.2 mg, 84% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 1.9 Hz, 1H), 7.72 (dd, J = 8.0, 1.9 Hz, 1H), 7.62-7.58 (m, 2H), 7.48-7.41 (m, 3H), 7.40-7.35 (m, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 2.20 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 156.9, 141.7, 139.7, 137.5, 130.9, 130.3, 129.7, 129.0 (2C), 128.9, 128.0, 127.2 (2C), 61.9, 61.4, 16.6, 14.2; HRMS (EI-TOF) m/z [M^+] calcd for $C_{18}H_{19}NO_3$ 297.1365; found 297.1366.

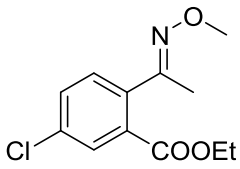
(*E*)-Ethyl 2-(1-(methoxyimino)ethyl)benzoate (3e)[3]



By following the general procedure, the reaction of **1e** (74.5 mg, 0.5 mmol) with **2** (156.4 mg, 1.0 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Ag_2CO_3 (276.1 mg, 1.0 mmol), $K_2S_2O_8$ (270.3 mg, 1.0 mmol), and D-CSA (57.9 mg, 0.25 mmol) afforded **3e** (85.8 mg, 78% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.7, 1.2 Hz, 1H), 7.51 (td, J = 7.5, 1.4 Hz, 2H), 7.42 (td, J = 7.6, 1.3 Hz, 1H), 7.34 (dd, J = 7.6, 1.1 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 2.17 (s, 3H), 1.36 (t, J = 7.1

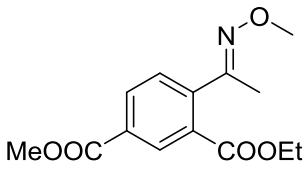
Hz, 3H).

(*E*)-Ethyl 5-chloro-2-(1-(methoxyimino)ethyl)benzoate (3f)



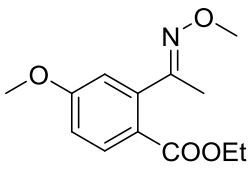
By following the general procedure, the reaction of **1f** (91.2 mg, 0.5 mmol) with **2** (157.0 mg, 1.0 mmol), $Pd(OAc)_2$ (11.5 mg, 0.05 mmol), Ag_2CO_3 (274.6 mg, 1.0 mmol), $K_2S_2O_8$ (271.2 mg, 1.0 mmol), and D-CSA (58.6 mg, 0.25 mmol) afforded **3f** (90.3 mg, 71% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 2.2 Hz, 1H), 7.48 (dd, J = 8.2, 2.2 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 2.14 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 156.3, 137.2, 134.7, 131.9 (2C), 130.7, 130.3, 62.0, 61.8, 16.6, 14.2; HRMS (EI-TOF) m/z [M^+] calcd for $C_{12}H_{14}NO_3{}^{35}Cl$ 255.0662; found 255.0665.

(*E*)-3-Ethyl 1-methyl 4-(1-(methoxyimino)ethyl)isophthalate (3g)



By following the general procedure, the reaction of **1g** (103.7 mg, 0.5 mmol) with **2** (158.1 mg, 1.0 mmol), $Pd(OAc)_2$ (11.9 mg, 0.05 mmol), Ag_2CO_3 (274.4 mg, 1.0 mmol), $K_2S_2O_8$ (270.8 mg, 1.0 mmol), and D-CSA (58.4 mg, 0.25 mmol) afforded **3g** (76.8 mg, 55% yield). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 1.7 Hz, 1H), 8.16 (dd, J = 8.0, 1.7 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 2.17 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.0, 156.5, 142.8, 132.7, 131.5, 130.8, 130.5, 129.6, 62.1, 61.7, 52.6, 16.5, 14.2; HRMS (EI-TOF) m/z [M^+] calcd for $C_{14}H_{17}NO_5$ 279.1107; found 279.1113.

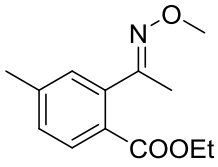
(*E*)-Ethyl 4-methoxy-2-(1-(methoxyimino)ethyl)benzoate (3h)[3]



By following the general procedure, the reaction of **1h** (88.7 mg, 0.5 mmol) with **2** (156.9 mg, 1.0 mmol), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol), Ag_2CO_3 (276.1 mg, 1.0 mmol), $K_2S_2O_8$ (271.3 mg, 1.0 mmol), and D-CSA (58.2 mg, 0.25 mmol) afforded **3h** (106.8 mg, 85% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 1H), 6.91 (dd, J = 8.7, 2.6 Hz, 1H), 6.81 (d, J = 2.6 Hz, 1H), 4.30 (q, J = 7.1 Hz,

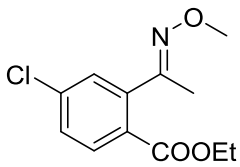
2H), 3.96 (s, 3H), 3.86 (s, 3H), 2.15 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).

(*E*)-Ethyl 2-(1-(methoxyimino)ethyl)-4-methylbenzoate (3i)[3]



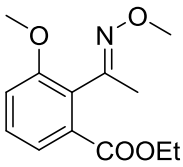
By following the general procedure, the reaction of **1i** (79.7 mg, 0.5 mmol) with **2** (156.4 mg, 1.0 mmol), $Pd(OAc)_2$ (11.7 mg, 0.05 mmol), Ag_2CO_3 (274.4 mg, 1.0 mmol), $K_2S_2O_8$ (274.1 mg, 1.0 mmol), and D-CSA (57.9 mg, 0.25 mmol) afforded **3i** (98.7 mg, 84% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 1H), 7.22 (dd, J = 7.9, 0.8 Hz, 1H), 7.14 (d, J = 0.8 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 2.39 (s, 3H), 2.14 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).

(*E*)-Ethyl 4-chloro-2-(1-(methoxyimino)ethyl)benzoate (3j)[3]



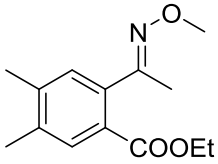
By following the general procedure, the reaction of **1j** (92.1 mg, 0.5 mmol) with **2** (156.7 mg, 1.0 mmol), $Pd(OAc)_2$ (12.0 mg, 0.05 mmol), Ag_2CO_3 (274.9 mg, 1.0 mmol), $K_2S_2O_8$ (270.9 mg, 1.0 mmol), and D-CSA (58.1 mg, 0.25 mmol) afforded **3j** (88.2 mg, 69% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 1H), 7.40 (dd, J = 8.4, 2.1 Hz, 1H), 7.34 (d, J = 2.1 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 2.14 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H).

(*E*)-Ethyl 3-methoxy-2-(1-(methoxyimino)ethyl)benzoate (3k)



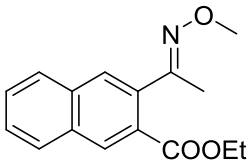
By following the general procedure, the reaction of **1k** (89.8 mg, 0.5 mmol) with **2** (157.1 mg, 1.0 mmol), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol), Ag_2CO_3 (275.1 mg, 1.0 mmol), $K_2S_2O_8$ (270.7 mg, 1.0 mmol), and D-CSA (58.0 mg, 0.25 mmol) afforded **3k** (91.7 mg, 73% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.8, 0.8 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 2.10 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 157.8, 155.6, 132.7, 129.5, 127.5, 121.9, 114.2, 61.7, 61.2, 56.1, 16.5, 14.2; HRMS (EI-TOF) m/z [M^+] calcd for $C_{13}H_{17}NO_4$ 251.1158; found 251.1163.

(*E*)-Ethyl 2-(1-(methoxyimino)ethyl)-4,5-dimethylbenzoate (3l)



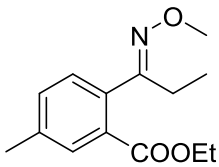
By following the general procedure, the reaction of **1l** (88.8 mg, 0.5 mmol) with **2** (156.6 mg, 1.0 mmol), $Pd(OAc)_2$ (11.7 mg, 0.05 mmol), Ag_2CO_3 (276.1 mg, 1.0 mmol), $K_2S_2O_8$ (271.2 mg, 1.0 mmol), and D-CSA (58.1 mg, 0.25 mmol) afforded **3l** (96.0 mg, 77% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.10 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 2.29 (s, 6H), 2.13 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 157.8, 141.4, 137.2, 136.7, 131.6, 130.6, 127.2, 61.8, 61.1, 19.9, 19.5, 17.1, 14.3; HRMS (EI-TOF) m/z [M^+] calcd for $C_{14}H_{19}NO_3$ 249.1365; found 249.1362.

(*E*)-Ethyl 3-(1-(methoxyimino)ethyl)-2-naphthoate (3m)[3]



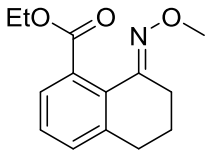
By following the general procedure, the reaction of **1m** (99.0 mg, 0.5 mmol) with **2** (157.0 mg, 1.0 mmol), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol), Ag_2CO_3 (275.2 mg, 1.0 mmol), $K_2S_2O_8$ (271.0 mg, 1.0 mmol), and D-CSA (58.4 mg, 0.25 mmol) afforded **3m** (113.9 mg, 85% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H) 7.82 (s, 1H), 7.61-7.51 (m, 2H), 4.39 (q, J = 7.1 Hz, 2H), 4.00 (s, 3H), 2.23 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H).

(*E*)-Ethyl 2-(1-(methoxyimino)propyl)-5-methylbenzoate (3n)



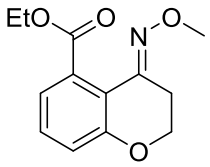
By following the general procedure, the reaction of **1n** (88.3 mg, 0.5 mmol) with **2** (157.2 mg, 1.0 mmol), $Pd(OAc)_2$ (11.6 mg, 0.05 mmol), Ag_2CO_3 (275.1 mg, 1.0 mmol), $K_2S_2O_8$ (271.2 mg, 1.0 mmol), and D-CSA (58.0 mg, 0.25 mmol) afforded **3n** (96.7 mg, 84% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 1.1 Hz, 1H), 7.32 (dd, J = 7.8, 1.1 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 3.91 (s, 3H), 2.67 (q, J = 7.6 Hz, 2H), 2.39 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 162.5, 138.6, 134.7, 132.5, 130.9, 130.4, 129.7, 61.8, 61.2, 23.6, 21.2, 14.2, 10.3; HRMS (EI-TOF) m/z [M^+] calcd for $C_{14}H_{19}NO_3$ 249.1365; found 249.1355.

(*E*)-Ethyl 8-(methoxyimino)-5,6,7,8-tetrahydronaphthalene-1-carboxylate (3o)[3]



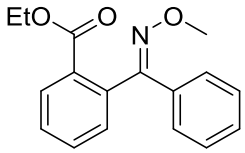
By following the general procedure, the reaction of **1o** (87.9 mg, 0.5 mmol) with **2** (157.5 mg, 1.0 mmol), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol), Ag_2CO_3 (275.6 mg, 1.0 mmol), $K_2S_2O_8$ (270.7 mg, 1.0 mmol), and D-CSA (58.9 mg, 0.25 mmol) afforded **3o** (92.3 mg, 75% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.23-7.18 (m, 1H), 4.32 (q, J = 7.2 Hz, 2H), 3.92 (s, 3H), 2.76-2.69 (m, 4H), 1.88-1.81 (m, 2H), 1.36 (t, J = 7.2 Hz, 3H).

(*E*)-Ethyl 4-(methoxyimino)chroman-5-carboxylate (3p)



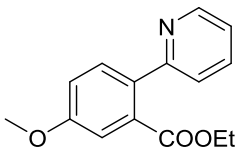
By following the general procedure, the reaction of **1p** (88.4 mg, 0.5 mmol) with **2** (157.5 mg, 1.0 mmol), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol), Ag_2CO_3 (276.1 mg, 1.0 mmol), $K_2S_2O_8$ (270.4 mg, 1.0 mmol), and D-CSA (58.0 mg, 0.25 mmol) afforded **3p** (87.2 mg, 70% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.9 Hz, 1H), 6.98-6.93 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 4.22 (t, J = 6.3 Hz, 2H), 3.93 (s, 3H), 2.93 (t, J = 6.3 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 157.3, 146.8, 132.3, 130.3, 121.0, 119.3, 115.9, 65.1, 62.3, 61.5, 24.7, 14.2; HRMS (EI-TOF) m/z [M^+] calcd for $C_{13}H_{15}NO_4$ 249.1001; found 249.0992.

(*E*)-Ethyl 2-((methoxyimino)(phenyl)methyl)benzoate (3q)



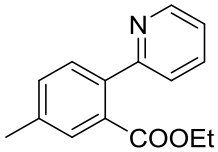
By following the general procedure, the reaction of **1q** (105.9 mg, 0.5 mmol) with **2** (157.2 mg, 1.0 mmol), $Pd(OAc)_2$ (11.6 mg, 0.05 mmol), Ag_2CO_3 (275.0 mg, 1.0 mmol), $K_2S_2O_8$ (271.6 mg, 1.0 mmol), and D-CSA (58.3 mg, 0.25 mmol) afforded **3q** (92.7 mg, 78% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 7.6, 1.3 Hz, 1H), 7.54-7.48 (m, 3H), 7.45 (td, J = 7.5, 1.5 Hz, 1H), 7.40 (dd, J = 7.5, 1.3 Hz, 1H), 7.38-7.32 (m, 3H), 4.11 (q, J = 7.1 Hz, 2H), 3.99 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 156.2, 137.7, 133.3, 132.3, 131.4, 131.1, 130.2 (2C), 130.0, 129.3, 128.9, 127.9 (2C), 62.6, 61.2, 14.1; HRMS (EI-TOF) m/z [M^+] calcd for $C_{17}H_{17}NO_3$ 283.1208; found 283.1202.

Ethyl 2-(pyridin-2-yloxy)benzoate (3r)



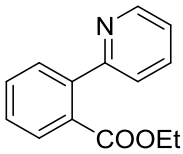
By following the general procedure, the reaction of **1r** (92.8 mg, 0.5 mmol) with **2** (157.7 mg, 1.0 mmol), $Pd(OAc)_2$ (11.5 mg, 0.05 mmol), Ag_2CO_3 (276.4 mg, 1.0 mmol), $K_2S_2O_8$ (272.4 mg, 1.0 mmol), and D-CSA (58.0 mg, 0.25 mmol) afforded **3r** (52.4 mg, 41% yield). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.71 (ddd, J = 7.9, 7.5, 1.8 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.43 (ddd, J = 7.9, 1.1, 0.9 Hz, 1H), 7.33 (d, J = 2.7 Hz, 1H), 7.21 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 7.07 (dd, J = 8.5, 2.7 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 159.6, 158.6, 149.0, 136.2, 133.5, 133.2, 131.1, 122.8, 121.7, 117.0, 114.7, 61.2, 55.7, 13.9; HRMS (APCI-Orbitrap): m/z $[M + H]^+$ calcd for $C_{15}H_{16}NO_3^+$ 258.1125; found 258.1125.

Ethyl 5-methyl-2-(pyridin-2-yl)benzoate (3s)[3]



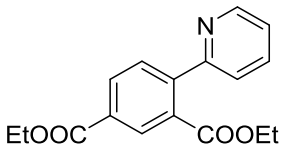
By following the general procedure, the reaction of **1s** (84.6 mg, 0.5 mmol) with **2** (156.7 mg, 1.0 mmol), $Pd(OAc)_2$ (11.7 mg, 0.05 mmol), Ag_2CO_3 (274.2 mg, 1.0 mmol), $K_2S_2O_8$ (270.1 mg, 1.0 mmol), and D-CSA (58.4 mg, 0.25 mmol) afforded **3s** (84.7 mg, 70% yield). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 4.9 Hz, 1H), 7.72 (td, J = 7.7, 1.6 Hz, 1H), 7.63 (s, 1H), 7.47-7.42 (m, 2H), 7.36 (d, J = 7.7 Hz, 1H), 7.23 (dd, J = 7.1, 4.9 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H).

Ethyl 2-(pyridin-2-yl)benzoate (3t)[3]



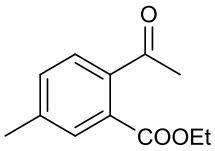
By following the general procedure, the reaction of **1t** (77.6 mg, 0.5 mmol) with **2** (153.1 mg, 1.0 mmol), $Pd(OAc)_2$ (11.4 mg, 0.05 mmol), Ag_2CO_3 (275.4 mg, 1.0 mmol), $K_2S_2O_8$ (271.0 mg, 1.0 mmol), and D-CSA (58.5 mg, 0.25 mmol) afforded **3t** (83.8 mg, 74% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.8 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.75 (td, J = 7.7, 1.7 Hz, 1H), 7.59-7.53 (m, 2H), 7.51-7.44 (m, 2H), 7.28-7.24 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 1.05 (t, J = 7.2 Hz, 3H).

Diethyl 4-(pyridin-2-yl)isophthalate (3u)



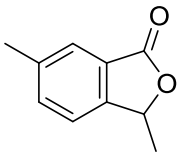
By following the general procedure, the reaction of **1u** (114.2 mg, 0.5 mmol) with **2** (156.3 mg, 1.0 mmol), $Pd(OAc)_2$ (11.7 mg, 0.05 mmol), Ag_2CO_3 (276.2 mg, 1.0 mmol), $K_2S_2O_8$ (271.6 mg, 1.0 mmol), and D-CSA (58.1 mg, 0.25 mmol) afforded **3u** (109.2 mg, 73% yield). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.7 Hz, 1H), 8.48 (d, J = 1.8 Hz, 1H), 8.22 (dd, J = 8.0, 1.8 Hz, 1H), 7.78 (ddd, J = 7.8, 7.6, 1.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.50 (dt, J = 7.8, 1.0 Hz, 1H), 7.30 (ddd, J = 7.6, 4.7, 1.0 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 165.7, 157.9, 149.3, 144.8, 136.5, 132.4, 132.0, 131.0, 130.5, 130.0, 123.0, 122.7, 61.5, 61.4, 14.4, 13.9; HRMS (APCI-Orbitrap): m/z $[M + H]^+$ calcd for $C_{17}H_{18}NO_4^+$ 300.1230; found 300.1229.

Ethyl 2-acetyl-5-methylbenzoate (4a)[4]



A 15 mL-vial equipped with a magnetic stirrer was charged with **3a** (47.0 mg, 0.2 mmol) and EtOH (1 mL). Then 37 wt. % formaldehyde solution (1 mL) and concentrated hydrochloric acid (160 μL) was added and the mixture was stirred and heated at 30 ℃ for 24 h. The reaction was diluted with ethyl acetate (10 mL). The mixture was concentrated under reduced pressure and then purified by flash column chromatography to give product **4a** (29.7 mg, 72%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.53 (s, 3H), 2.42 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 167.8, 141.1, 139.1, 132.2, 130.2, 130.1, 127.2, 61.8, 29.8, 21.4, 14.1; HRMS (APCI-Orbitrap): m/z $[M + H]^+$ calcd for $C_{12}H_{15}O_3^+$ 207.1016; found 207.1017.

3,5-Dimethylisobenzofuran-1(3H)-one (5a)[5]



Compound **4a** (48.2 mg, 0.234 mmol) was dissolved in EtOH (2 mL). Then, $NaBH_4$ (13.7 mg, 0.362 mmol) was added, and the solution heated to 60 ℃ for 3 h. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography to give the product **5a** (27.2 mg, 73%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 5.53 (q, J = 6.6 Hz, 1H), 2.47 (s, 3H), 1.61 (d, J = 6.6 Hz, 3H) ; ^{13}C NMR

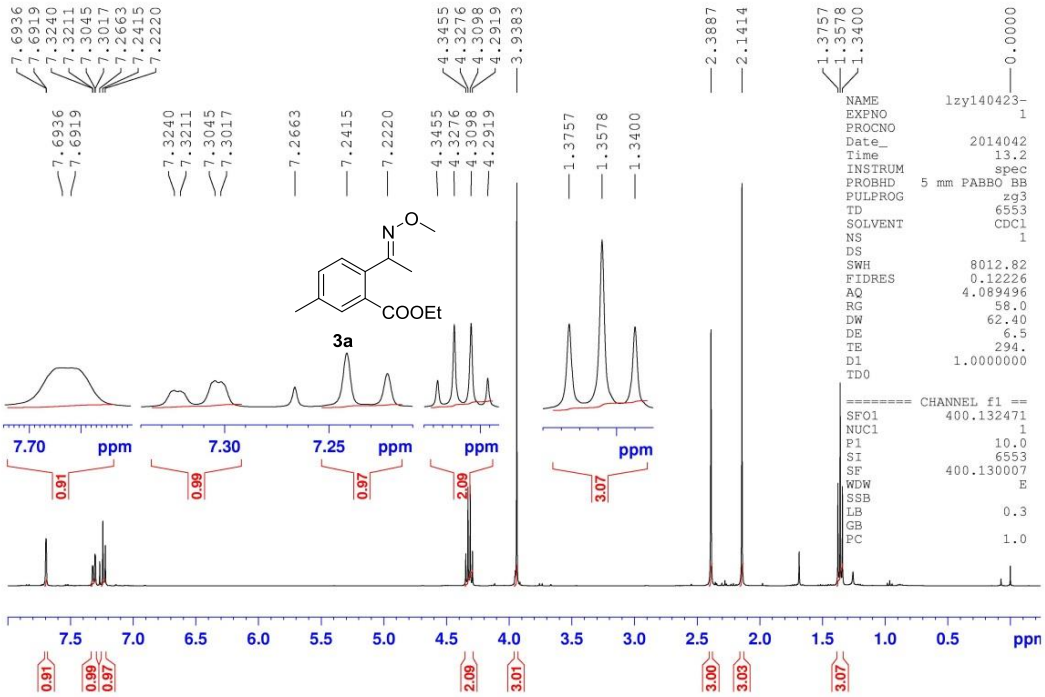
(100 MHz, $CDCl_3$) δ 170.8, 148.8, 139.4, 135.3, 126.1, 125.8, 121.4, 77.8, 21.4, 20.6; HRMS (APCI-Orbitrap): m/z $[M + H]^+$ calcd for $C_{10}H_{11}O_2^+$ 163.0754; found 163.0754.

6. References

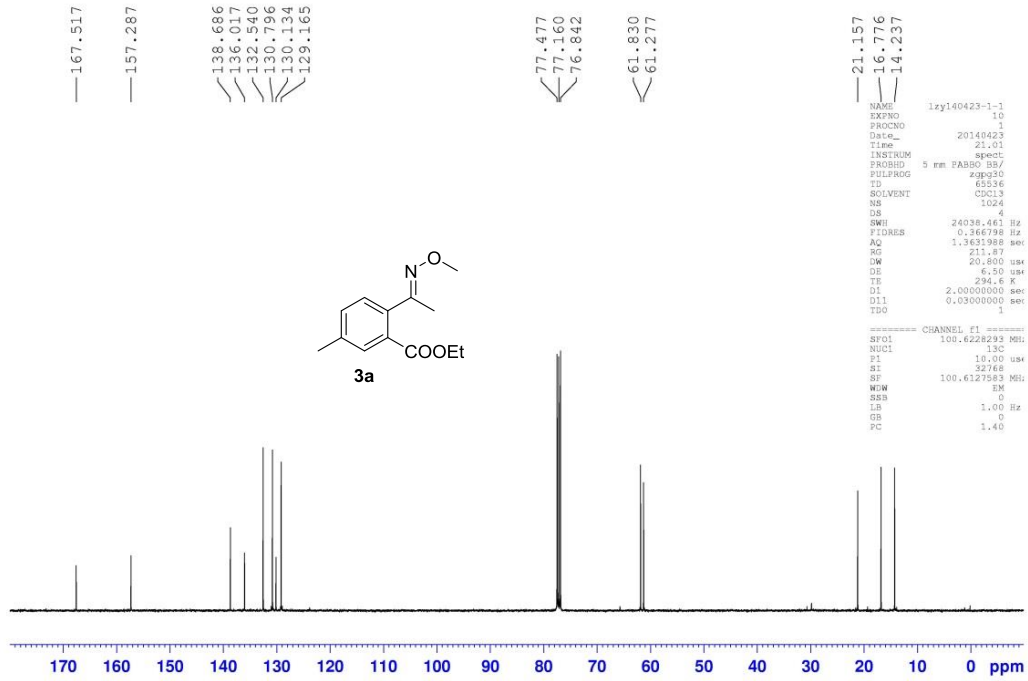
(1) Tsai, A. S.; Brasse, M.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2011**, *13*, 540.
(2) Shang, R.; Fu, Y.; Li, J.-B.; Zhang, S.-L.; Guo, Q.-X.; Liu, L. *J. Am. Chem. Soc.* **2009**, *131*, 5738.
(3) Yu, W.-Y.; Sit, W. N.; Lai, K.-M.; Zhou, Z.; Chan, A. S. C. *J. Am. Chem. Soc.* **2008**, *130*, 3304.
(4) Chan, W.-W.; Lo, S.-F.; Zhou, Z.; Yu, W.-Y. *J. Am. Chem. Soc.* **2012**, *134*, 13565.
(5) Salerno, C. P.; Cleaves, H. J. *Synth. Commun.* **2004**, *34*, 2379.

7. NMR Spectra

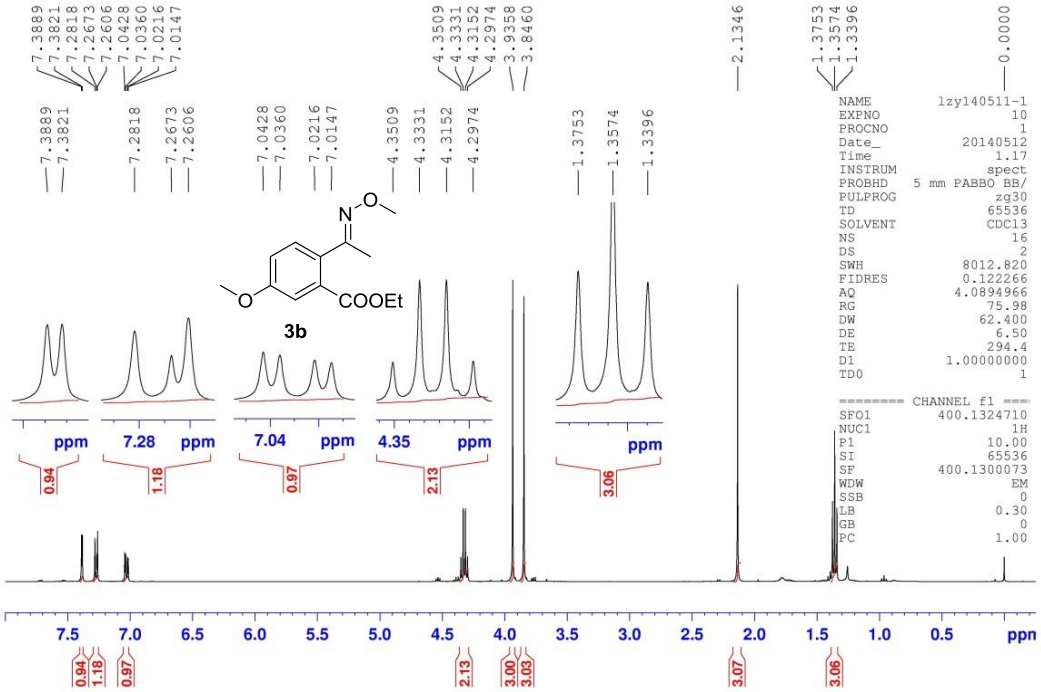
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3a



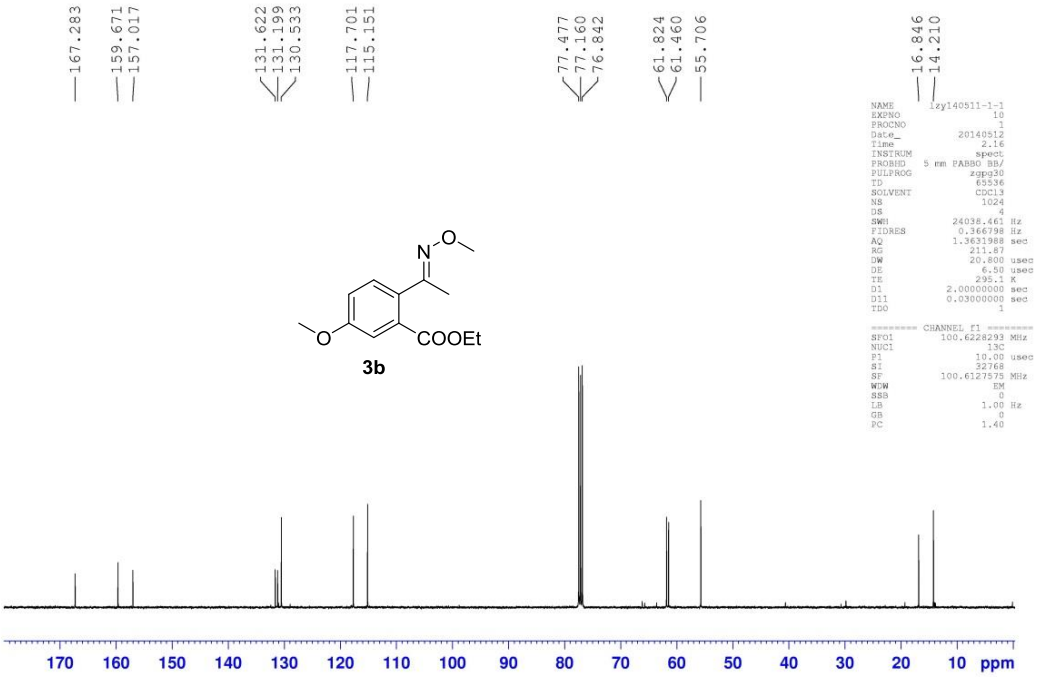
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3a



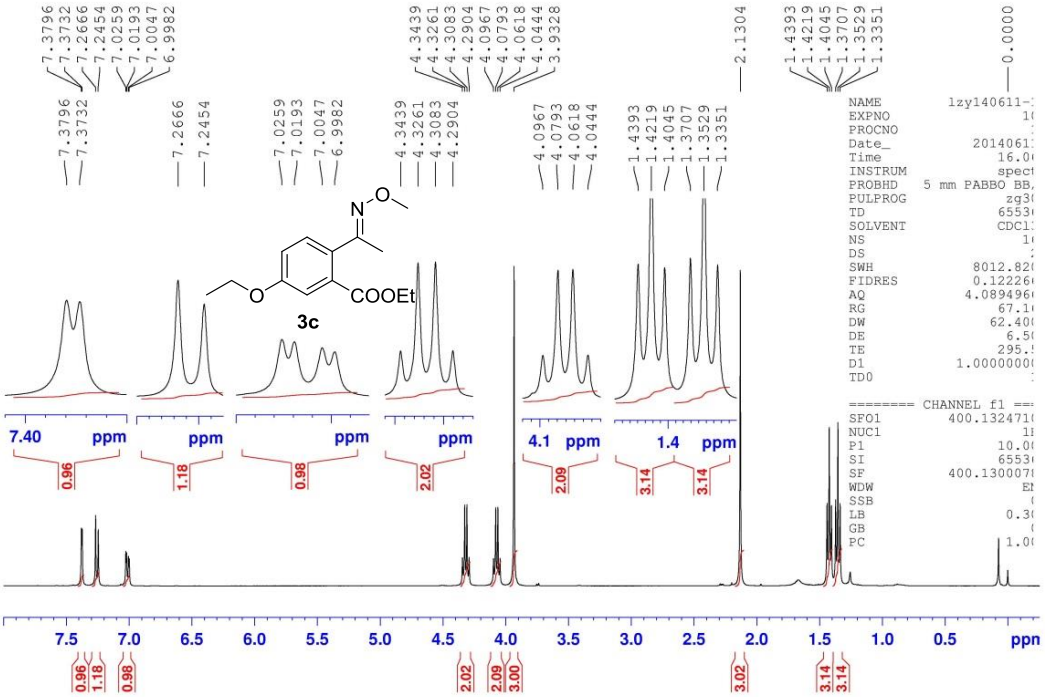
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3b



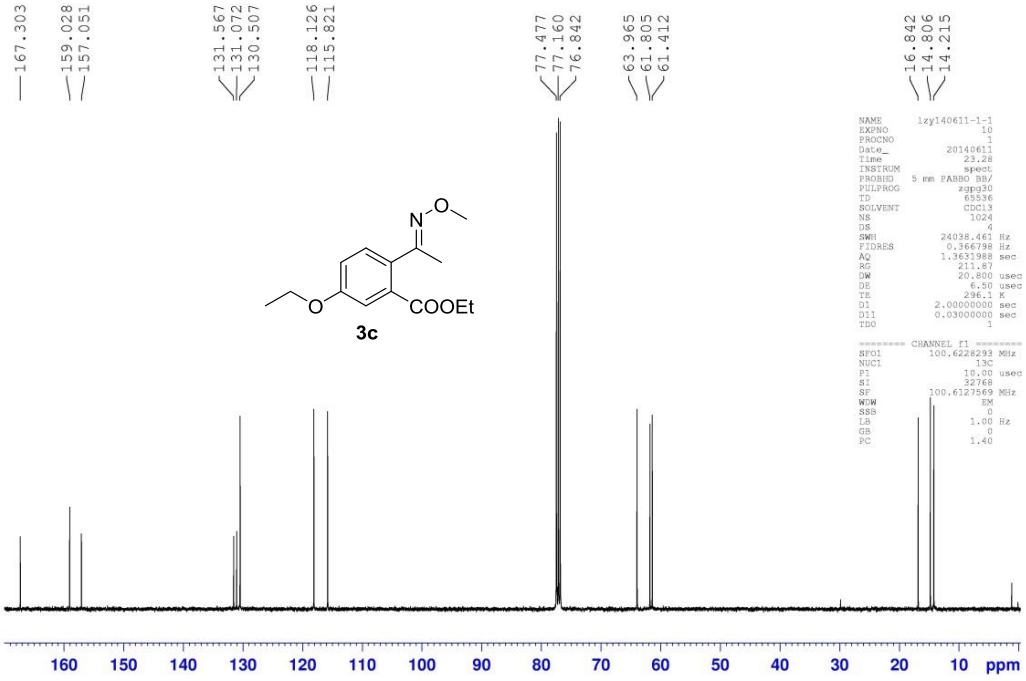
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3b



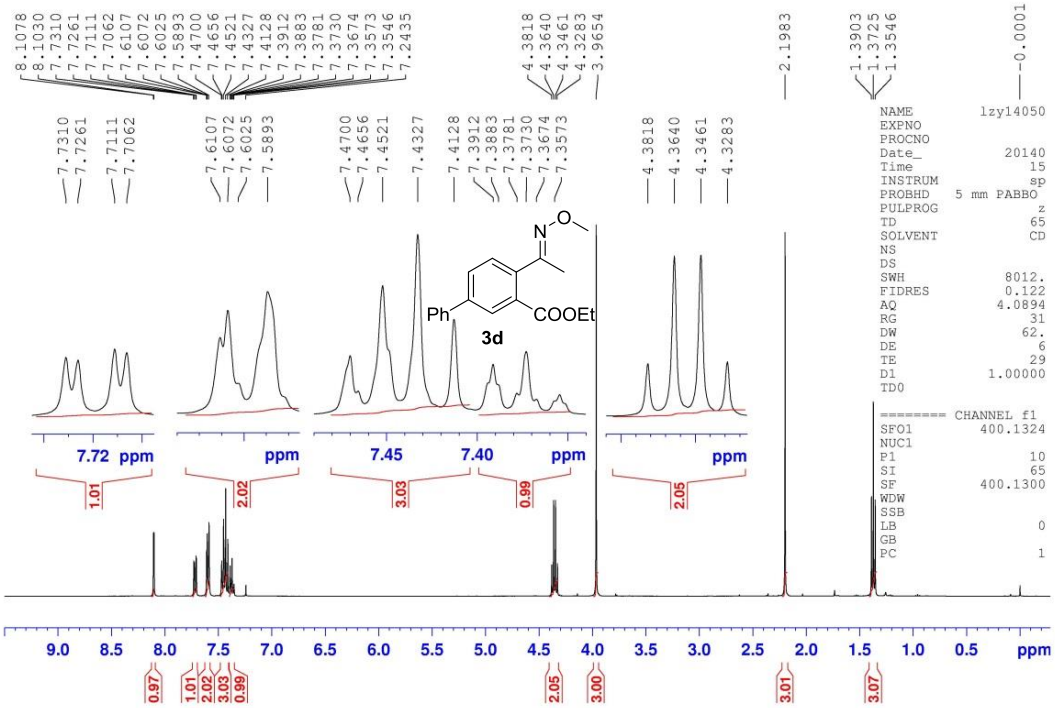
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3c



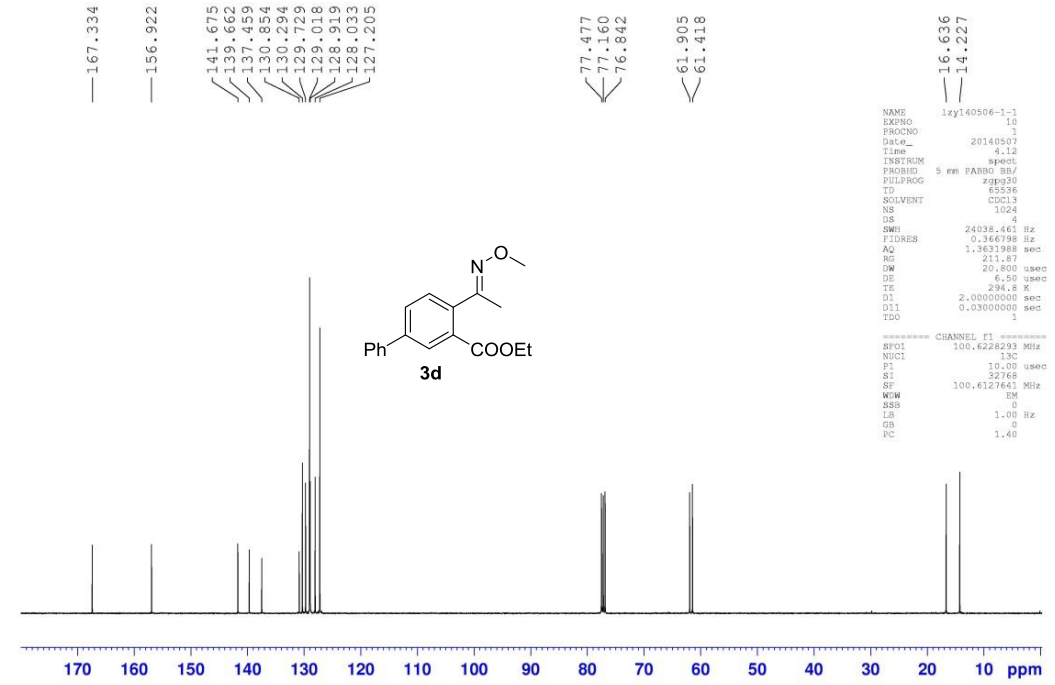
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3c



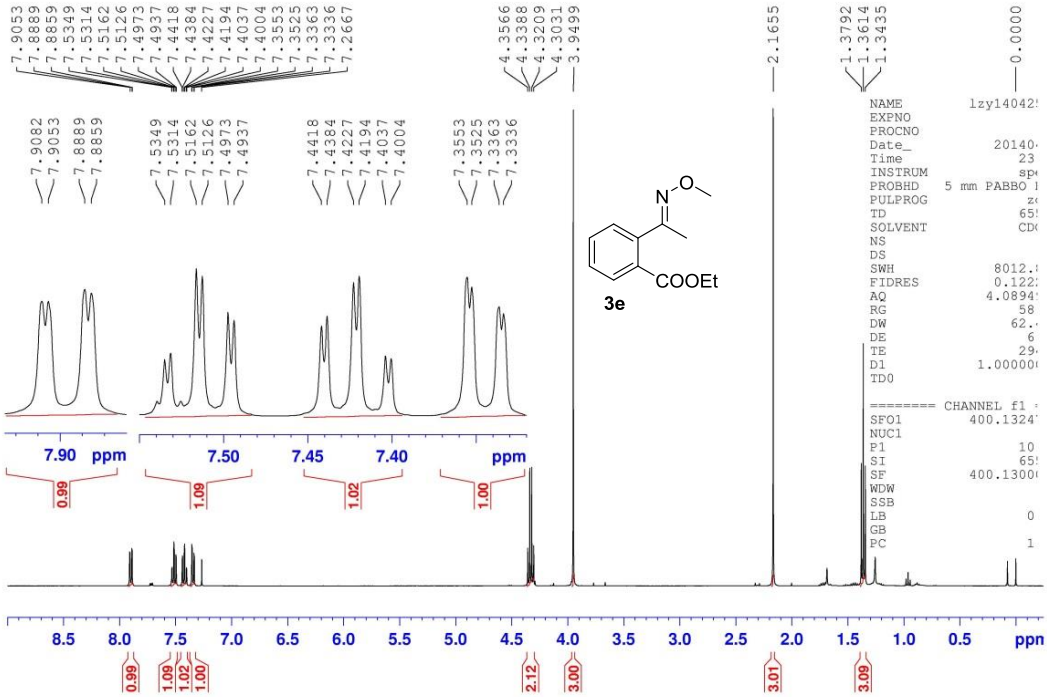
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3d



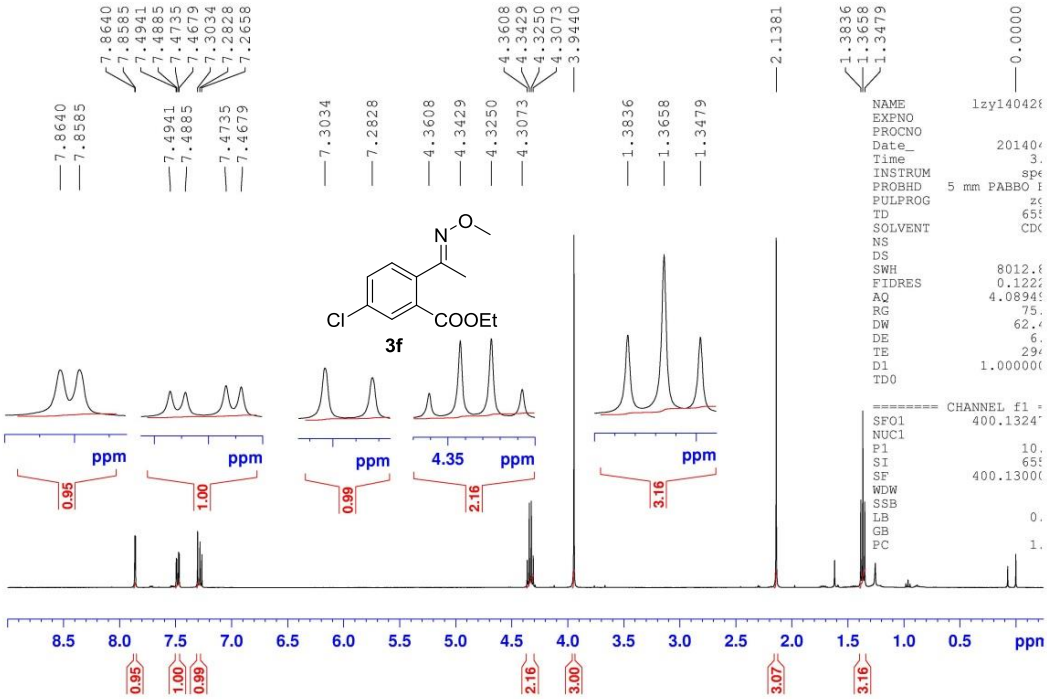
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3d



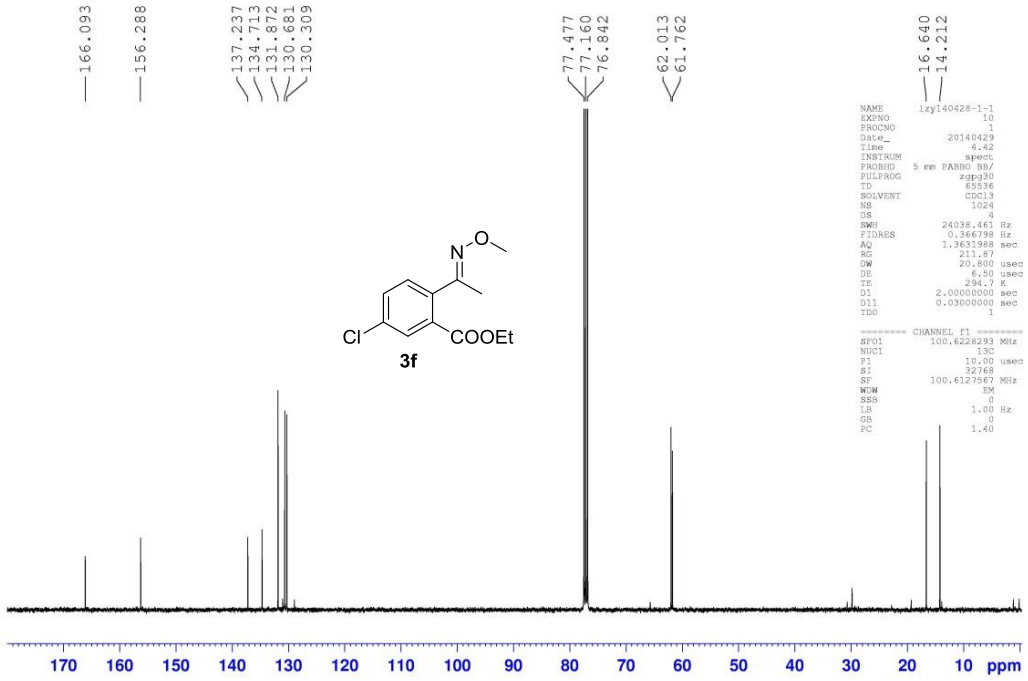
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3e



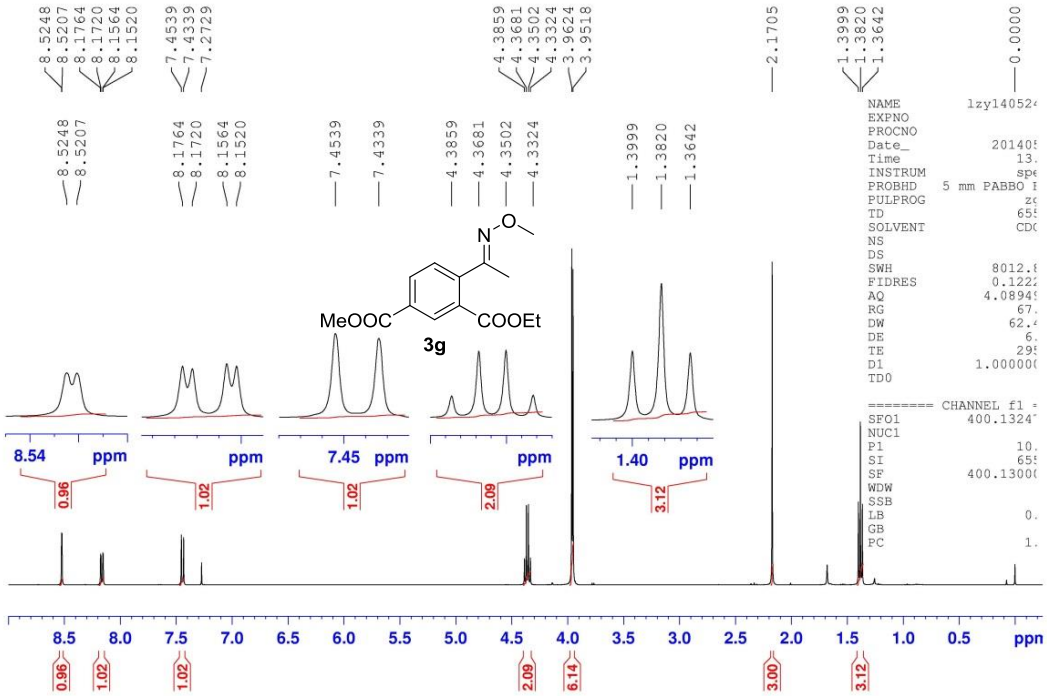
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3f



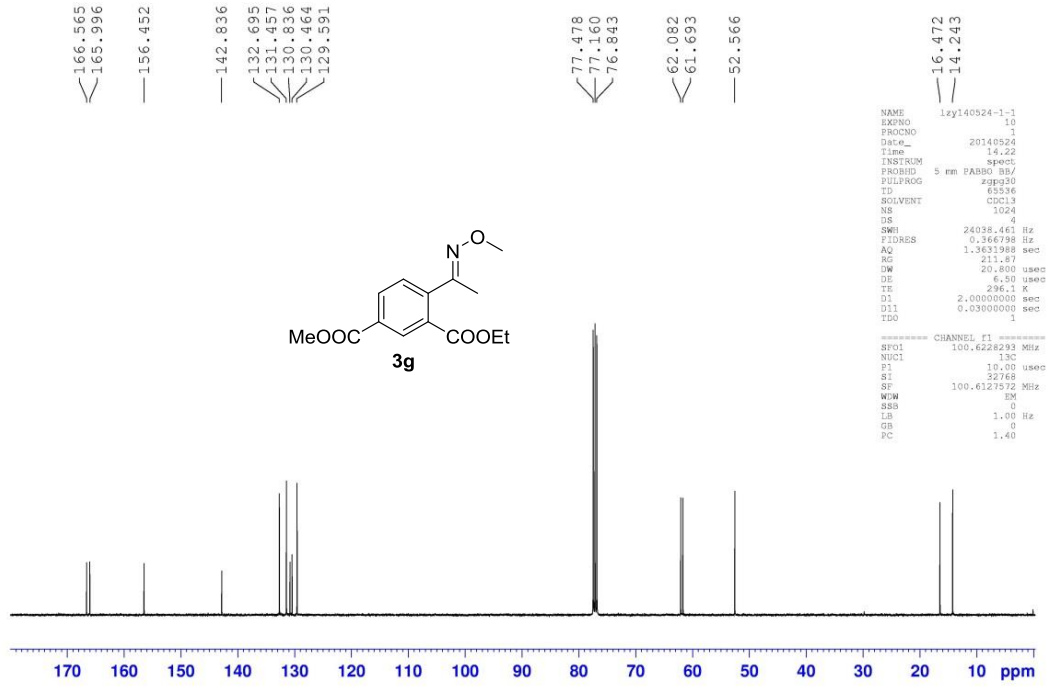
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3f



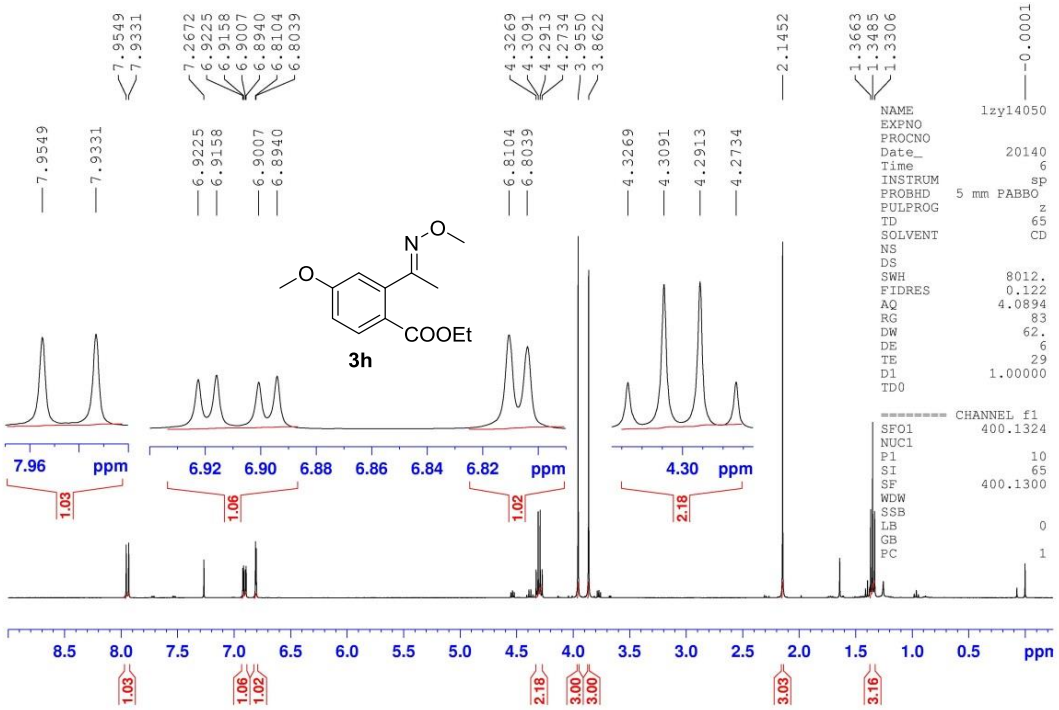
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3g



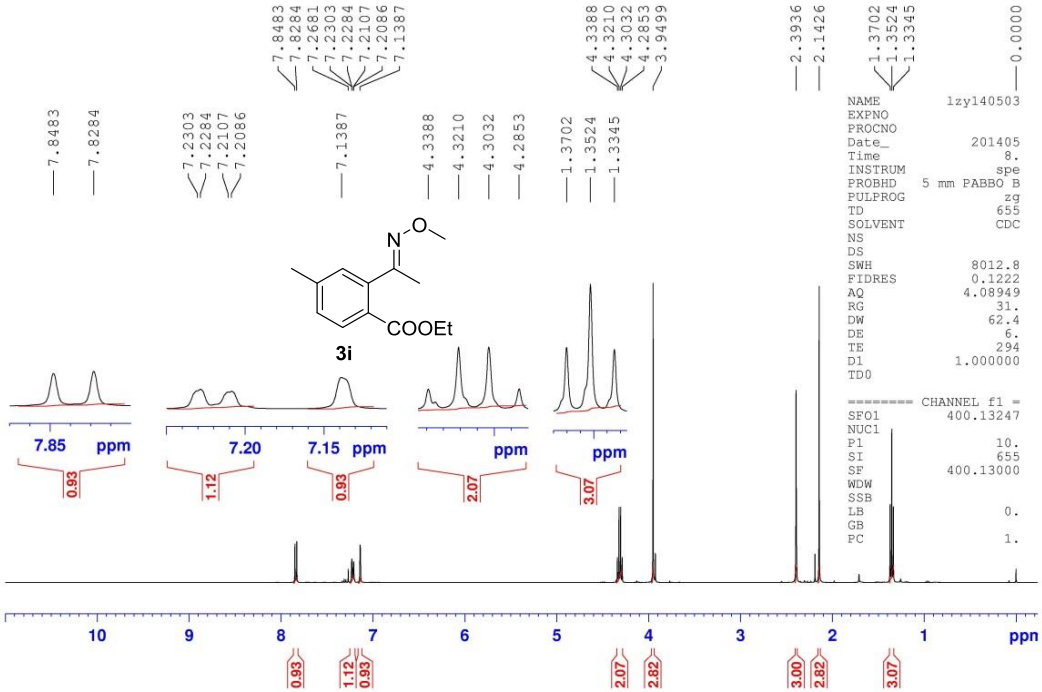
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3g



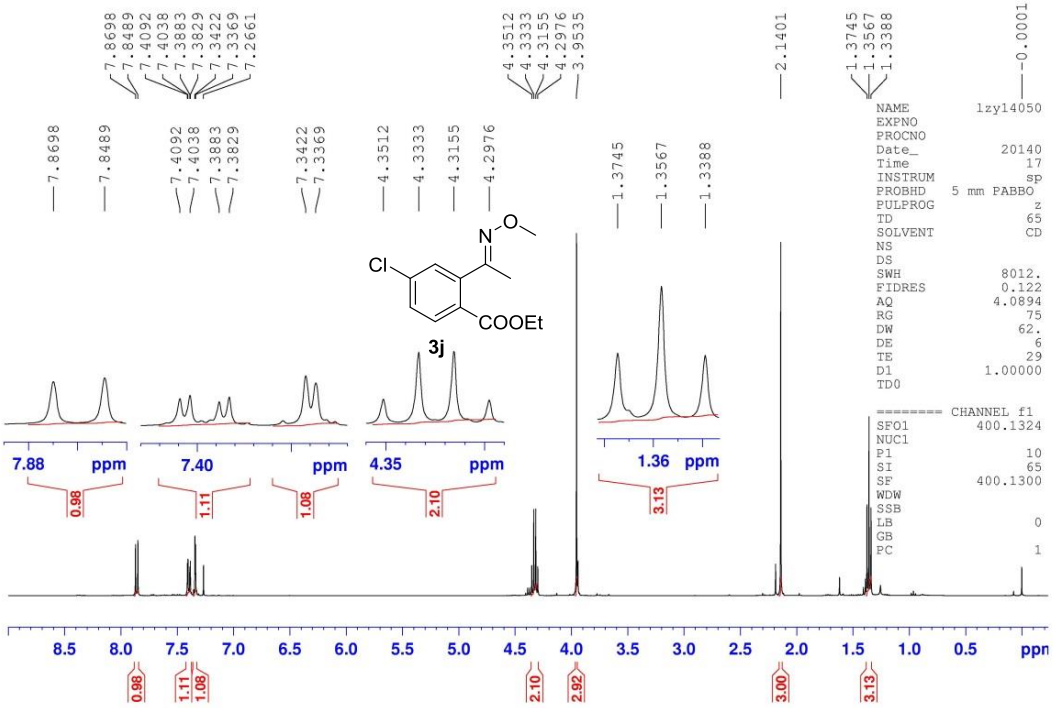
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3h



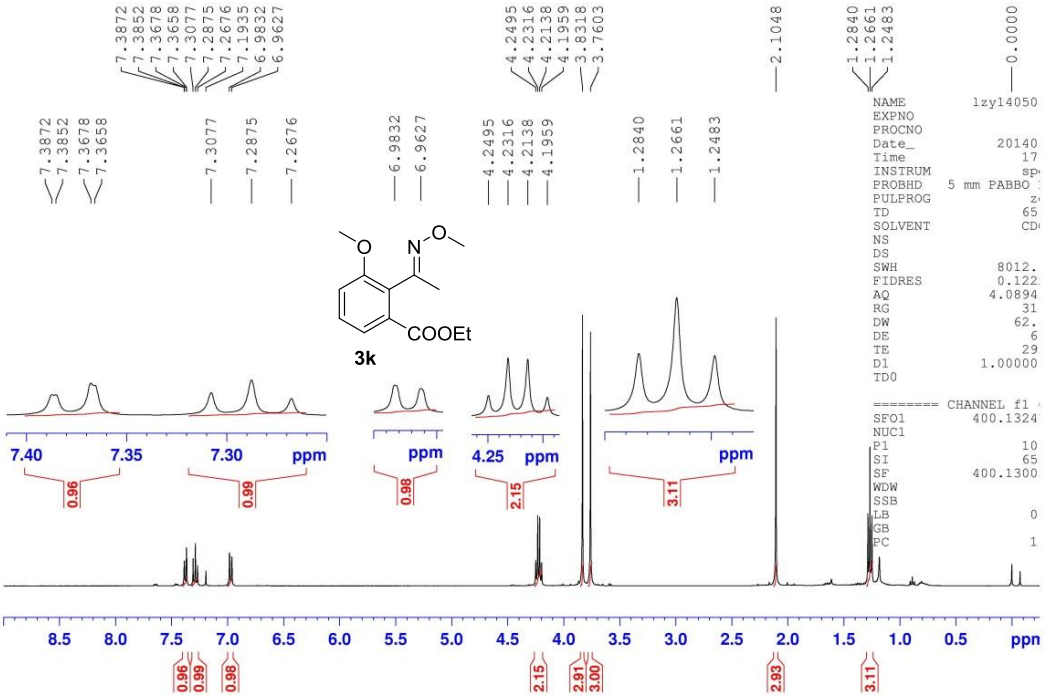
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3i



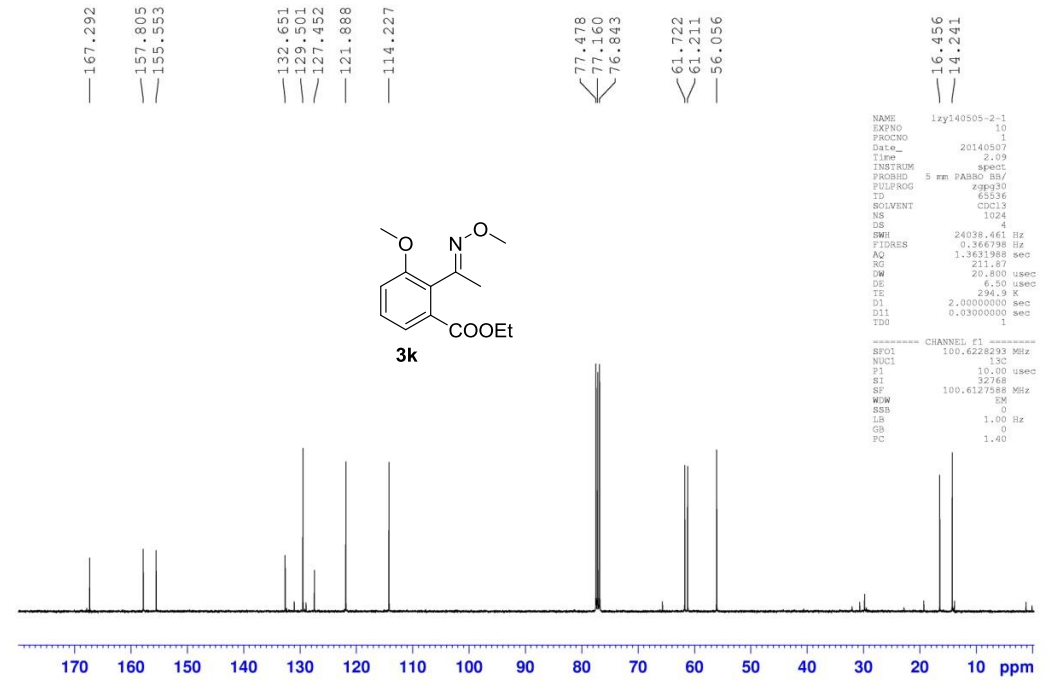
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3j



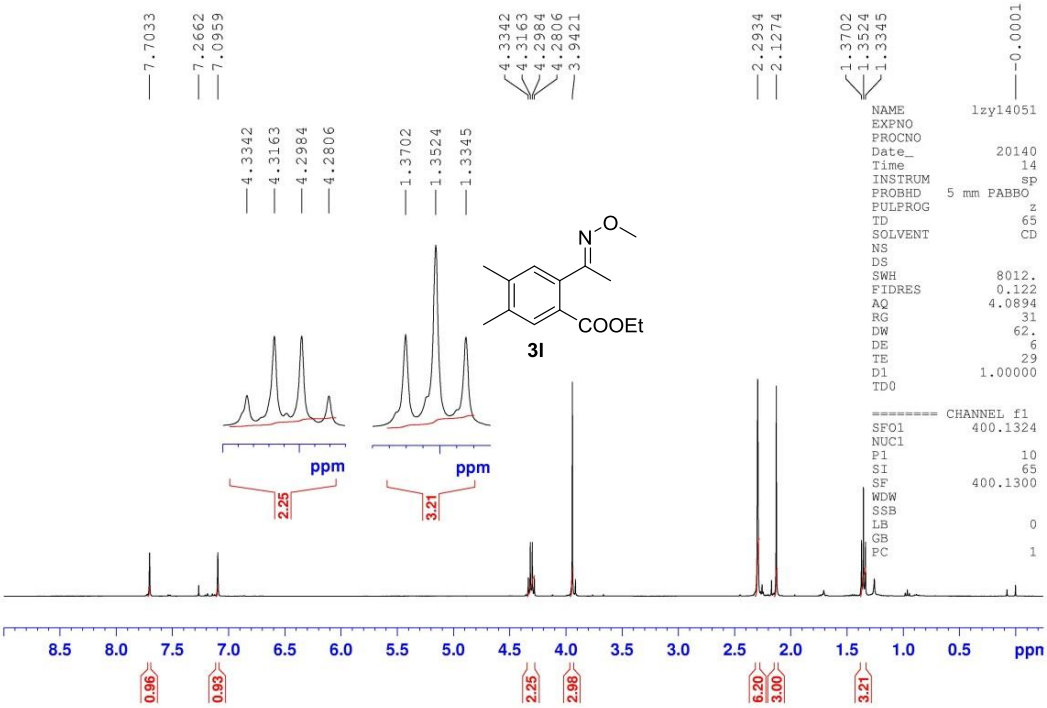
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3k



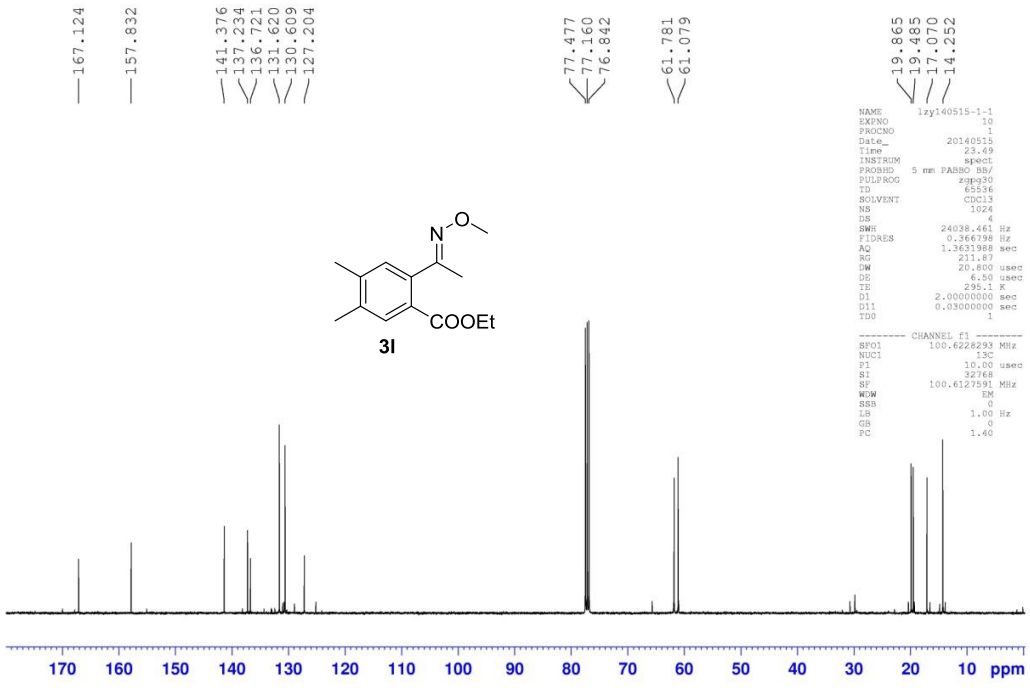
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3k



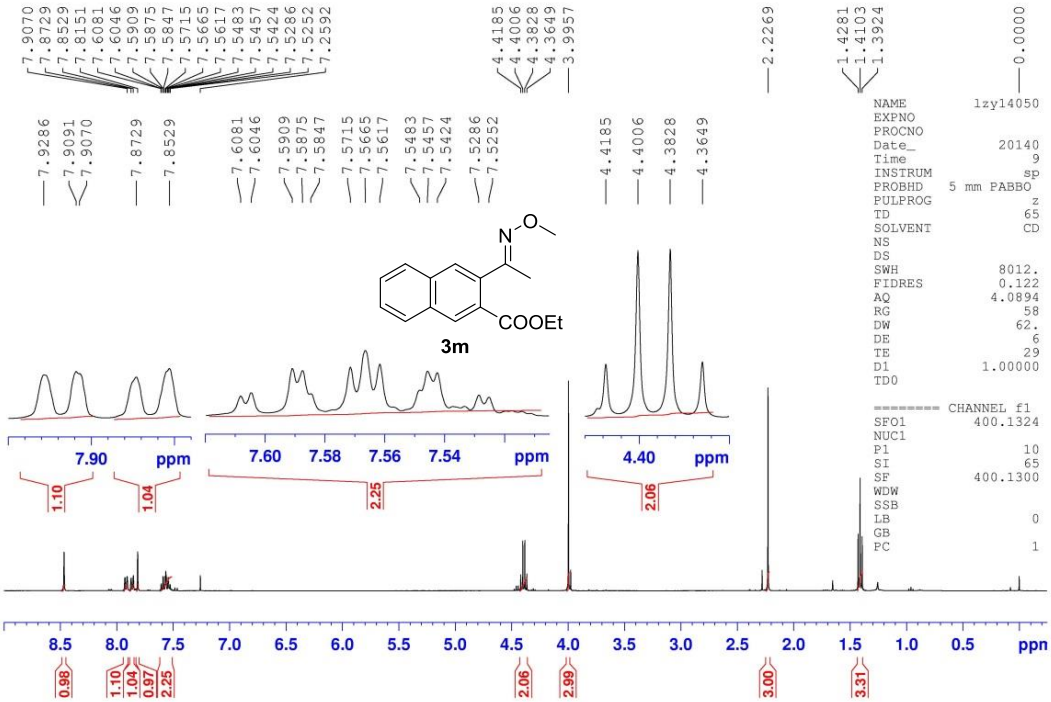
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3l



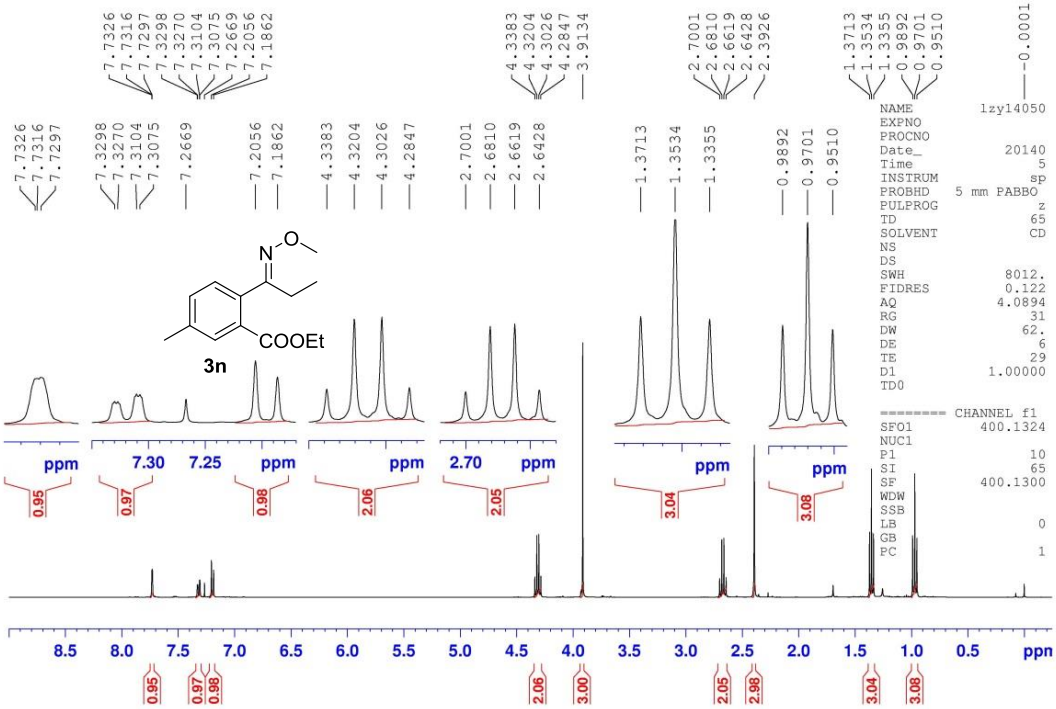
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3l



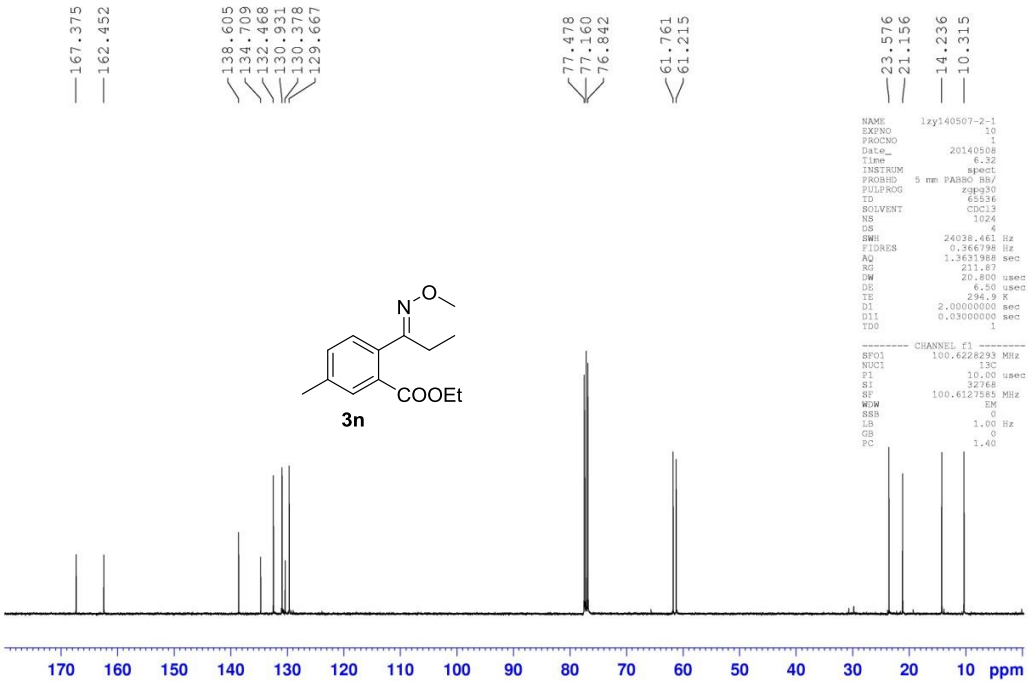
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3m



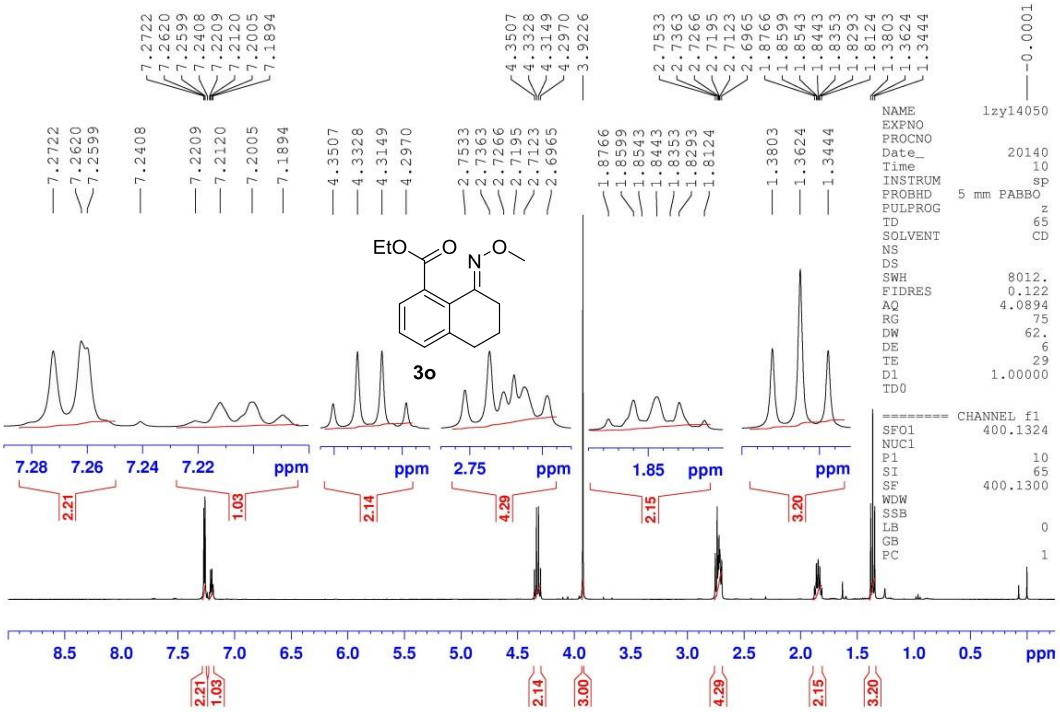
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3n



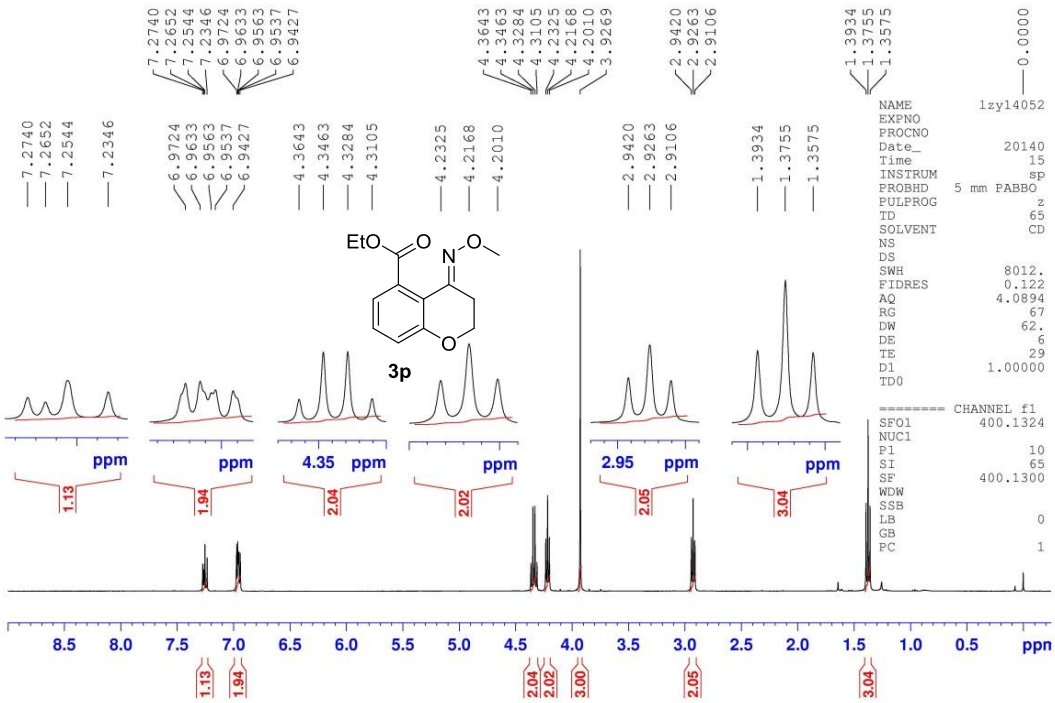
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3n



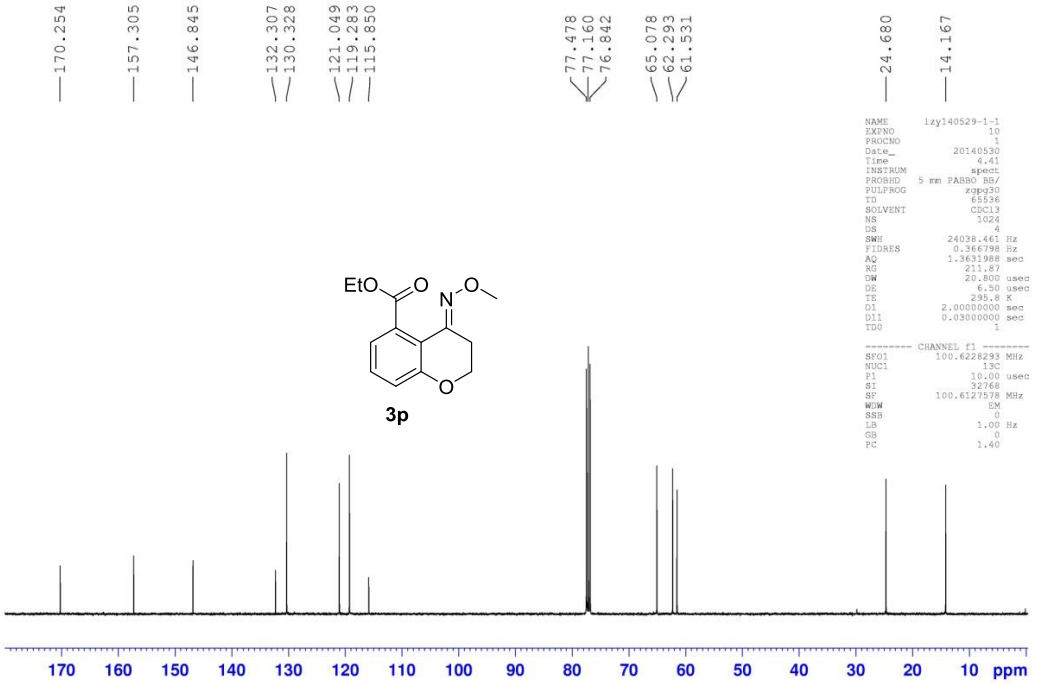
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3o



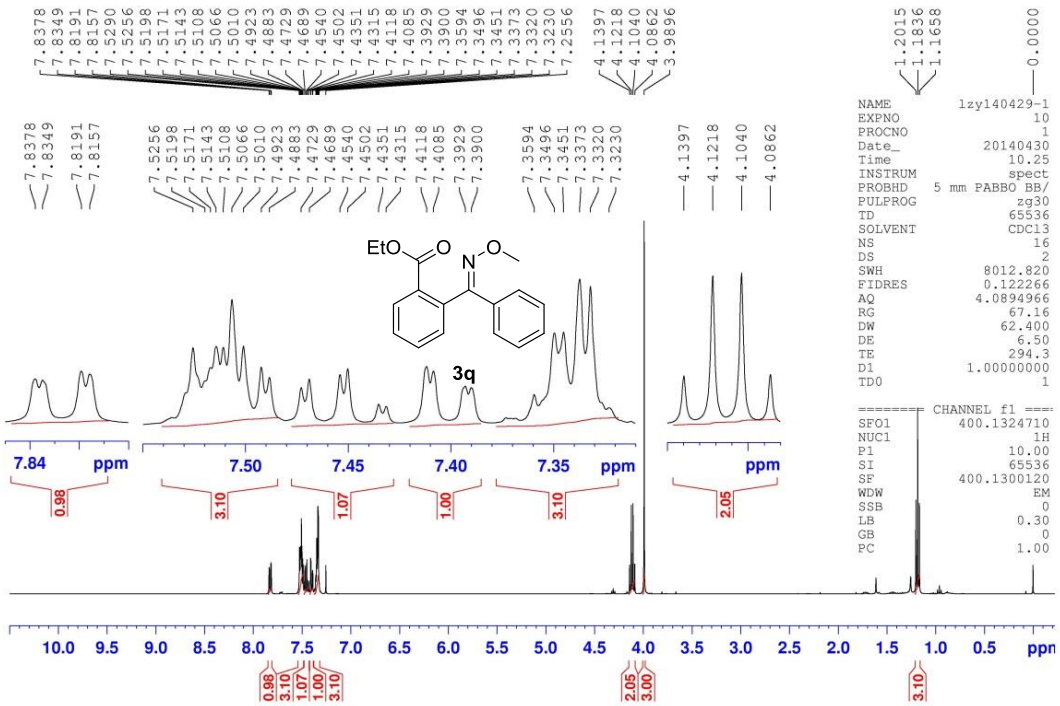
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3p



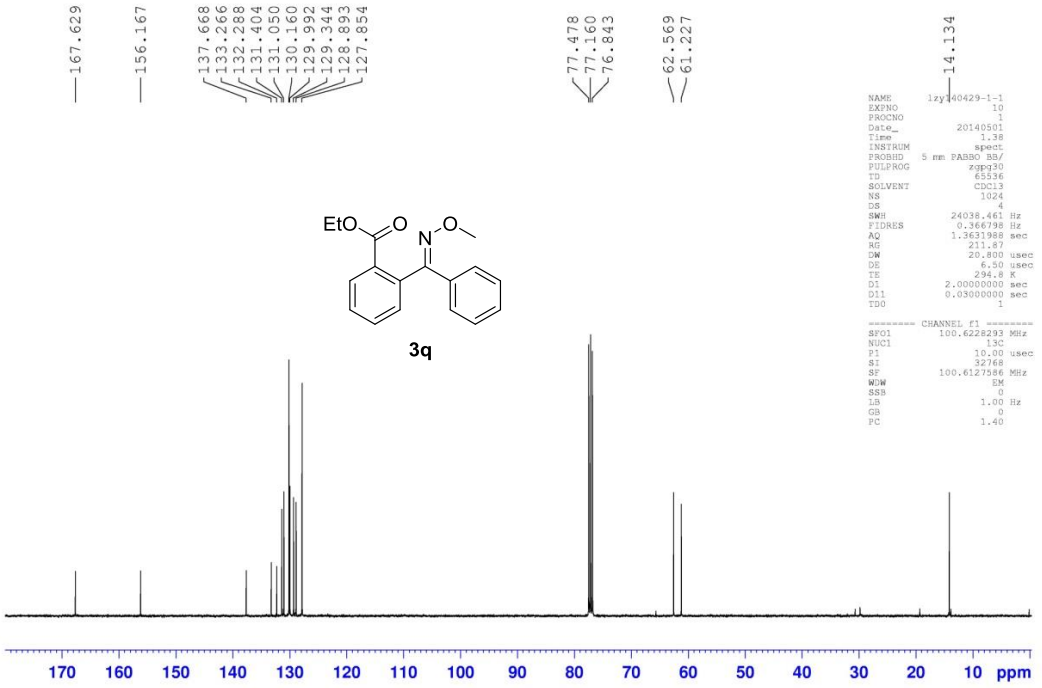
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3p



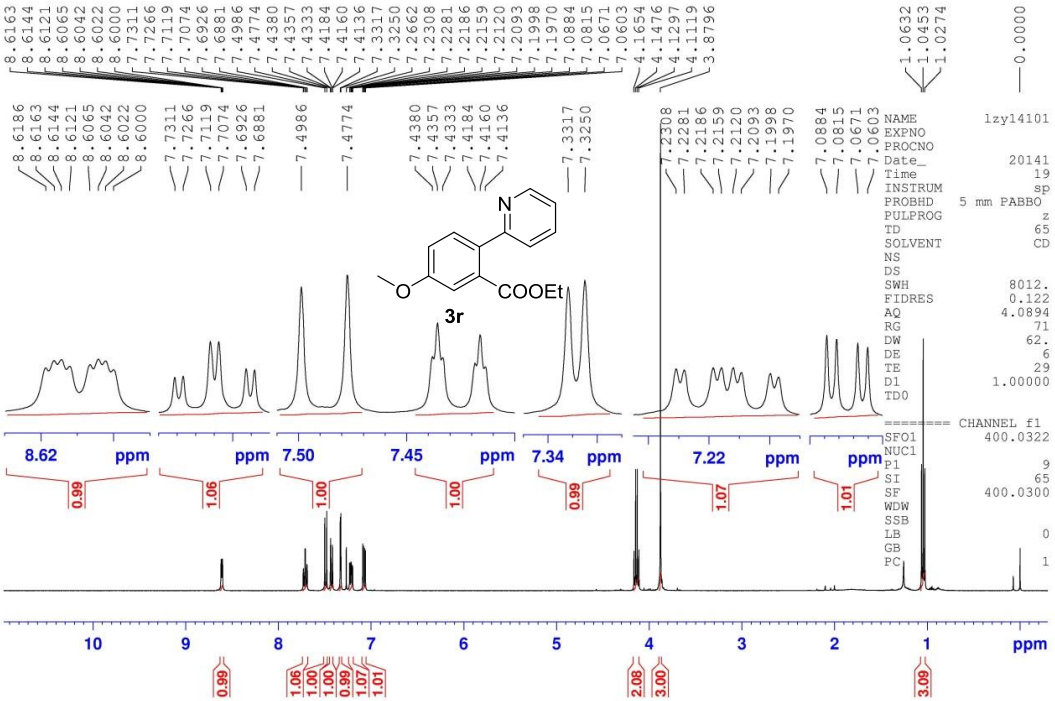
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3q



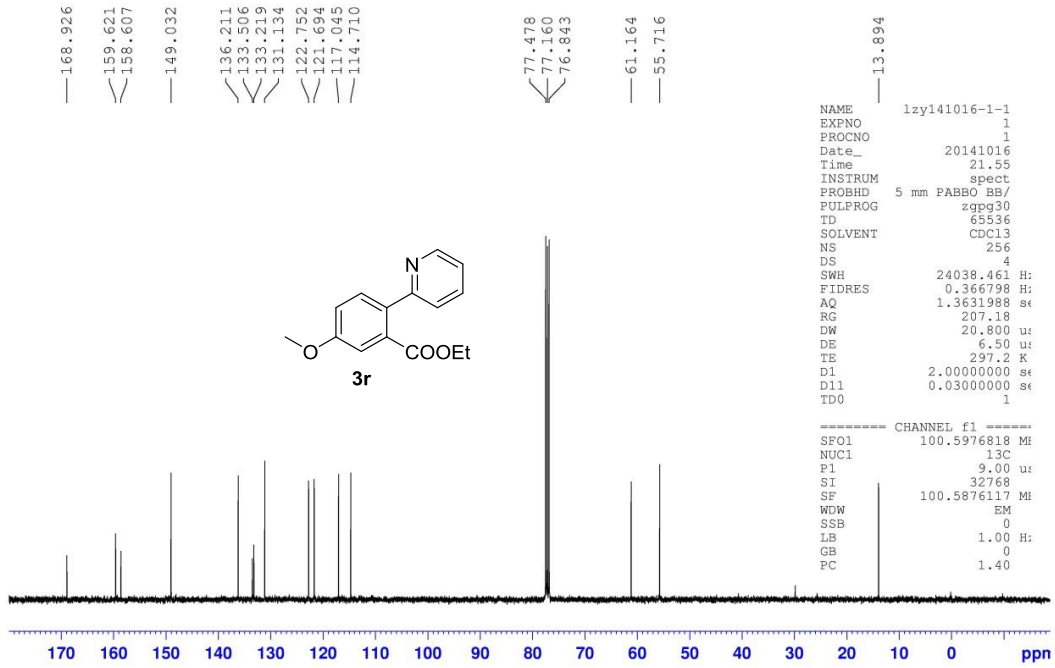
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3q



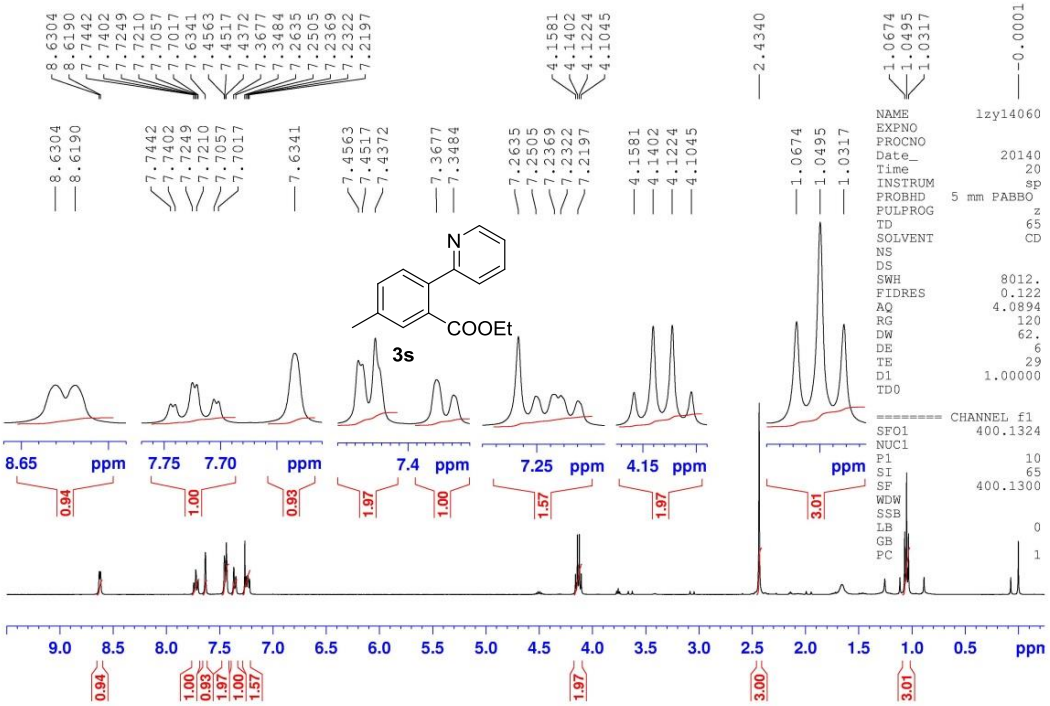
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3r



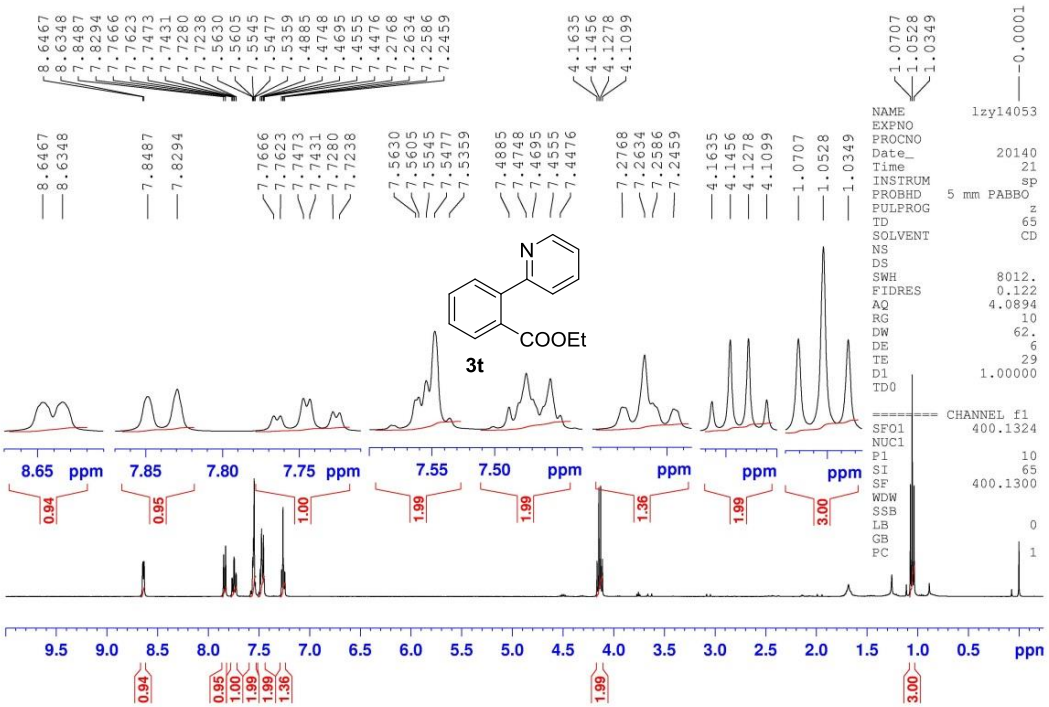
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3r



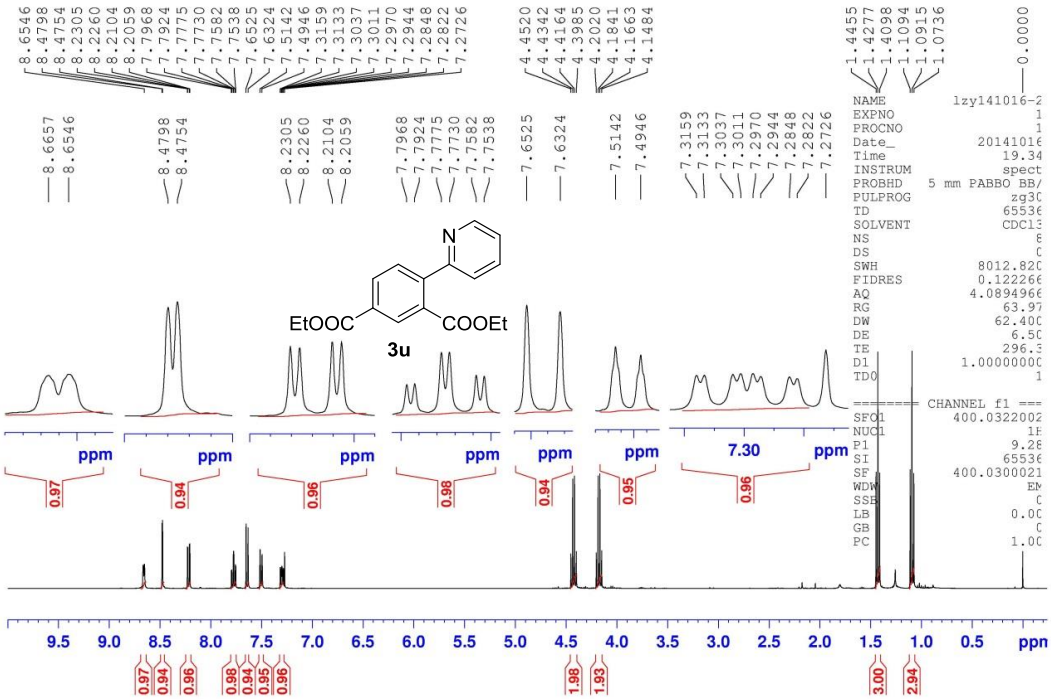
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3s



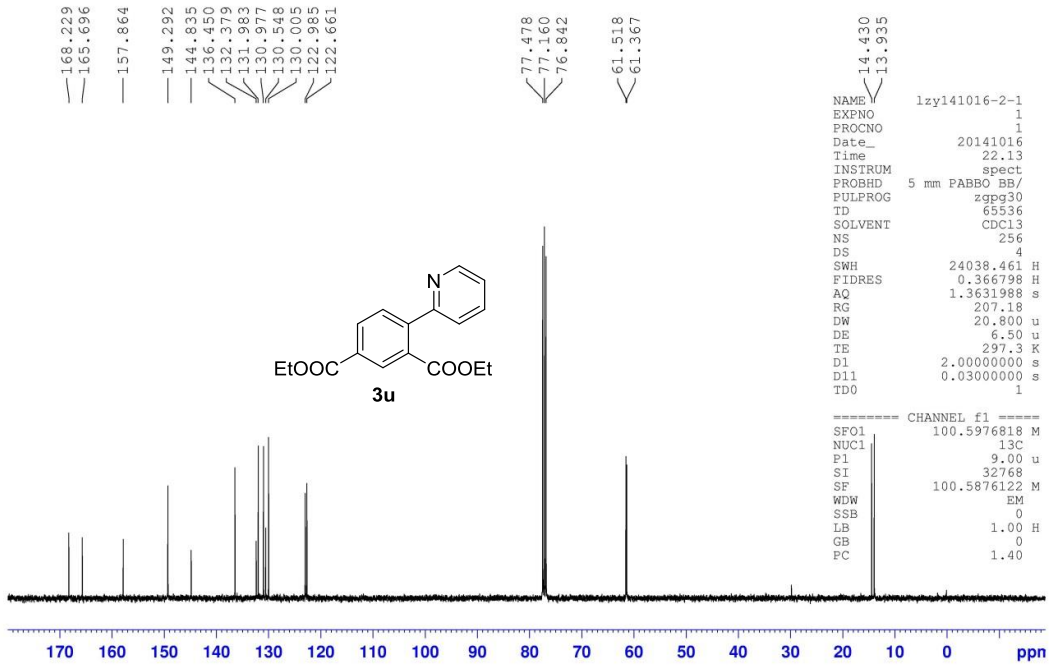
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3t



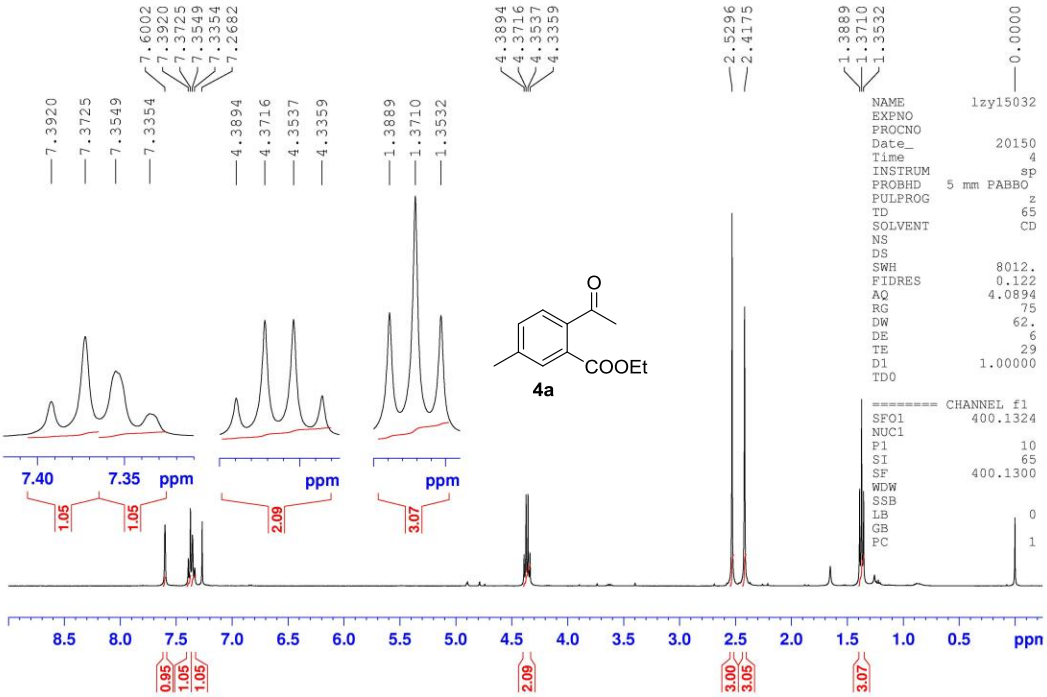
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3u



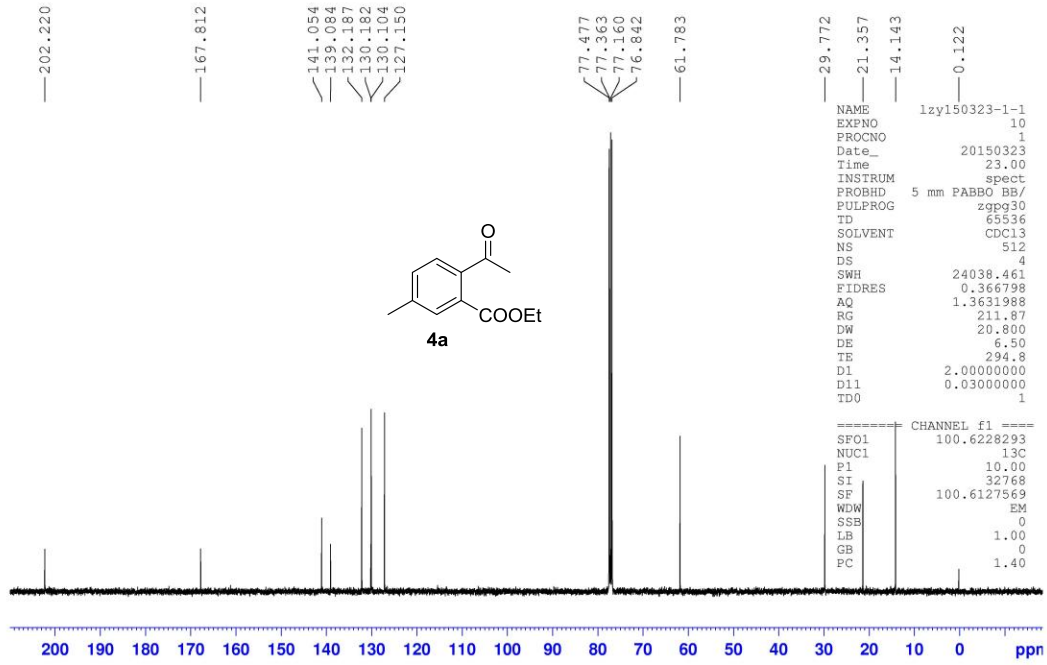
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3u



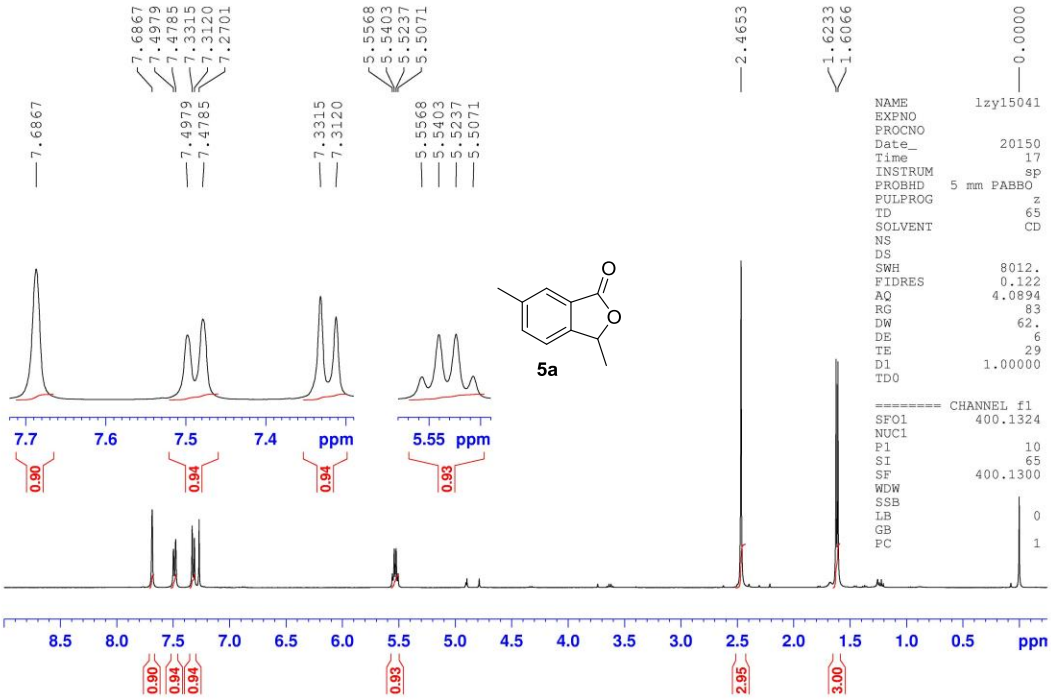
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4a



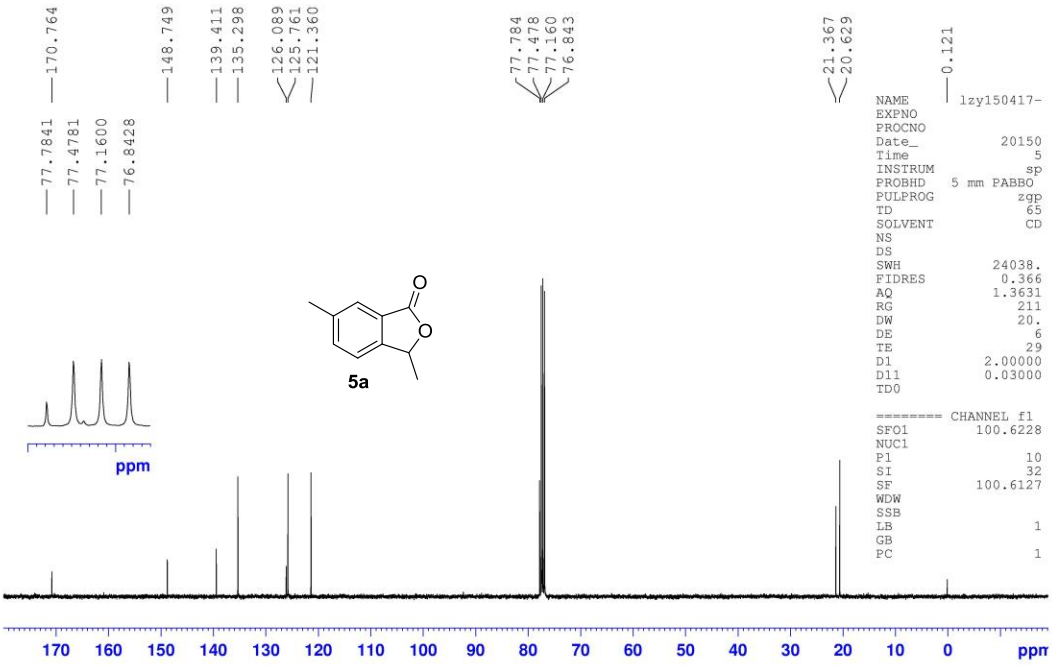
^{13}C NMR (100 MHz, $CDCl_3$) of compound 4a



^{1}H NMR (400 MHz, $CDCl_3$) of compound 5a



^{13}C NMR (100 MHz, $CDCl_3$) of compound 5a



^{1}H NMR (400 MHz, $CDCl_3$) of compound 3e and 3e-d_4