Supporting Information

Palladium-Catalyzed Arylic/Allylic Aminations: Permutable Domino Sequences for the Synthesis of Dihydroquinolines from Morita-Baylis-Hillman Adducts

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Contents

1. General Remarks

Unless special mention, all reactions were carried out under an argon atmosphere. Glassware was flame-dried under an argon gas flow prior to use. Palladium-mediated reactions were run in sealed tubes with magnetic stirring.

Anhydrous 1,4-dioxane was obtained by distillation over sodium/benzophenone and used freshly distilled.

Other reagents were commercially available and used without further purification, except for aniline which was purified by simple distillation.

TLC were performed on Merck 60 F254 silica gel and revealed with either a ultra-violet lamp (λ = 254 nm) or a specific color reagent (potassium permanganate, vanillin...). A silica gel Merck Geduran SI 60 (40-63 µm) was used for flash column chromatographies (FC). Preparative thin layer chromatographies were realized with PLC silica gel 60 F_{254} (1 mm, 20x20 cm).
NMR spectra (^{1}H, ^{13}C, ^{19}F) were recorded on a Bruker AM300 MHz or a Bruker AVANCE 400 MHz spectrometer. Chemical shifts are given in parts per million (ppm) using the $CDCl_3$ residual chloroform signal as reference ($\delta^{1}H$ = 7.26 ppm, $\delta^{13}C$ = 77.0 ppm). The terms m, s, d, t, and q represent multiplet, singlet, doublet, triplet, and quadruplet respectively. Coupling constants (*J*) are given in Hertz (Hz). IR spectra were recorded with a Tensor 27 (ATR diamond) Bruker spectrometer. IR spectra were reported as characteristic bands (cm^{-1}). High resolution mass spectra (HRMS) were recorded at the Institut Parisien de Chimie Moléculaire (FR 2769) of UPMC (electrospray source).

2. General Procedures

General Procedure 1 (GP1). *Morita-Baylis-Hillman reaction.* A solution of aldehyde (10 mmol, 1 equiv), acrylate (15 mmol, 1.5 equiv) and DABCO (10 mmol, 1 equiv) in MeOH (5 mL) was stirred at room temperature. After completion of the reaction, monitored by TLC, the reaction mixture was hydrolyzed with aqueous saturated NH_4Cl solution and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by column chromatography (Cyclohexane:EtOAc, 8:2) on silica gel to afford the desired product.

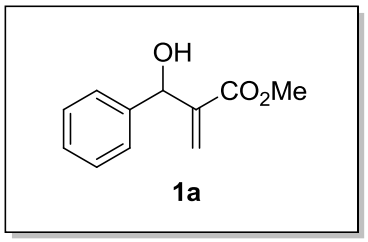
General Procedure 2 (GP2). *Allylic Amination reaction.* Under argon atmosphere, $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5 mol %) and XANTPhos (10 mol %) were stirred at room temperature for 15 minutes in 1,4-dioxane (0.4 M). A solution of MBH adducts (1 equiv) in 1,4-dioxane (0,4 M) and the aromatic amine (1.5 equiv) was added. The reaction mixture was stirred at 80 °C. After completion, the reaction was cooled down to room temperature, diluted with EtOAc and filtered through a plug of Celite.® The crude product was purified by preparative thin layer chromatography PLC (pentane:EtOAc, 8:2), to afford the desired allylamine.

General Procedure 3 (GP3). *Pd-catalyzed pseudo-domino reaction.* Under argon atmosphere, $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5 mol %), XANTPhos (10 mol %) and K_2CO_3 (2 equiv) were stirred at room temperature for 15 minutes in 1,4-dioxane (0.4 M). A solution of MBH adducts (1 equiv) in 1,4-dioxane (0,4 M) and the aromatic amine (1.5 equiv) was added. The reaction mixture was stirred at 80 °C during 20 hours, unless otherwise noted. After completion, the reaction was cooled down to room temperature, diluted with EtOAc and filtered through a plug of Celite.® The crude product was

purified by preparative thin layer chromatography PLC (pentane:EtOAc, 8:2), to afford the corresponding 1,2-dihydroquinoline.

3. Synthesis and Characterization of MBH adducts

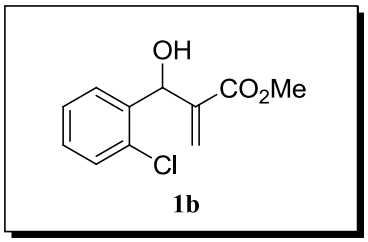
Methyl 2-(hydroxy(phenyl)methyl)acrylate (1a)



1a

Following GP1 during 3 days with benzaldehyde and methylacrylate to give 1.64 g (85%) of **1a** as a colorless oil. The spectroscopic data are in accordance with those reported in the literature.[1] **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.39-7.26 (m, 5H), 6.34 (s, 1H), 5.83 (s, 1H), 5.57 (d, *J* = 5.5 Hz, 1H), 3.73 (s, 3H), 2.98 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 166.8, 142.1, 141.4, 128.4, 127.8, 126.7, 125.9, 73.0, 51.9. **FTIR** (cm^{-1}) ν 3465, 3032, 2953, 1720, 1440.

Methyl 2-((2-chlorophenyl)(hydroxy)methyl)acrylate (1b)



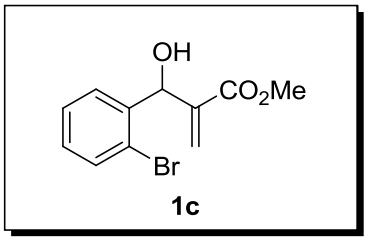
1b

Following GP1 during 3 days, with 2-chlorobenzaldehyde and methylacrylate to give 1.83 g (81%) of **1b** as a colorless oil. The spectroscopic data are in accordance with those reported in the literature.[2] **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.55 (d, *J* = 7.6 Hz, 1H), 7.37-7.24 (m, 3H) 6.34 (s, 1H), 5.99 (d, *J* = 4.8 Hz, 1H), 5.62 (s, 1H), 3.76 (s, 3H), 3.64 (d, *J* = 4.9 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ

[1] Holz, J.; Schäffner, B.; Zayas, O.; Spannenberg, A.; Börner, A. *Adv. Synth. Catal.* **2008**, *350*, 2533.
[2] Zhu, B.; Yan, L.; Pan, Y.; Lee, R.; Liu, H.; Han, Z.; Huang, K.-W.; Tan, C.-H.; Jiang, Z. *J. Org. Chem.* **2011**, *76*, 6894.

(ppm) 166.8, 140.6, 138.2, 132.7, 129.3, 128.8, 128.0, 126.9, 126.8, 69.0, 52.2. **FTIR** (cm^{-1}) ν 3438, 2998, 2953, 1722, 1440.

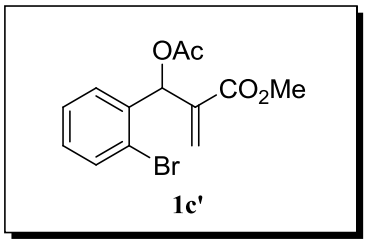
Methyl 2-((2-bromophenyl)(hydroxy)methyl)acrylate (1c)



1c

Following GP1 during 48 hours with 2-bromobenzaldehyde and methylacrylate to give 2.67 g (98%) of **1c** as a colorless oil. The spectroscopic data are in accordance with those reported in the literature.[3] **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.51 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.16-7.10 (m, 1H), 6.31 (s, 1H), 5.92 (d, *J* = 4.3 Hz, 1H), 5.56 (s, 1H), 3.73 (s, 3H), 3.57 (d, *J* = 3.7 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 167.0, 140.5, 139.7, 132.7, 129.3, 128.4, 127.7, 127.2, 123.1, 71.5, 52.2. **FTIR** (cm^{-1}) ν 3413, 2999, 1709, 1437, 1266.

Methyl 2-((2-bromophenyl)(hydroxy)methyl)acrylate (1c')



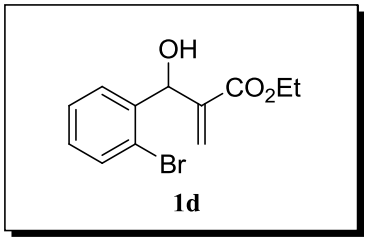
1c'

Under argon atmosphere, DMAP (16 mg, 0.13 mmol, 10 mol %) and acetic anhydride (153 mg, 1.5 mmol, 1.2 equiv) were stirred at room temperature for 5 minutes in 4 mL of DCM. The mixture was cooled to 0 °C and a solution of **1c** (330 mg, 1.22 mmol, 1 equiv) in 2.2 mL of DCM was added, followed by NEt_3 (192 mg, 1.9 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature. After completion of the reaction (TLC monitoring), the reaction mixture was tretated with H_2O and extracted with DCM. The combined organic layers were dried over anhydrous $MgSO_4$

[3] Coelho, F.; Almeida, W. P.; Veronese, D.; Mateus, C. R.; Lopes, E. C. S.; Rossi, R. C.; Silveira G. P. C.; Pavam, C. H. *Tetrahedron* **2002**, *58*, 7437.

and filtered through a plug of silica (Cyclohexane:EtOAC, 6:4) to give 210 mg (55%) of **1c'** as a colorless oil. The spectroscopic data are in accordance with those reported in the literature.[4] **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.50 (d, *J* = 8.0 Hz, 1H), 7.29-7.24 (m, 2H), 7.12 (d, *J* = 9.1 Hz, 1H), 6.92 (s, 1H), 6.40 (s, 1H), 5.54 (s, 1H), 3.67 (s, 1H), 2.04 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 168.8, 165.1, 138.0, 136.7, 132.9, 129.7, 128.3, 127.8, 127.3, 123.5, 51.9, 21.9, 20.6.

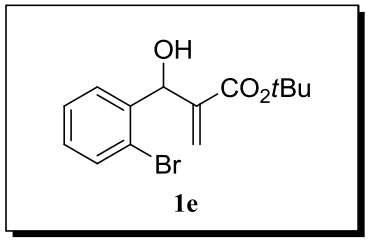
Ethyl 2-((2-bromophenyl)(hydroxy)methyl)acrylate (1d)



1d

Following GP1 during 2 days with 2-bromobenzaldehyde and ethyl acrylate in EtOH to give 2.17 g (76%) of **1d** as a colorless oil. The spectroscopic data are in accordance with those reported in the literature.[5] **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.53-7.50 (m, 2H), 7.31 (td , *J* = 7.7, 0.9 Hz, 1H), 7.14 (td, *J* = 7.7, 1.7 Hz, 1H), 6.33 (s, 1H), 5.93 (s, 1H), 5.58 (s, 1H), 4.19 (qd, *J* = 7.1, 1.8 Hz, 2H), 3.46 (d, *J* = 3.3 Hz,1H), 1.25 (t, *J* =7.1, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 166.4, 140.9, 140.0, 132.7, 129.2, 128.3, 127.5, 126.6, 123.1, 71.3, 61.0, 14.0. **FTIR** (cm^{-1}) ν 3413, 3062, 2980, 2952, 1702, 1439.

***tert*-Butyl 2-((2-bromophenyl)(hydroxy)methyl)acrylate (1e)**

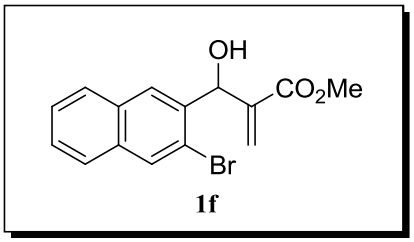


1e

[4] Cao, H.; Vieira, T. O.; Alper, H. *Org. Lett.* **2011**, *13*, 11.
[5] Coelho, F.; Veronese, D.; Pavam, C. H.; de Paula, V. I.; Buffon, R. *Tetrahedron* **2006**, *62*, 4563.

Following GP1 during 4 days with 2-bromobenzaldehyde and *tert*-butyl acrylate to give 2,53 g (81%) of **1e** as a colorless oil. The spectroscopic data are in accordance with those reported in the literature.[6] **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.55 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.16 (td, *J* = 7.7, 1.7 Hz, 1H), 6.27 (s, 1H), 5.90 (d, *J* = 4.0 Hz, 1H), 5,55 (s, 1H), 3,24 (d, *J* = 4.4 Hz, 1H), 1,43 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.7, 142.2, 140.3, 132.7, 129.2, 128.3, 127.6, 125.8, 123.3, 81.7, 71.7, 28.0. **FTIR** (cm^{-1}) ν 3419, 2976, 2930, 1707, 1631, 1469, 1438, 1367, 1282, 1145.

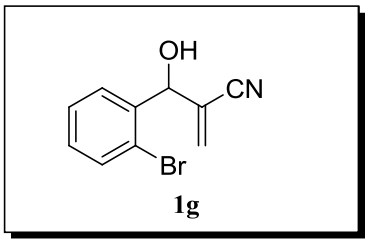
Methyl 2-((3-bromonaphthalen-2-yl)(hydroxy)methyl)acrylate (1f)



1f

Following GP1 during 3 days with 2-bromo-2-naphthaldehyde (517 mg, 2,20 mmol) and methyl acrylate to give 739 mg (96%) of **1f** as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.33 (d, *J* = 8.5 Hz, 1H), 7.83-7.81 (m, 2H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.60-7.57 (m, 1H), 7.54-7.52 (m, 1H), 6.36 (s, 1H), 6,28 (s, 1H), 5,59 (s, 1H), 3,77 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 166.9, 140.7, 137.7, 134.1, 132.1, 128.1, 127.9, 127.4, 127.4, 127.1, 126.7, 125.0, 123.2, 72.26, 52.07. **FTIR** (cm^{-1}) ν 3458, 3057, 1721, 1630, 1501, 1438, 1328, 1258, 1149.

2-((2-bromophenyl)(hydroxy)methyl)acrylonitrile (1g)



1g

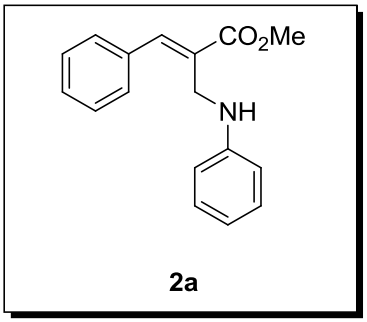
Following GP1 during 3 days with 2-bromobenzaldehyde and acrylonitrile to give 2,24 g (94%) of **1g** as a colorless oil. The spectroscopic data are in accordance with those reported in the literature.[3] **^{1}H**

[6] Furukawa, T.; Nishimine, T.; Tokunaga, E.; Hasegawa, K.; Shiro, M.; Shibata, M. *Org. Lett.* **2011**, *13*, 3972.

NMR (300 MHz, $CDCl_3$) δ (ppm) 7.60-7.53 (m, 2H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.27-7.15 (ddd, *J* = 7.8, 7.5, 1.7 Hz, 1H), 6.06-6.01 (m, 2H), 5.69 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 138.1, 133.1, 131.7, 130.3, 128.3, 128.2, 124.6, 122.8, 116.8, 72.6. **FTIR** (cm^{-1}) ν 3419, 3066, 2922, 2229, 1928, 1590, 1439.

4. Synthesis and Characterization of allylic amination products

***(E)*-methyl 3-phenyl-2-((phenylamino)methyl)acrylate (2a)**

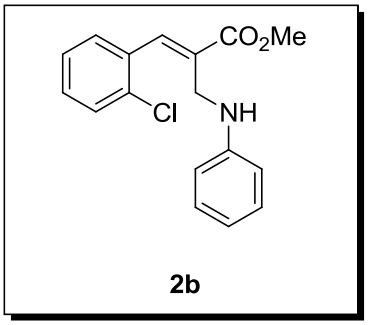


2a

Following GP2 with **1a** (100 mg, 0.52 mmol) and aniline (73 mg, 0.78 mmol) to give 137 mg (98%) of **2a** as a yellow oil. The spectroscopic data were consistent with those reported in the literature.[7] **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.90 (s, 1H), 7.50-7.36 (m, 5H), 7.15 (t, *J* = 7.2 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 2H), 4.18-4.11 (m, 3H), 3.84 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 168.2, 147.7, 142.9, 134.8, 129.5, 129.2, 129.1, 128.8, 128.7, 117.8, 113.4, 52.2, 40.9. **FTIR** (cm^{-1}) ν 3388, 3023, 2949, 1712, 1600, 1503, 1432, 1201, 1103. **HRMS (ESI)** calcd for $C_{17}H_{18}NO_2$ ($[M+H]^+$): 268.1332; found 268.1332.

***(E)*-methyl 3-(2-chlorophenyl)-2-((phenylamino)methyl)acrylate (2b)**

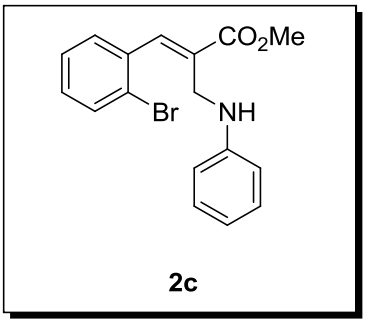
[7] Paira, M.; Mandal, S. K.; Roy, S. C. *Tetrahedron Lett*. **2008**, *49*, 2432.



2b

Following GP2 during 2 days with **1b** (371 mg, 1.64 mmol) and aniline (230 mg, 2.46 mmol) to give 455 mg (91%) of **2b** as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.92 (s, 1H), 7.46-7.38 (m, 2H), 7.33-7.20 (m, 2H), 7.13-7.04 (m, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 7.7 Hz, 2H), 4.16-4.05 (m, 1H), 4.02 (s, 2H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 168.2, 147.7, 142.9, 134.8, 129.5, 129.2, 129.1, 128.7, 128.7, 117.8, 113.4, 52.2, 41.0. **FTIR** (cm^{-1}) ν 3392, 3053, 2950, 1707, 1601, 1503, 1469, 1434, 1229, 1103. **HRMS (ESI)** calcd for $C_{17}H_{16}ClNO_2Na$ ($[M+Na]^+$): 324.0762; found 324.0764.

***(E)*-methyl 3-(2-bromophenyl)-2-((phenylamino)methyl)acrylate (2c)**



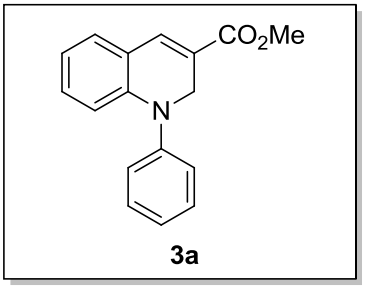
2c

Following GP2 with **1c** (100 mg, 0.32 mmol) and aniline (45 mg, 0.48 mmol) to give 65 mg (56%) of **2c** as a yellow oil. The spectroscopic data were consistent with those reported in the literature.[8] **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.88 (s, 1H), 7.66 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.66 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.33 (td, *J* = 7.5, 1.2 Hz, 1H), 7.28-7.21 (m, 1H), 7.16-7.08 (m, 2H), 6.71 (td, *J* = 7.3, 1.8 Hz, 1H), 6.49-6.43 (m, 2H), 4.04 (s, 2H), 3.86 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 167.8, 147.5, 141.6, 135.1, 132.8, 130.9, 130.6, 129.1, 127.4, 124.1, 117.9, 113.5, 52.3, 41.1. **FTIR** (cm^{-1}). ν 2955, 2825, 1796, 1564, 1278, 715, 667.

[8] Wang, Y.; Liu, L.; Wang, D.; Chen, Y-J.; *Org. Biomol. Chem.*, **2012**,*10*, 6908.

5. Synthesis and Characterization of 1,2-dihydroquinoline products

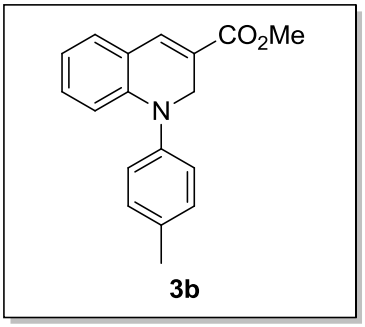
Methyl 1-phenyl-1,2-dihydroquinoline-3-carboxylate (3a)



3a

Following GP3 with **1c** (220 mg, 0.80 mmol) and aniline (112 mg, 1.2 mmol) to give 123 mg (58%) of **3a** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.48 (s, 1H), 7.41-7.37 (m, 2H), 7.29-7.26 (m, 2H), 7.18-7.12 (m, 2H), 7.07-7.03 (m, 1H), 6.73 (t, *J* = 7.9 Hz, 2H), 4.62 (s, 2H), 3.80 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.7, 145.4, 140.4, 135.3, 131.1, 129.6, 129.4, 124.5, 123.7, 122.4, 122.1, 119.1, 114.8, 51.8, 48.9. **FTIR** (cm^{-1}) ν 3028, 2949, 1702, 1485, 1201. **HRMS (ESI)** calcd for $C_{17}H_{15}NO_2Na$ ($[M+Na]^+$): 288.0995; found 288.0984.

Methyl 1-*p*-tolyl-1,2-dihydroquinoline-3-carboxylate (3b)

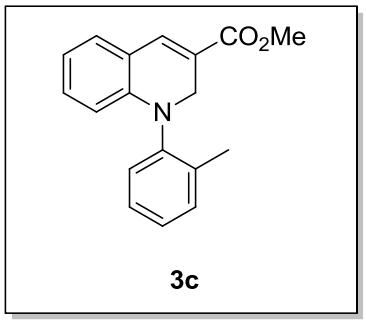


3b

Following GP3 with **1c** (184 mg, 0.68 mmol) and *p*-toluidine (139 mg, 1.3 mmol) to give 114 mg (60%) of **3b** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.46 (s, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 4.61 (s, 2H), 3.80 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.8, 145.9, 142.9, 135.3, 134.5, 131.1, 130.1, 131.1, 130.1, 129.6, 124.1, 122.0, 121.8, 118.6,

114.4, 51.5, 49.1, 20.9. **FTIR** (cm^{-1}) ν 3028, 2949, 1703, 1510, 1486, 1158. **HRMS (ESI)** calcd for $C_{18}H_{17}NO_2Na$ ($[M+Na]^+$): 302.1151; found 302.1150.

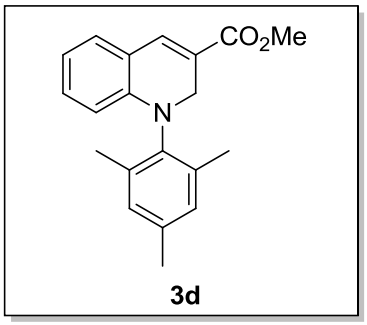
Methyl 1-*o*-tolyl-1,2-dihydroquinoline-3-carboxylate (3c)



3c

Following GP3 with **1c** (162 mg, 0.60 mmol) and *o*-toluidine (96 mg, 0.90 mmol) to give 82 mg (50 %) of **3c** as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.48 (s, 1H), 7.36-7.27 (m, 4H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.99 (m, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 5.98 (d, *J* = 8.2 Hz, 1H), 4.64 (d, *J* = 18.9 Hz, 2H), 3.82 (s, 3H), 2.21 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.8, 146.0, 143.4, 136.0, 135.8, 131.6, 129.7, 127.7, 127.4, 127.0, 120.9, 120.2, 117.5, 112.5, 51.7, 49.8, 17.8. **FTIR** (cm^{-1}) ν 3402, 3068, 2999, 2952, 1708, 1438. **HRMS (ESI)** calcd for $C_{18}H_{17}NO_2Na$ ($[M+Na]^+$): 302.1151; found 302.1161.

Methyl 1-mesityl-1,2-dihydroquinoline-3-carboxylate (3d)

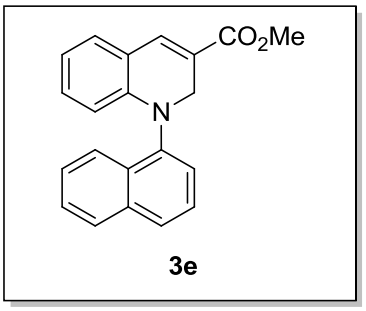


3d

Following GP3 with **1c** (200 mg, 0.74 mmol) and 2,4,6-trimethylaniline (150 mg, 1.11 mmol) to give 46 mg (20 %) of **3d** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.41 (s, 1H), 7.01-6.98 (m, 3H), 6.92-6.89 (m, 1H), 6.50 (t, *J* = 7.4 Hz, 1H), 5.81 (d, *J* = 8.2 Hz, 1H), 4.57 (s, 2H), 3.78 (s, 3H), 2.32 (s, 3H), 2.18 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.9, 145.5, 138.4, 137.2, 137.1, 136.0, 132.2, 130.0, 119.5, 118.1, 116.4, 110.7, 51.7, 49.0, 29.7, 21.0, 17.9. **FTIR** (cm^{-1}) ν 3068,

2952, 2367, 1703, 1491, 1233. **HRMS (ESI)** calcd for $C_{20}H_{21}NO_2Na$ ($[M+Na]^+$): 330.1465; found 330.1455.

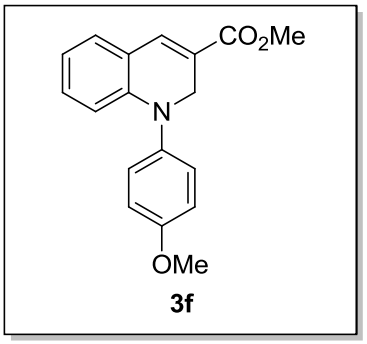
Methyl 1-(naphthalen-1-yl)-1,2-dihydroquinoline-3-carboxylate (3e)



3e

Following GP3 during 40 hours with **1c** (264 mg, 0.97 mmol) and 1-naphtylamine (197 mg, 1.38 mmol) to give 76 mg (25 %) of **3e** as a yellow oil**. ^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.99 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.59-7.53 (m, 4H), 7.51-7.45 (m, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 5.94 (d, *J* = 8.2 Hz, 1H), 4.84 (d, *J* = 14.6 Hz, 1H), 4.76 (d, *J* = 14.6 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.8, 146.9, 141.7, 135.8, 135.1, 131.5, 129.9, 129.6, 128.5, 127.3, 126.5, 126.4, 126.3, 124.8, 123.4, 121.4, 120.3, 117.8, 113.5, 51.7, 50.7. **FTIR** (cm^{-1}) ν 2949, 2851, 1700, 1486, 1197. **HRMS (ESI)** calcd for $C_{21}H_{17}NO_2Na$ ($[M+Na]^+$): 338.1151; found 338.1153.

Methyl 1-(4-methoxyphenyl)-1,2-dihydroquinoline-3-carboxylate (3f)

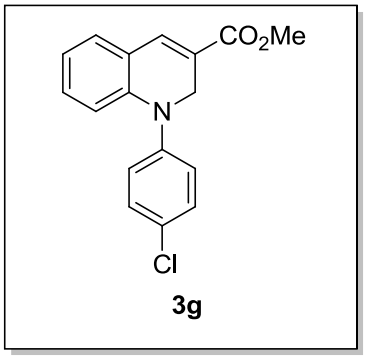


3f

Following GP3 with **1c** (228 mg, 0.84 mmol) and *p*-anisidine (155 mg, 1.26 mmol) to give 140 mg (56%) of **3f** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.45 (s, 1H), 7.21 (d, *J* = 8.9 Hz, 2H), 7.08 (dd, *J* = 1.4, 7.5 Hz, 1H), 7.02-7.00 (m, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 8.3 Hz, 1H) 4.60 (s, 2H), 3.83 (s, 3H), 3.80 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ

(ppm) 165.7, 157.1, 146.5, 138.4, 135.4, 131.3, 129.6, 129.0, 126.3, 121.3, 118.1, 115.1, 114.9, 114.8, 113.6, 55.5, 51.7, 49.8. **FTIR** (cm^{-1}) ν 2950, 2836, 1700, 1509, 1220. **HRMS (ESI)** calcd for $C_{18}H_{17}NO_3Na$ ($[M+Na]^+$): 318.1101; found 318.1093.

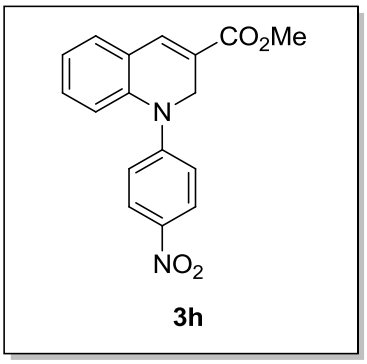
Methyl 1-(4-chlorophenyl)-1,2-dihydroquinoline-3-carboxylate (3g)



3g

Following GP3 with **1c** (119 mg, 0.44 mmol) and *p*-chloroaniline (84.2 mg, 0.66 mmol) to give 93 mg (70%) of **3g** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.47 (s, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 8.6 Hz, 1H), 6.78-6.71 (m, 2H) 4.57 (s, 2H), 3.80 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.6, 144.7, 144.1, 135.1, 131.1, 129.6, 129.4, 129.2, 124.7, 122.7, 122.3, 119.6, 114.9, 51.9, 48.8. **FTIR** (cm^{-1}) ν 2950, 2850, 1703, 1491, 1225. **HRMS (ESI)** calcd for $C_{17}H_{14}ClNO_2Na$ ($[M+Na]^+$): 322.0605; found 322.0602.

Methyl 1-(4-nitrophenyl)-1,2-dihydroquinoline-3-carboxylate (3h)

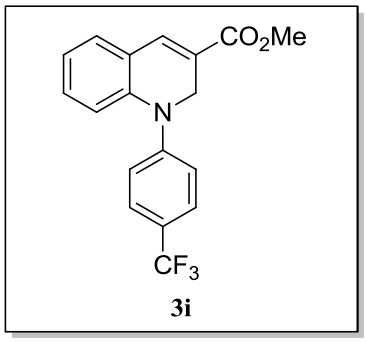


3h

Following GP3 with **1c** (122 mg, 0.45 mmol) and *p*-nitroaniline (93.5 mg, 0.68 mmol) to give 78 mg (56 %) of **3h** as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 8.19 (d, *J* = 9.3 Hz, 2H), 7.53 (m, 1H), 7.30-7.14 (m, 5H), 6.99 (td, *J* = 7.4, 1.6 Hz, 1H), 4.63 (s, 2H), 3.83 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) 165.6, 151.8, 141.3, 134.7, 131.3, 130.0, 125.2, 124.4, 123.0, 120.1, 118.6, 52.4,

47.3. **FTIR** (cm^{-1}) ν 2918, 2850, 1706, 1590, 1500, 1325, 1225. **HRMS (ESI)** calcd for $C_{17}H_{14}N_2O_4Na$ ($[M+Na]^+$): 333.0846; found 333.0852.

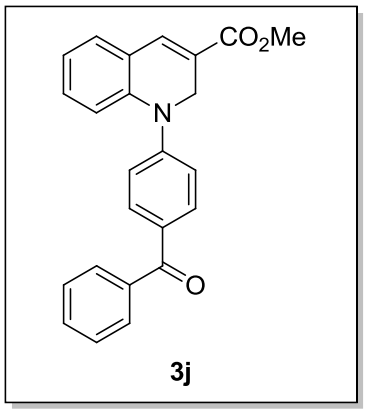
Methyl 1-(4-(trifluoromethyl)phenyl)-1,2-dihydroquinoline-3-carboxylate (3i)



3i

Following GP3 with **1c** (144 mg, 0.5 mmol) and *p*-(trifluoromethyl)aniline (120 mg, 0.75 mmol) to give 86 mg (51%) of **3i** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.5 (d, *J* = 8.5 Hz, 2H), 7.51 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.20 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.15-7.10 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.87 (td, *J* = 7.5, 1.1 Hz, 1H) 4.61 (s, 2H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.4, 148.8, 143.3, 134.8, 130.9, 129.6, 126.4 (q, J_{C-F} = 3.6 Hz), 124.9 (q, J_{C-F} = 33.9 Hz), 124.2 (q, J_{C-F} = 271.8 Hz), 123.9, 123.2, 121.8, 120.9, 116.2, 51.9, 48.2. **^{19}F NMR (380 MHz, $CDCl_3$)** δ (ppm) 61.95. **FTIR** (cm^{-1}) ν 2953, 1703, 1598, 1486, 1226. **HRMS (ESI)** calcd for $C_{18}H_{14}F_3NO_2Na$ ($[M+Na]^+$): 356.0869; found 356.0872.

Methyl 1-(4-benzoylphenyl)-1,2-dihydroquinoline-3-carboxylate (3j)

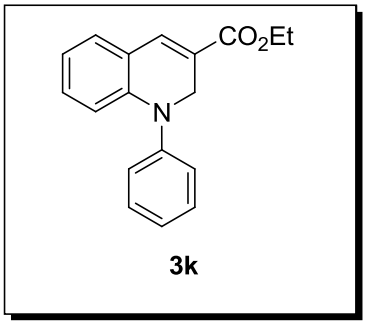


3j

Following GP3 with **1c** (165 mg, 0.61 mmol) and (4-aminophenyl)(phenyl)methanone (183 mg, 0.68 mmol) to give 120 mg (53 %) of **3j** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.84 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 7.0 Hz, 2H), 7,58 (t, *J* = 7.4 Hz, 1H), 7.52-7.47 (m, 3H), 7.31 (d, *J* = 8.7 Hz,

2H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.22-7.11 (m, 2H), 6.90 (t, *J* = 7.9 Hz, 1H), 4.65 (s, 2H), 3.82 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 195.3, 165.4, 149.7, 142.8, 138.1, 134.8, 132.0, 131.8, 131.5, 130.8, 129.8, 129.5, 128.2, 124.2, 123.5, 121.3, 120.5, 117.0, 115.0, 52.0, 48.0. **FTIR** (cm^{-1}) ν 2950, 2850, 1704, 1650, 1508, 1280. **HRMS (ESI)** calcd for $C_{24}H_{19}NO_3Na$ ($[M+Na]^+$): 392.1257; found 392.1271.

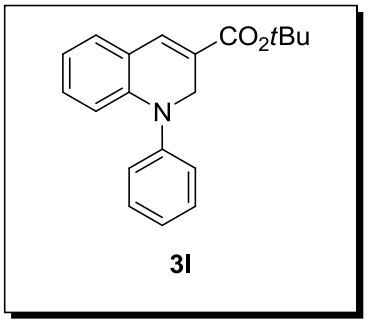
Ethyl 1-phenyl-1,2-dihydroquinoline-3-carboxylate (3k)



3k

Following GP3 with **1d** (125 mg, 0.44 mmol) and aniline (62 mg, 0.66 mmol) to give 70 mg (57 %) of **3k** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.48 (s, 1H), 7.39 (m, 2H), 7.28 (dd, *J* = 8.6, 1.1 Hz, 2H), 7.18-7.13 (m, 2H), 7.06-7.02 (m, 1H), 6.75-6.71 (m, 2H), 4.62 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.2, 145.5, 145.3, 134.9, 130.9, 129.4, 129.3, 124.3, 123.7, 122.5, 122.4, 119.0, 114.7, 60.6, 48.9, 14.3. **FTIR** (cm^{-1}) ν 2980, 1697, 1485, 1261. **HRMS (ESI)** calcd for $C_{18}H_{17}NO_2Na$ ($[M+Na]^+$): 302.1151; found 302.1155.

***Tert*-butyl 1-phenyl-1,2-dihydroquinoline-3-carboxylate (3l)**

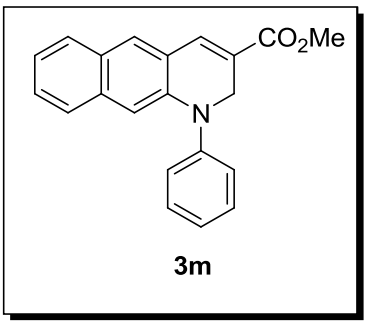


3l

Following GP3 with **1e** (238 mg, 0.76 mmol) and aniline (106 mg, 1.14 mmol) to give 103 mg (45 %) of **3l** as a yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.40-7.36 (m, 3H), 7.29-7.26 (m, 2H), 7.17-7.11 (m, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.74-6.71 (m, 2H), 4.57 (s, 2H), 1.53 (s, 9H). **^{13}C NMR**

(101 MHz, $CDCl_3$) δ (ppm) 164.6, 145.7, 145.1, 134.1, 130.7, 129.3, 124.2, 123.6, 122.7, 119.0, 114.7, 80.8, 48.9, 28.2. **FTIR** (cm^{-1}) ν 3391, 2975, 1693, 1150. **HRMS (ESI)** calcd for $C_{20}H_{21}NO_2Na$ ($[M+Na]^+$): 330.1465; found 330.1462.

Methyl 1-phenyl-1,2-dihydrobenzo[g]quinoline-3-carboxylate (3m)



3m

Following GP3 with **1f** (125 mg, 0.39 mmol) and aniline (62 mg, 0.66 mmol) to give 12 mg (10 %) of **3m** as a yellow oil. **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) 7.78 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 4.2 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.26-7.24 (m, 1H), 7.16 (t, *J* = 7.8 Hz, 2H), 6.98-6.90 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 4.74 (s, 2H), 3.78 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 165.8, 149.8, 139.7, 135.2, 134.8, 129.0, 128.3, 127.6, 126.7, 125.9, 125.8, 125.6, 125.2, 124.3, 123.2, 122.0, 121.3, 51.8, 50.6. **FTIR** (cm^{-1}) ν 3055, 2950, 1704, 1490, 1202. **HRMS (ESI)** calcd for $C_{21}H_{17}NO_2Na$ ($[M+Na]^+$): 338.1151; found 338.1143.

Parameters		
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2	Temperature	300.0
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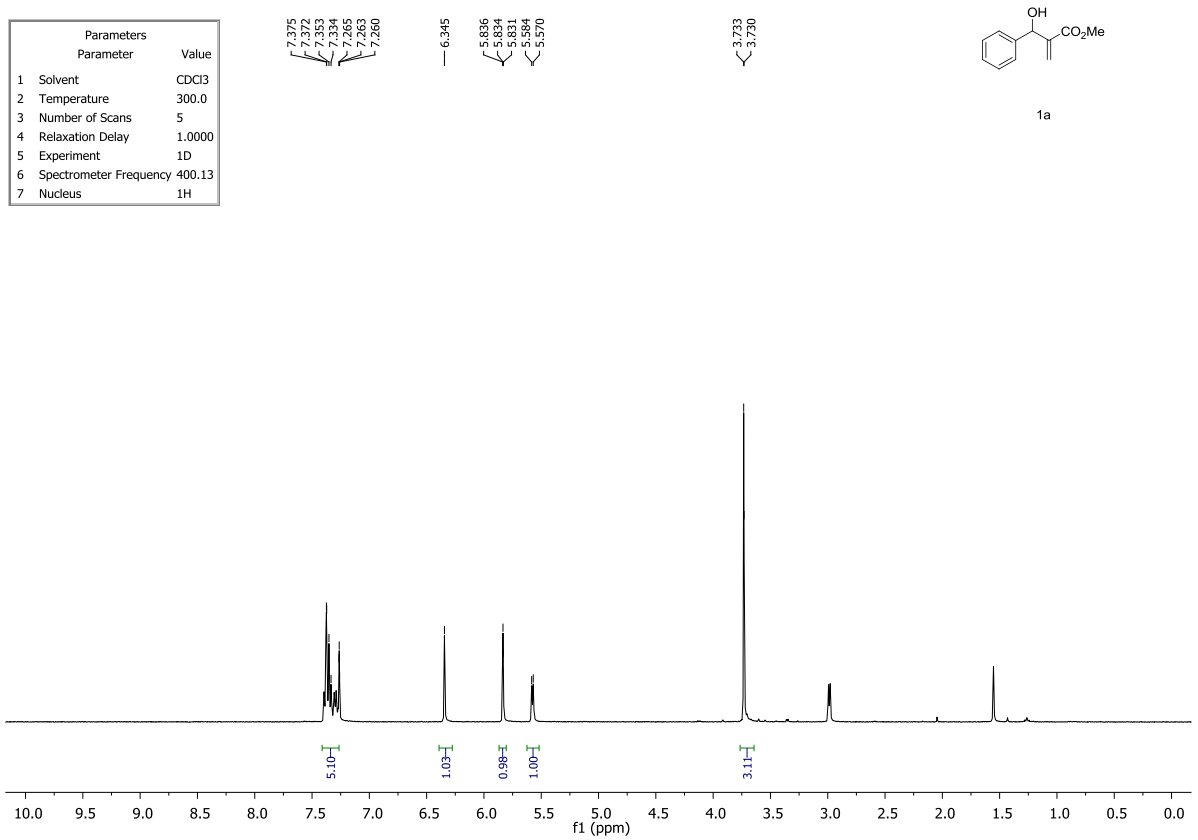
4	Relaxation Delay	1.0000
5	Experiment	1D
6	Spectrometer Frequency	400.13
7	Nucleus	1H



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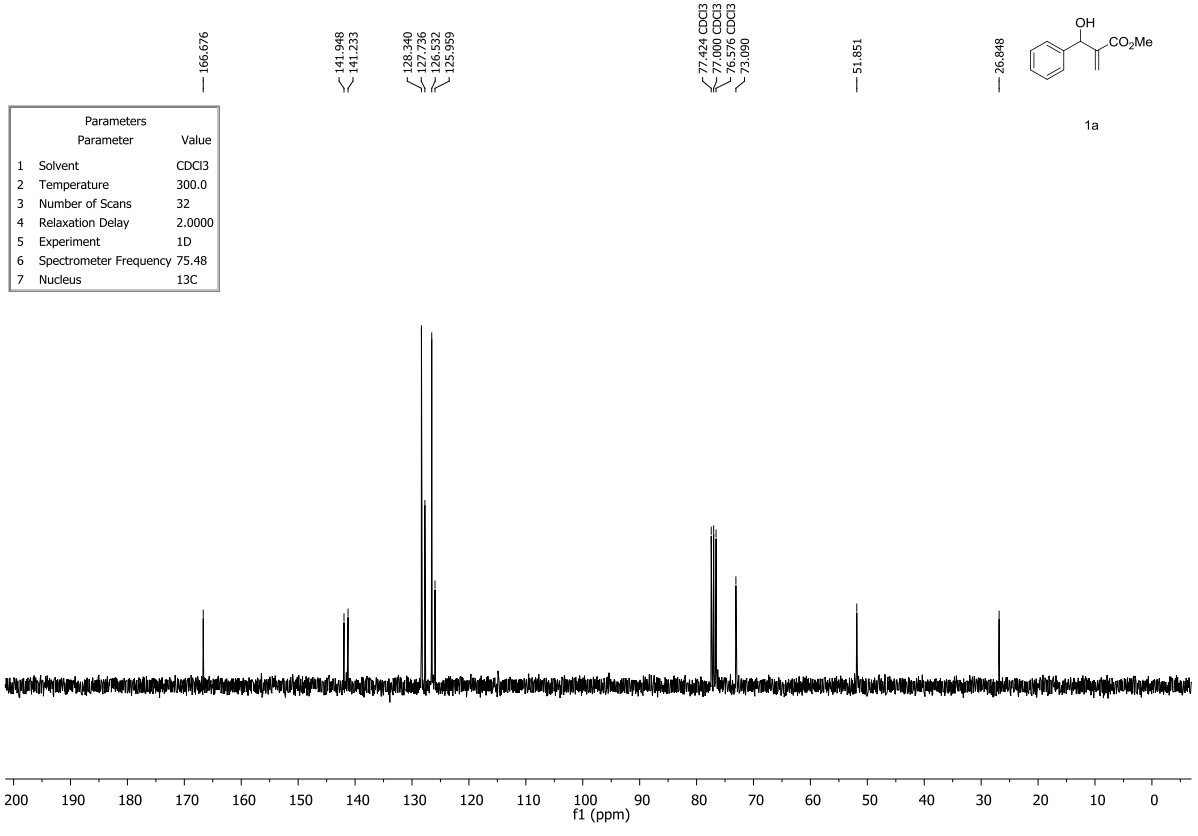

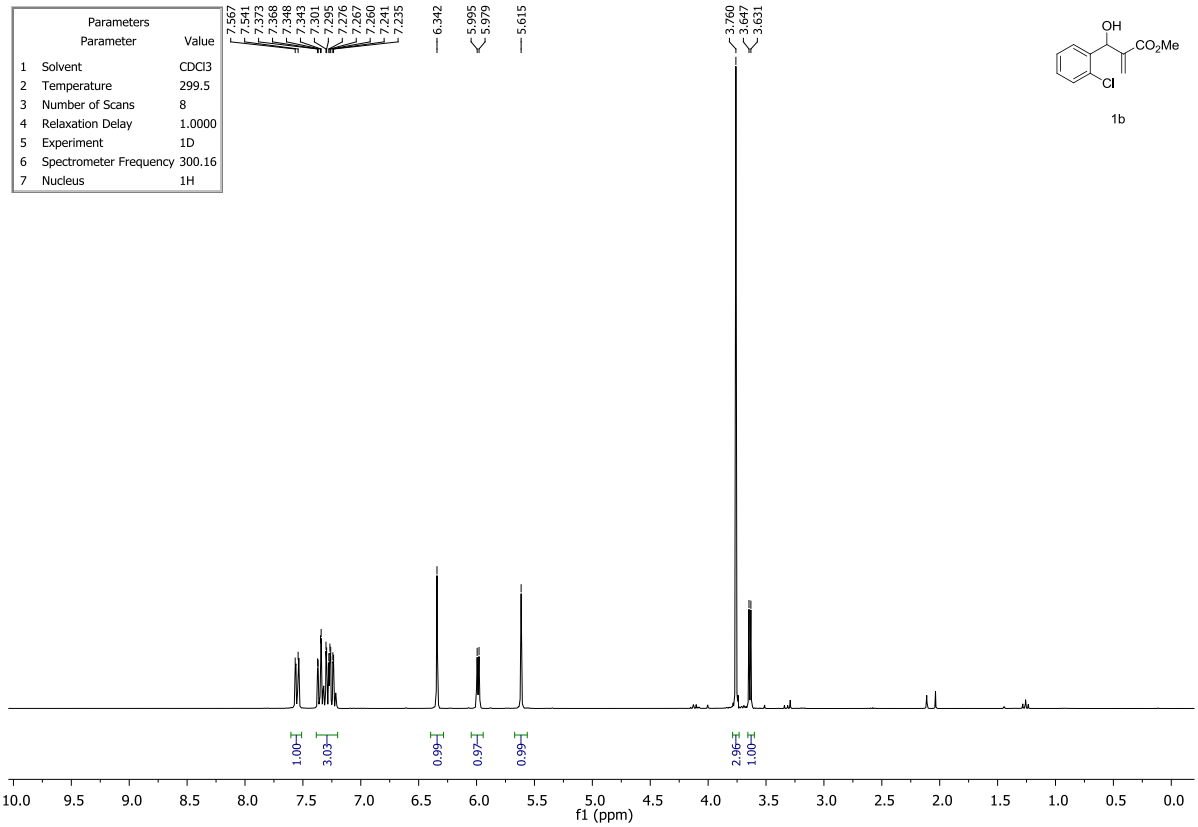
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6 Spectrometer Frequency 300.16
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7.343
7.301
7.295
7.276
7.267
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5.979
5.615
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3.647
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OH
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Cl
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3.03
0.99
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0.99
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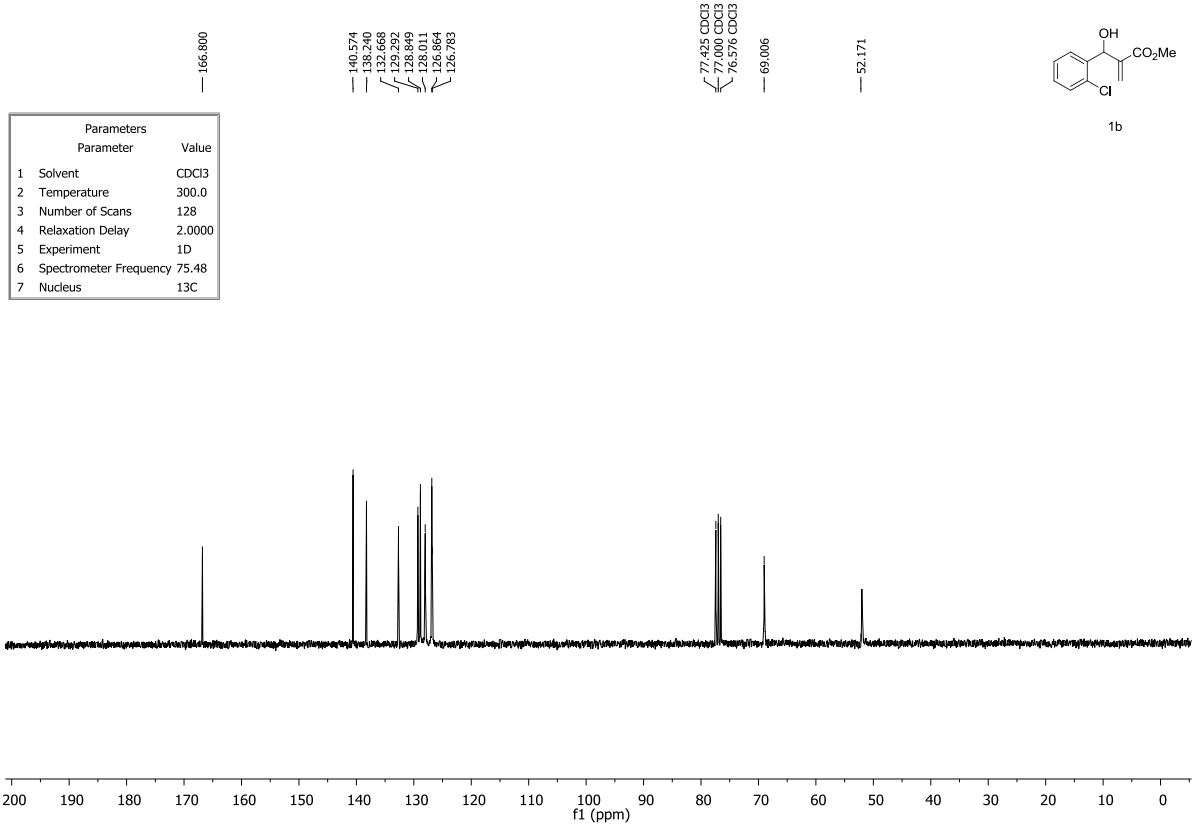
1.00
f1 (ppm)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5 Experiment 1D
6 Spectrometer Frequency 75.48
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OH
CO2Me
Cl
1b
f1 (ppm)

Parameters		
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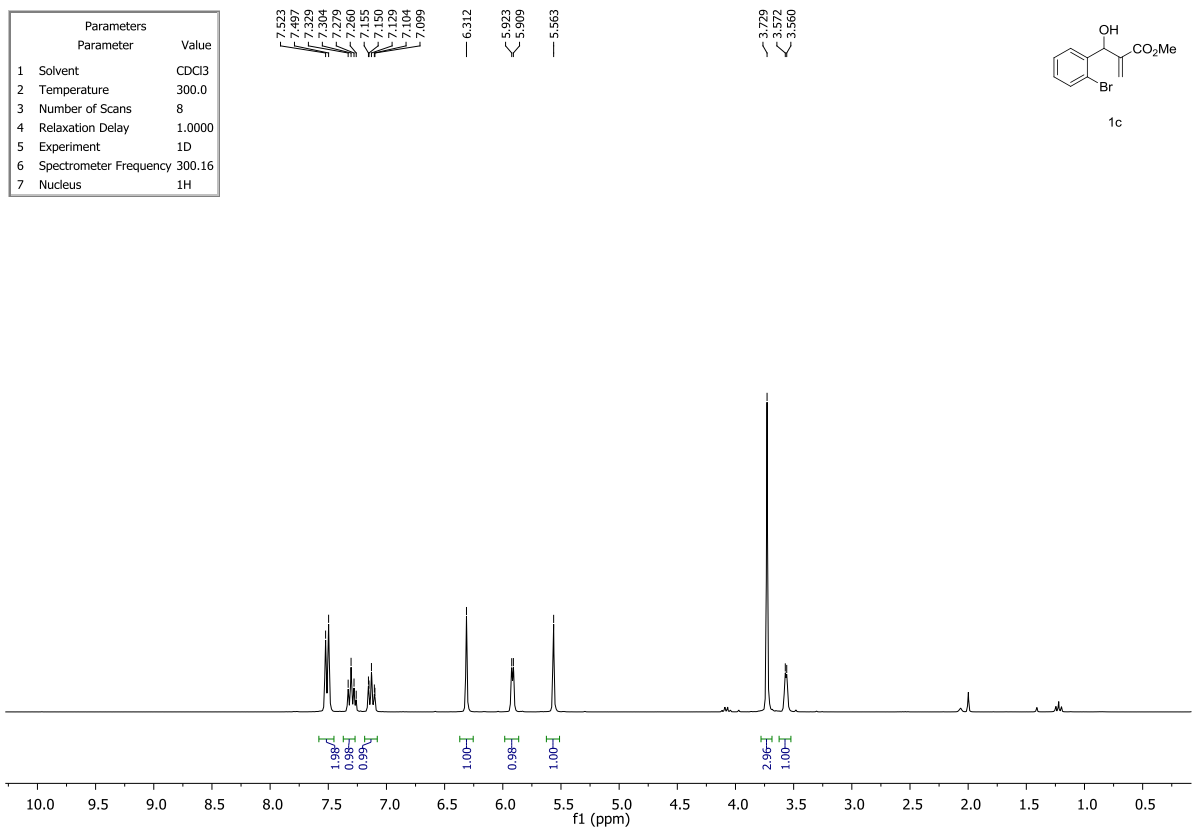

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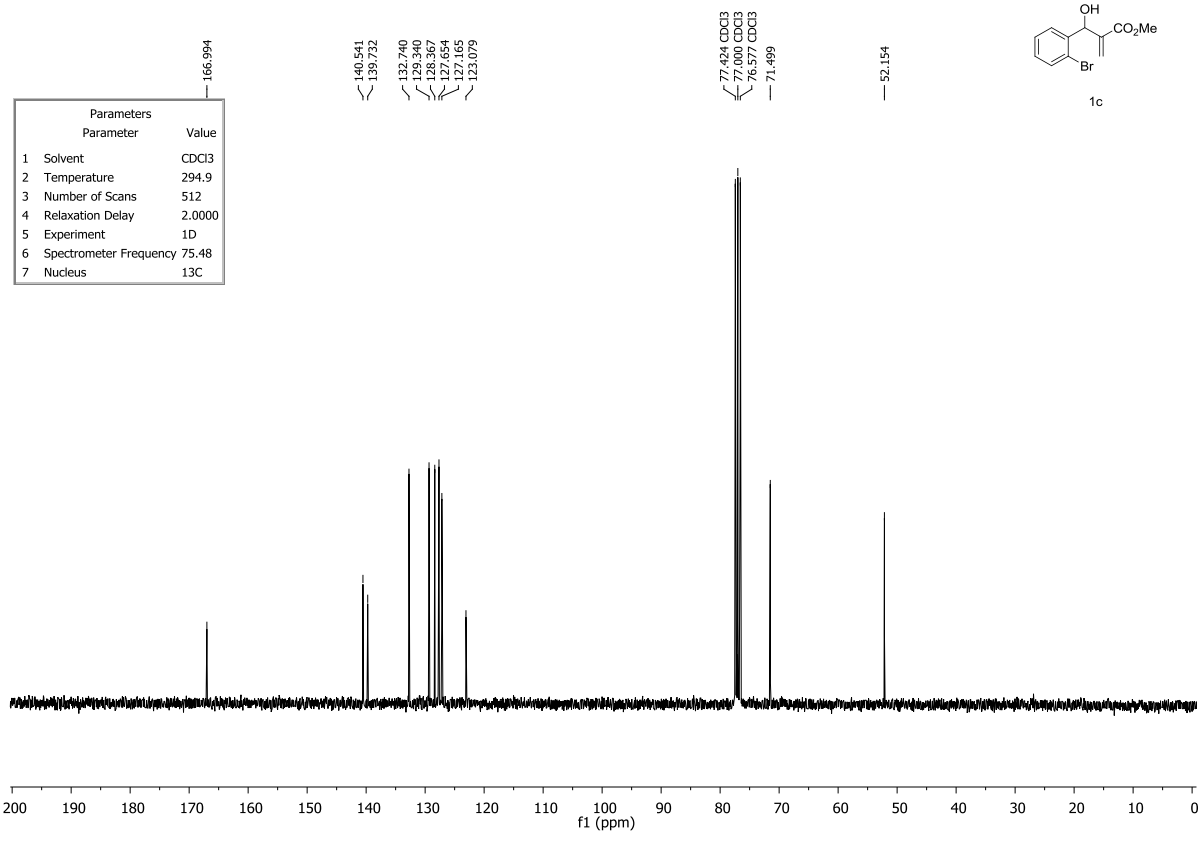

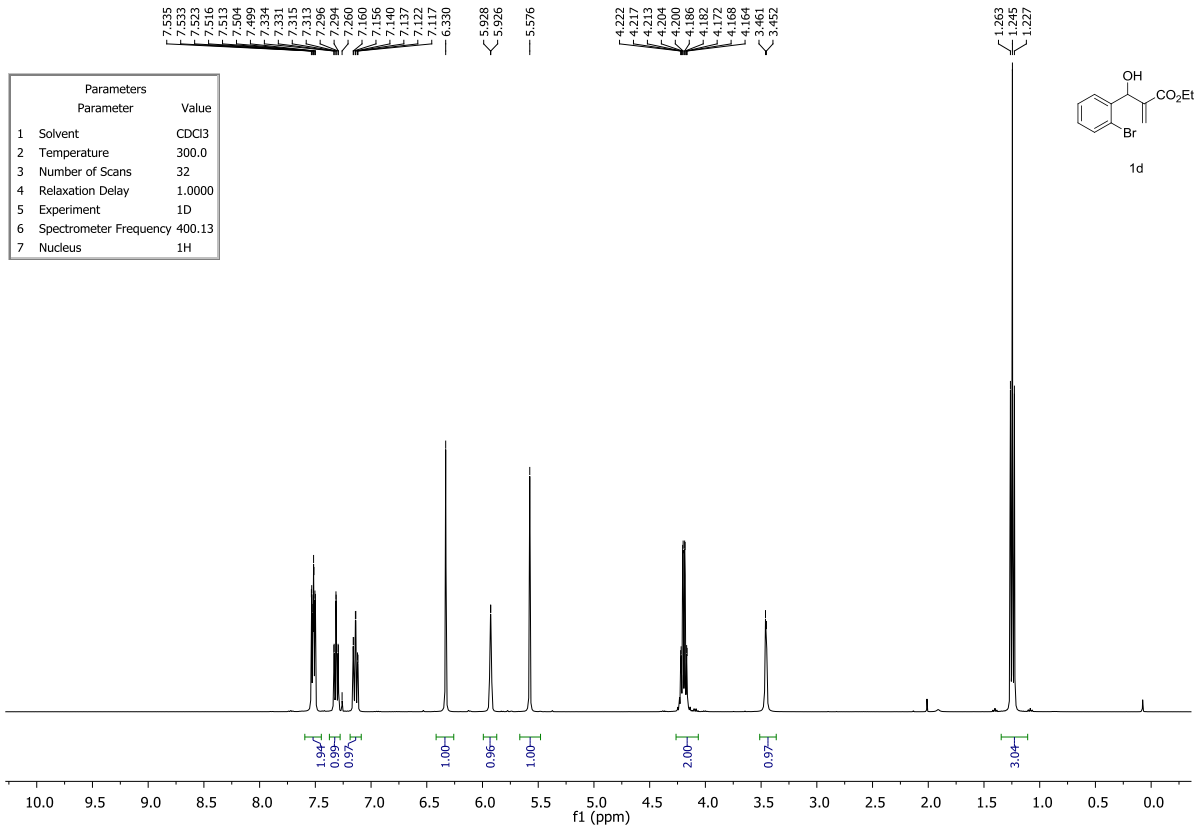
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7.122
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4.222
4.217
4.213
4.204
4.200
4.186
4.182
4.172
4.168
4.164
3.461
3.452
1.263
1.245
1.227
Parameters
Parameter Value
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6 Spectrometer Frequency 400.13
7 Nucleus 1H
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CO2Et
Br
1d
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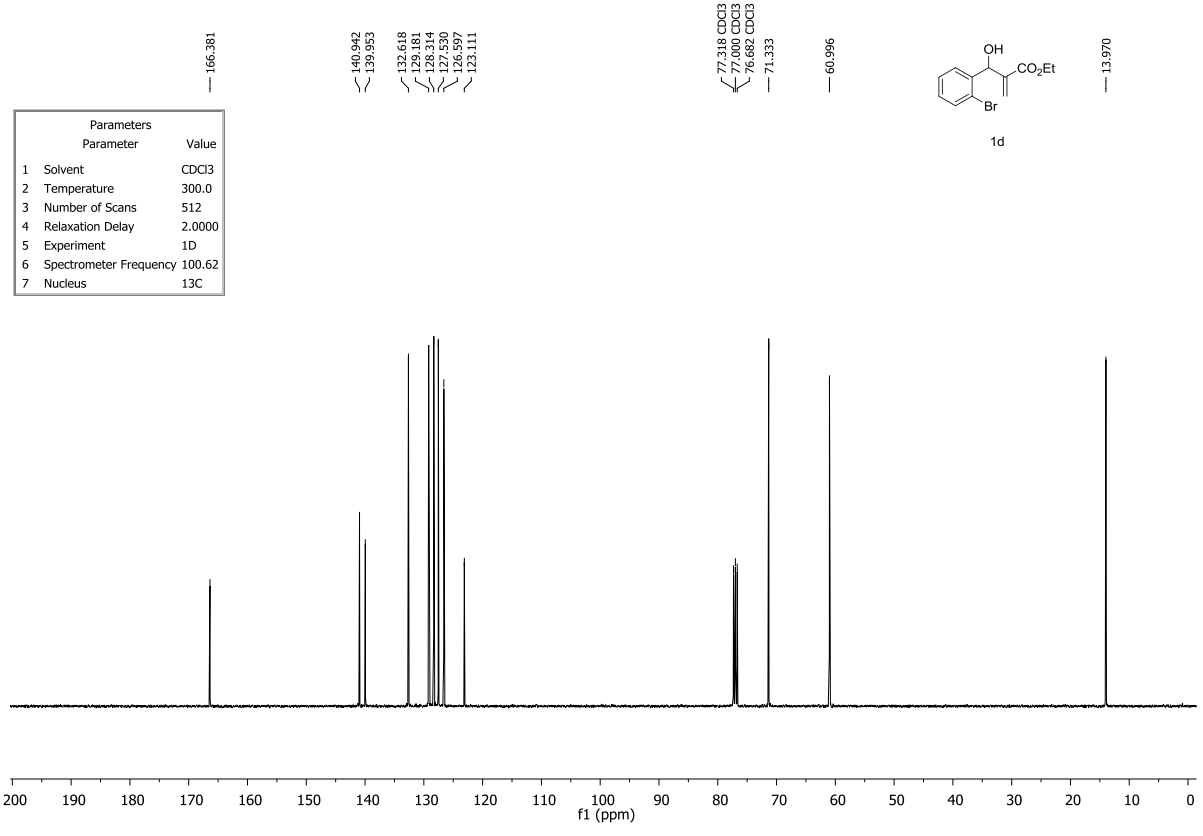
0.99
0.97
1.00
0.96
1.00
2.00
0.97
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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60.996
13.970
Parameters
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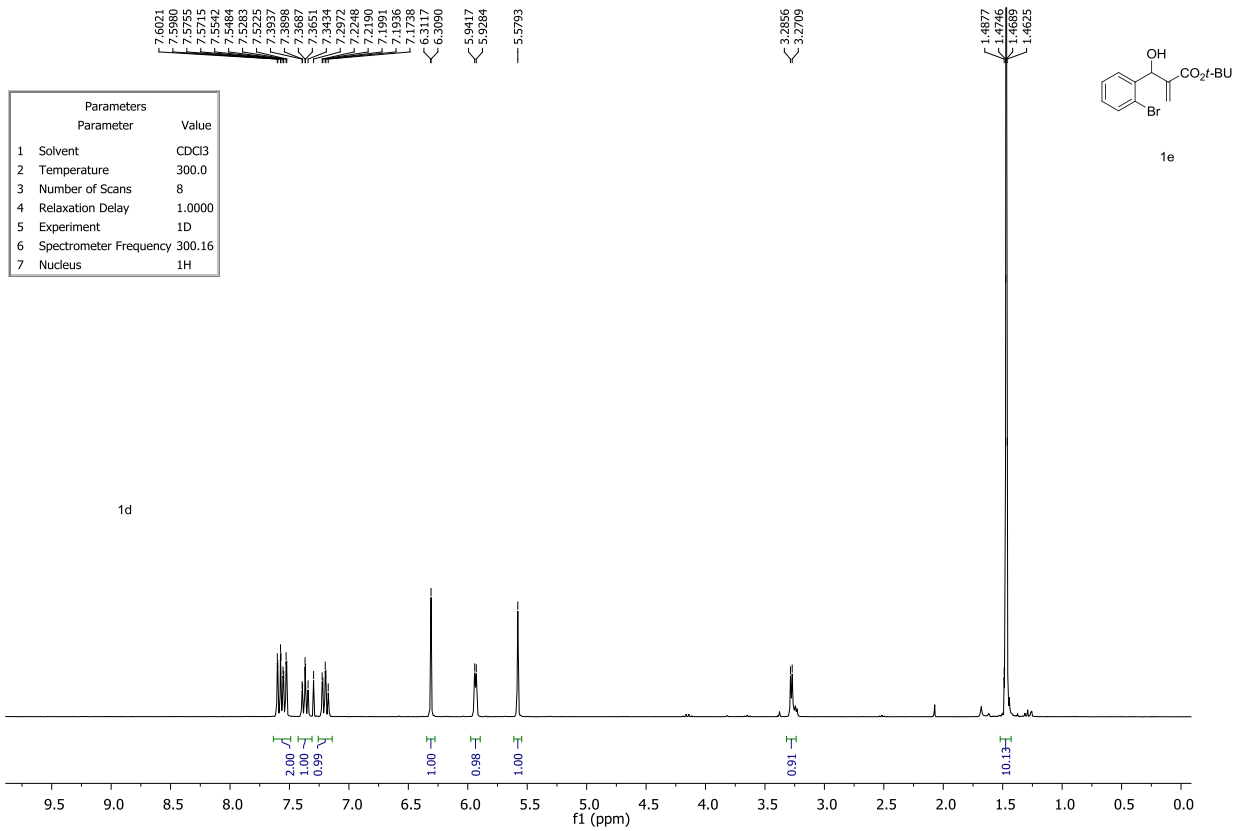
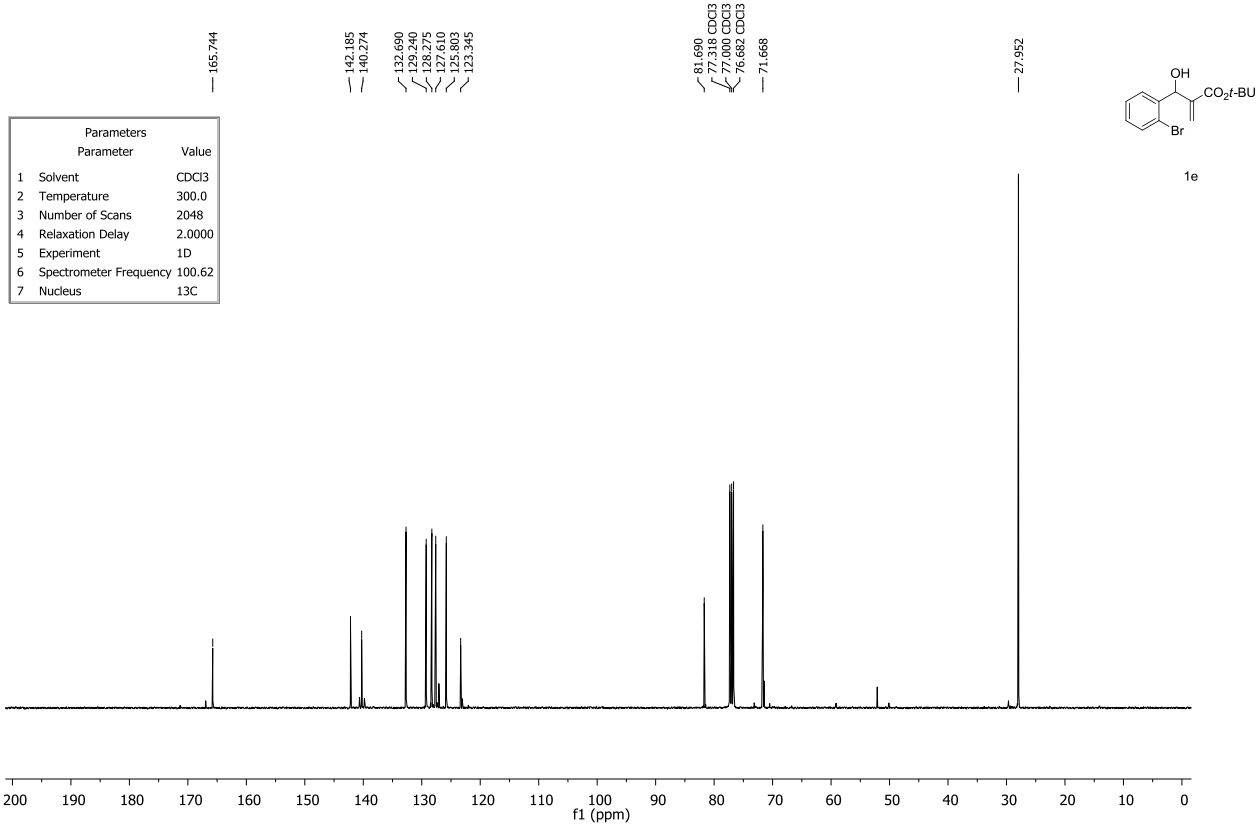
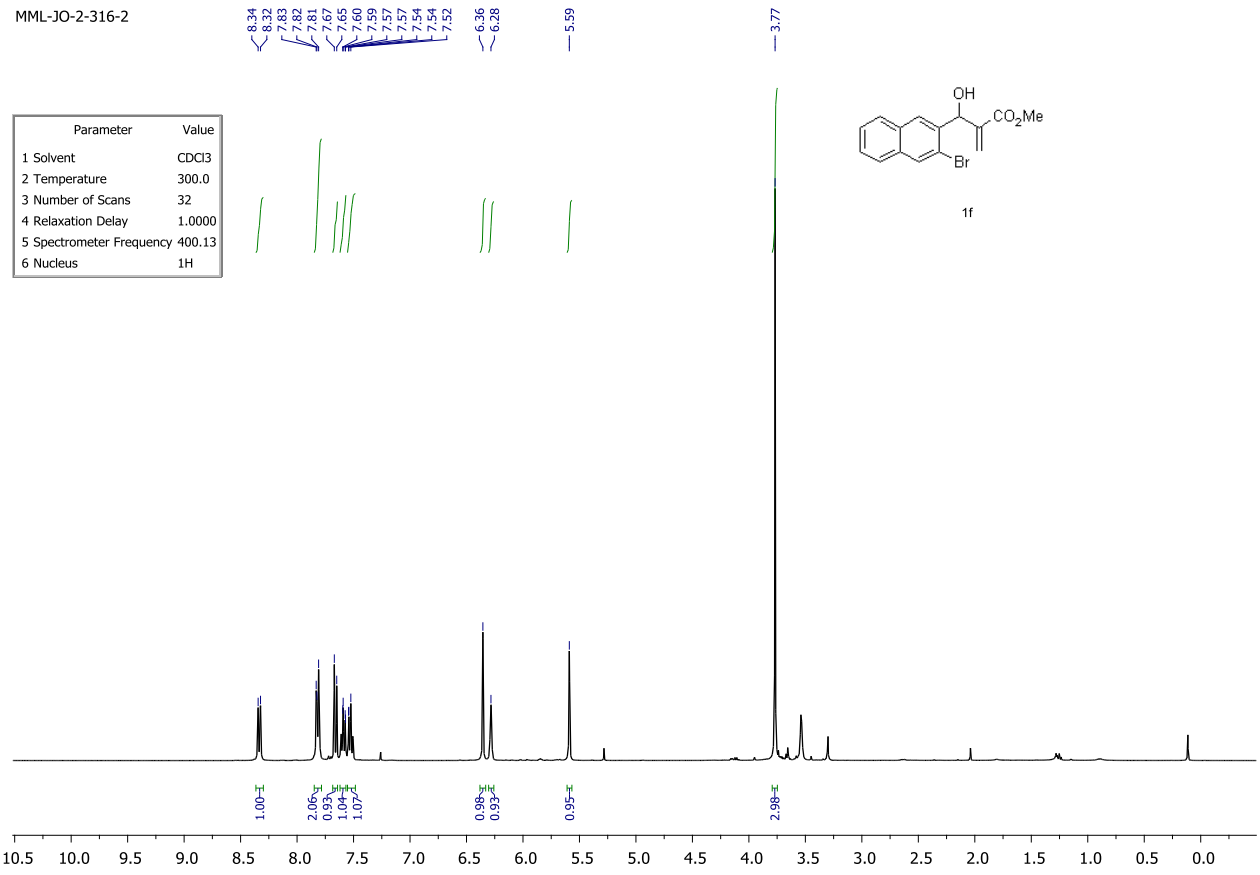
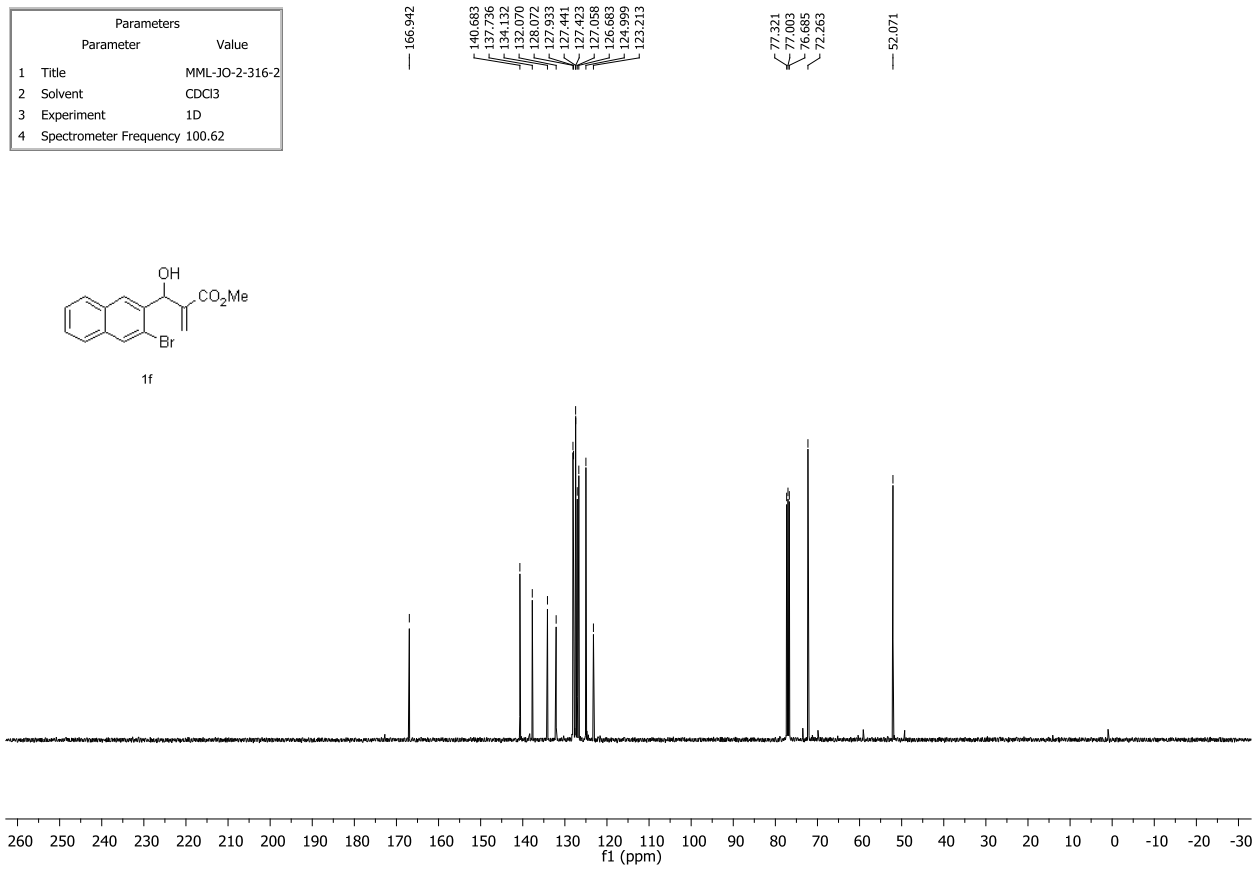
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
OH
CO2Et
Br
1d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.6021
7.5980
7.5755
7.5715
7.5542
7.5484
7.5283
7.5225
7.3937
7.3898
7.3687
7.3651
7.3434
7.2972
7.2248
7.2190
7.1991
7.1936
7.1738
6.3117
6.3090
5.9417
5.9284
5.5793
3.2856
3.2709
1.4877
1.4746
1.4689
1.4625
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 300.16
7 Nucleus 1H
1d
OH
CO2t-BU
Br
1e
2.00
1.00
0.99
1.00
0.98
1.00
0.91
10.13
9.5 9.0 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)

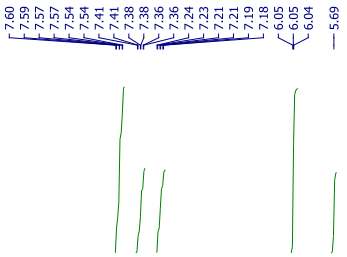

165.744
142.185
140.274
132.690
129.240
128.275
127.610
125.803
123.345
81.690
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
71.668
27.952
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 2048
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
OH
CO2t-BU
Br
1e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

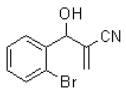

MML-JO-2-316-2
8.34
8.32
7.83
7.82
7.81
7.67
7.65
7.60
7.59
7.57
7.57
7.54
7.54
7.52
6.36
6.28
5.59
3.77
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 32
4 Relaxation Delay 1.0000
5 Spectrometer Frequency 400.13
6 Nucleus 1H
OH
CO2Me
Br
1f
1.00
2.06
0.99
1.04
1.07
0.98
0.93
0.95
2.98
10.5 10.0 9.5 9.0 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


Parameters
Parameter Value
1 Title MML-JO-2-316-2
2 Solvent CDCl3
3 Experiment 1D
4 Spectrometer Frequency 100.62
166.942
140.683
137.736
134.132
132.070
128.072
127.933
127.441
127.423
127.058
126.683
124.999
123.213
77.321
77.003
76.685
72.263
52.071
OH
CO2Me
Br
1f
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

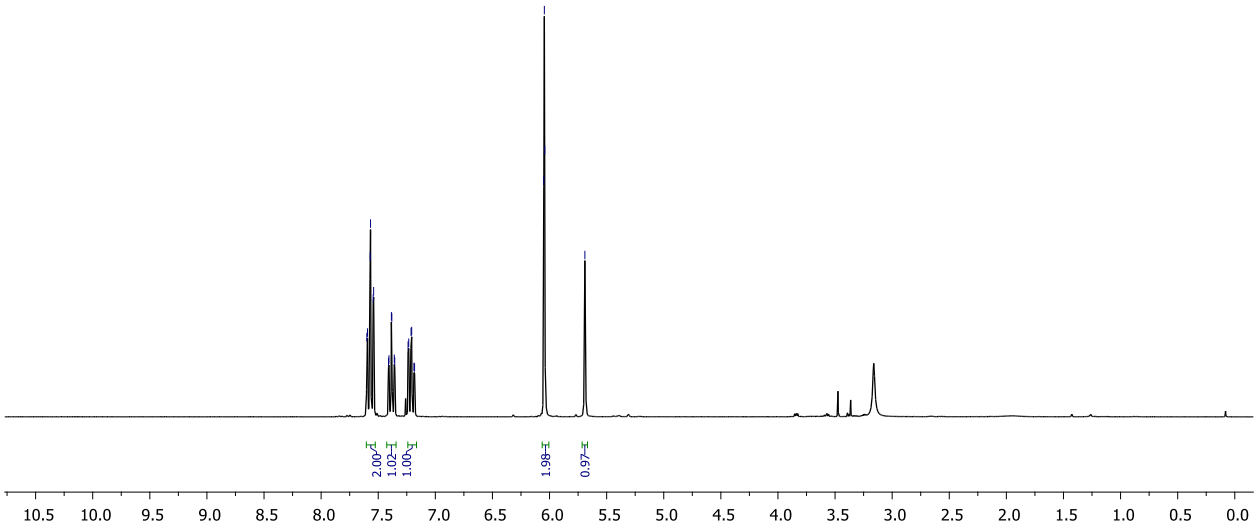
jo-2-301

Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.1
3 Number of Scans	8
4 Relaxation Delay	1.0000
5 Spectrometer Frequency	300.16
6 Nucleus	1H



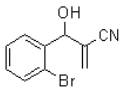


1g

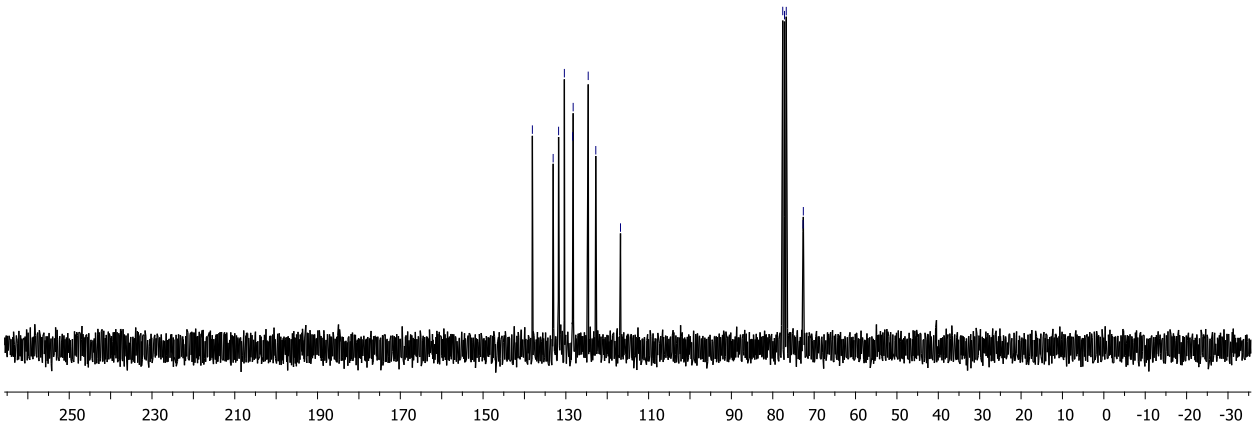


jo-2-301

Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.0
3 Number of Scans	64
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	75.48
6 Nucleus	13C

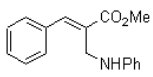


1g



jo-2-197
1H routine 8 scans

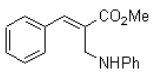
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.0
3 Number of Scans	8
4 Relaxation Delay	1.0000
5 Spectrometer Frequency	300.16
6 Nucleus	1H



2a

JO-2-197

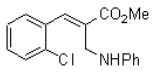
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.0
3 Number of Scans	512
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	75.48
6 Nucleus	13C



2a

mml075-f2

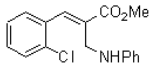
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.0
3 Number of Scans	8
4 Relaxation Delay	1.0000
5 Spectrometer Frequency	300.16
6 Nucleus	1H



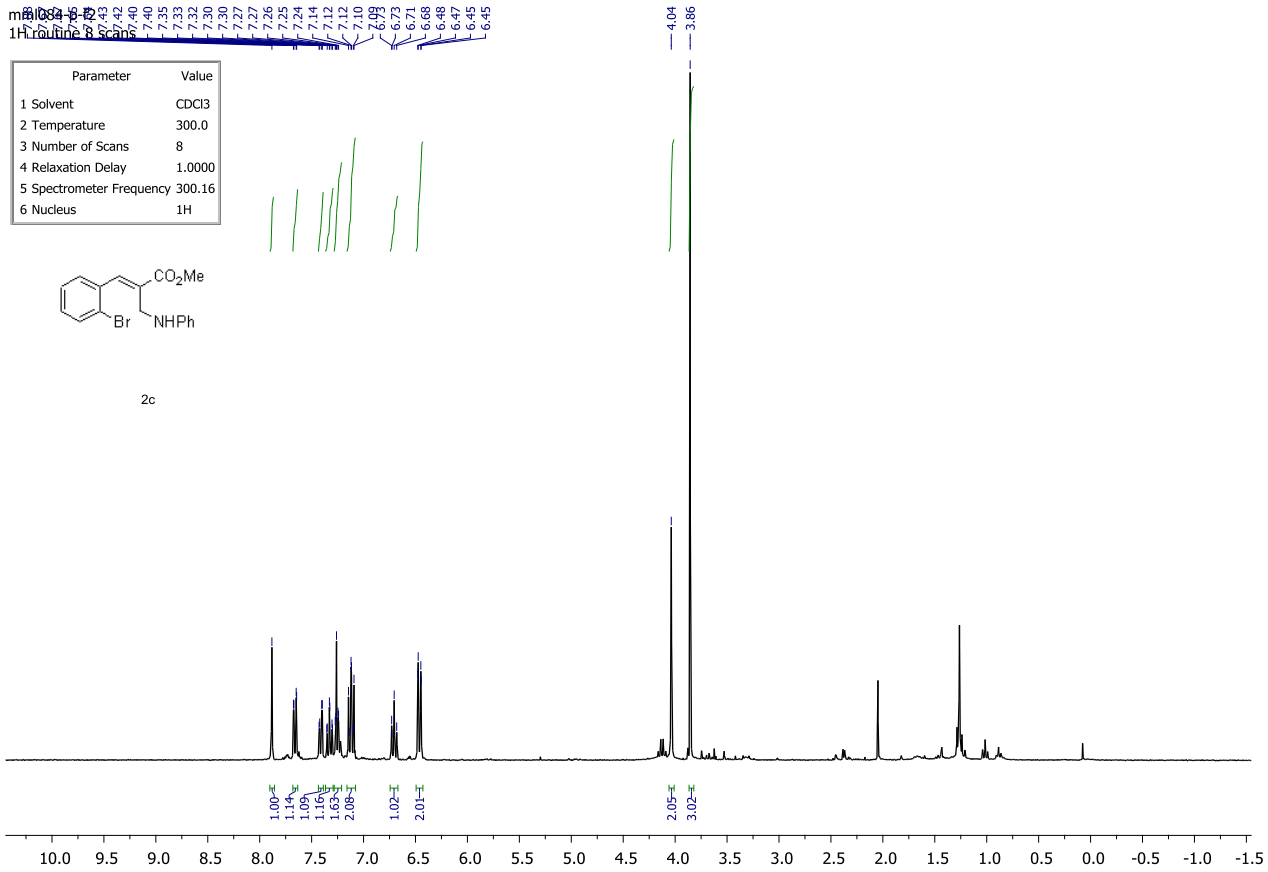
2b

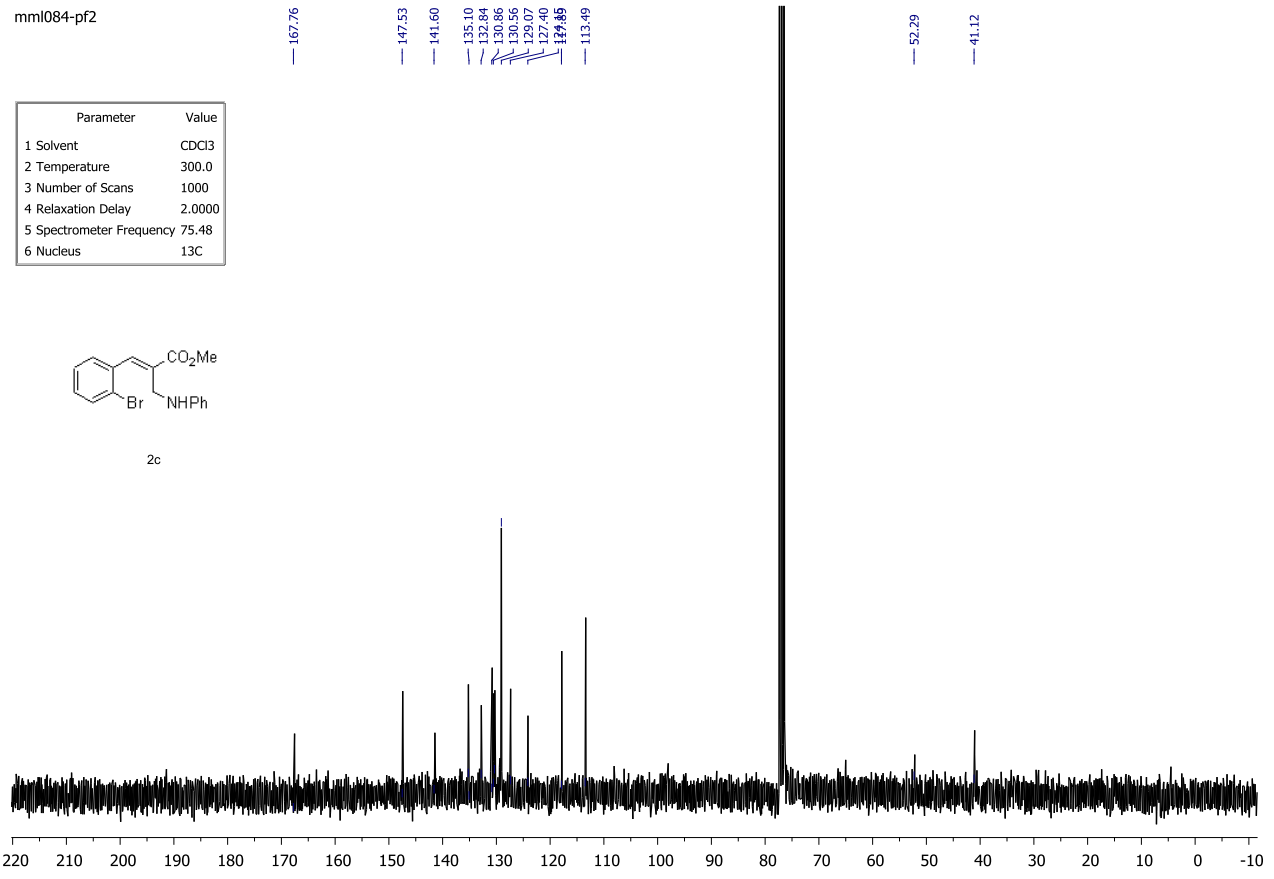
mml075-f2
13C routine
decouple 1H
32 scans

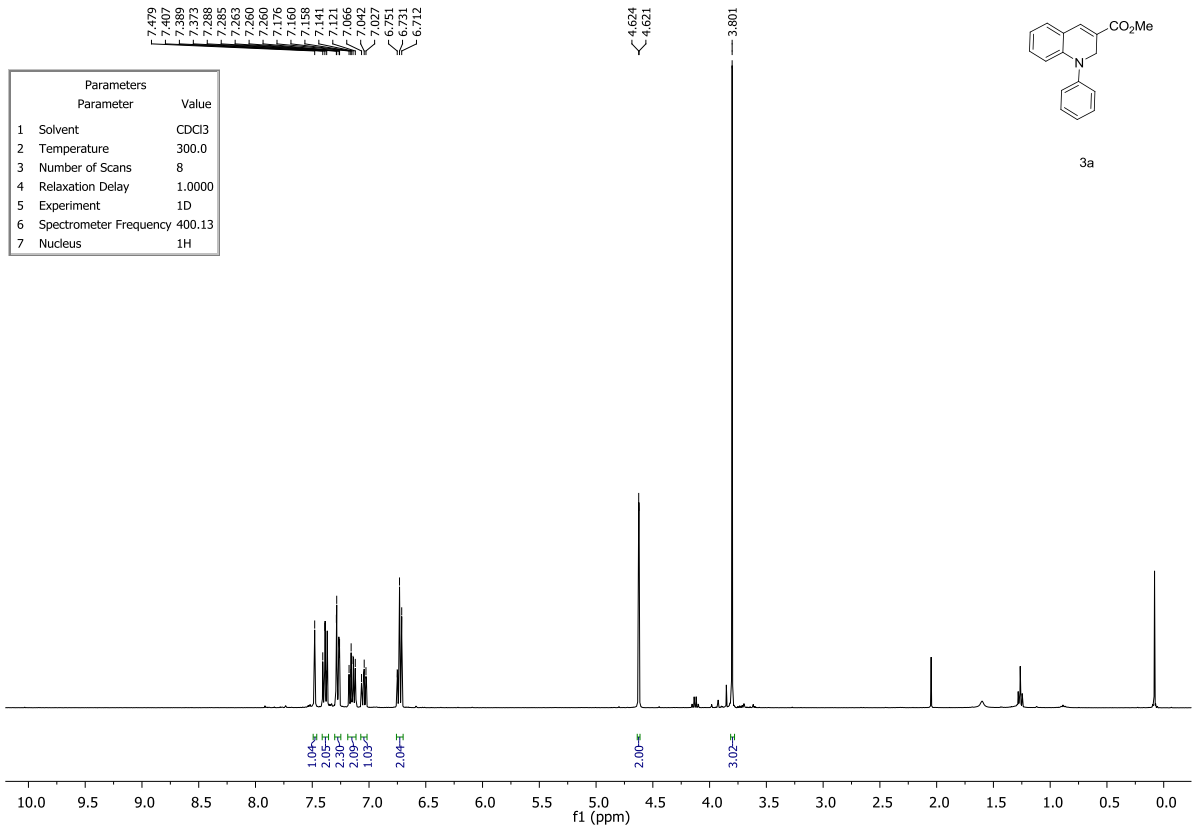
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.1
3 Number of Scans	32
4 Relaxation Delay	2.0000
5 Spectrometer Frequency	100.61
6 Nucleus	13C

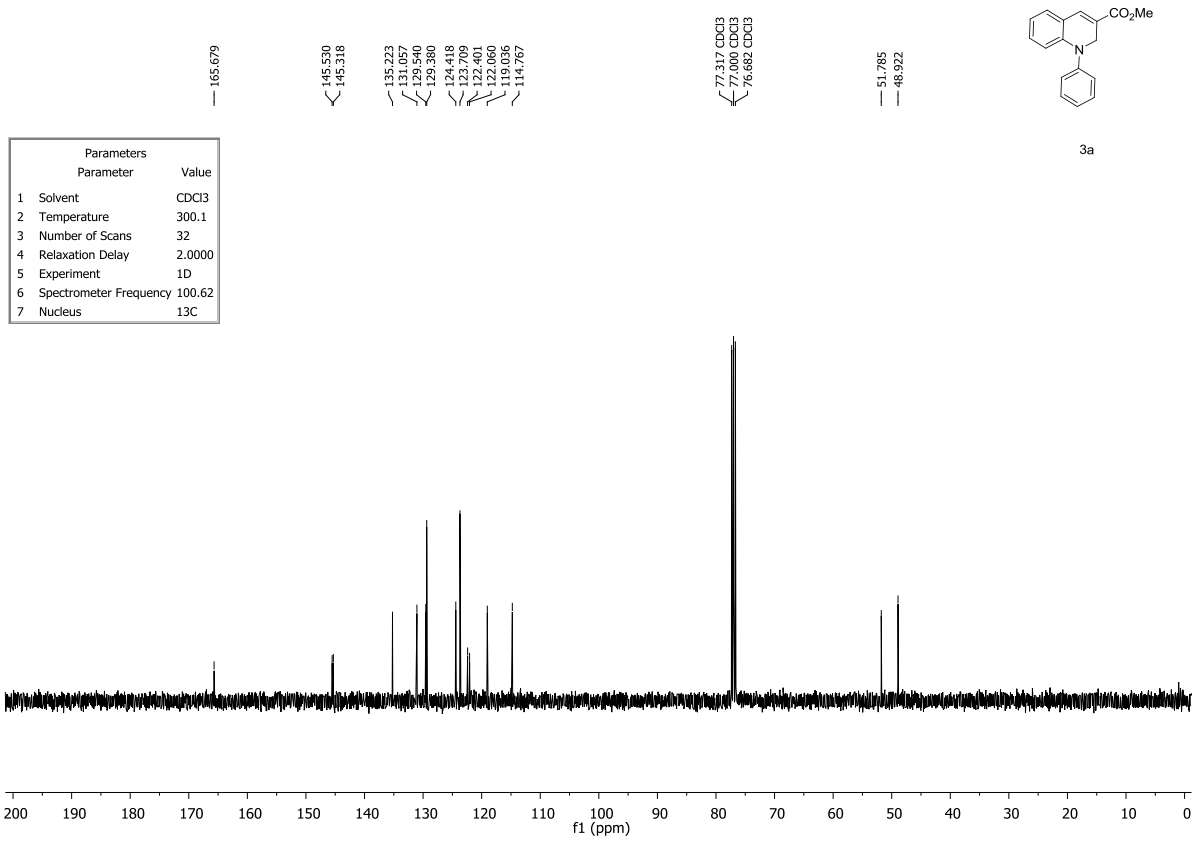


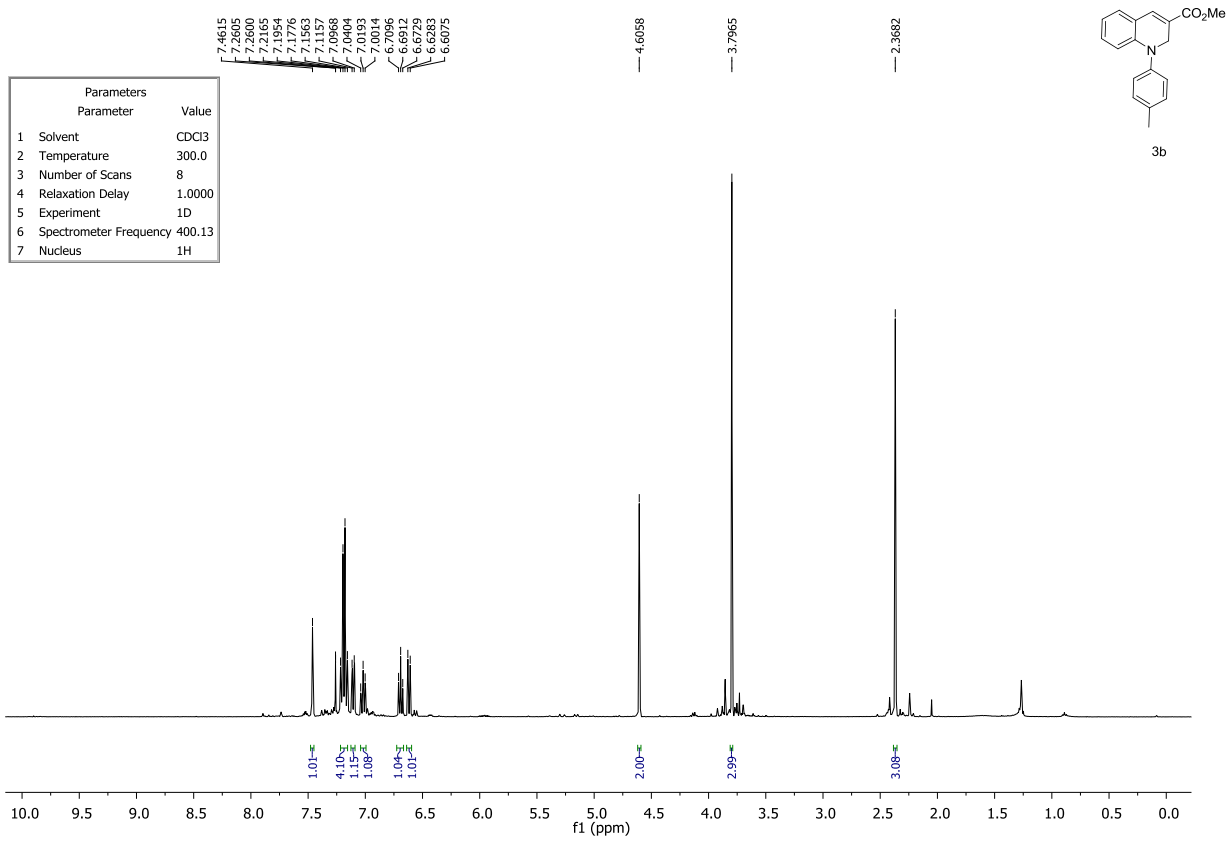
2b

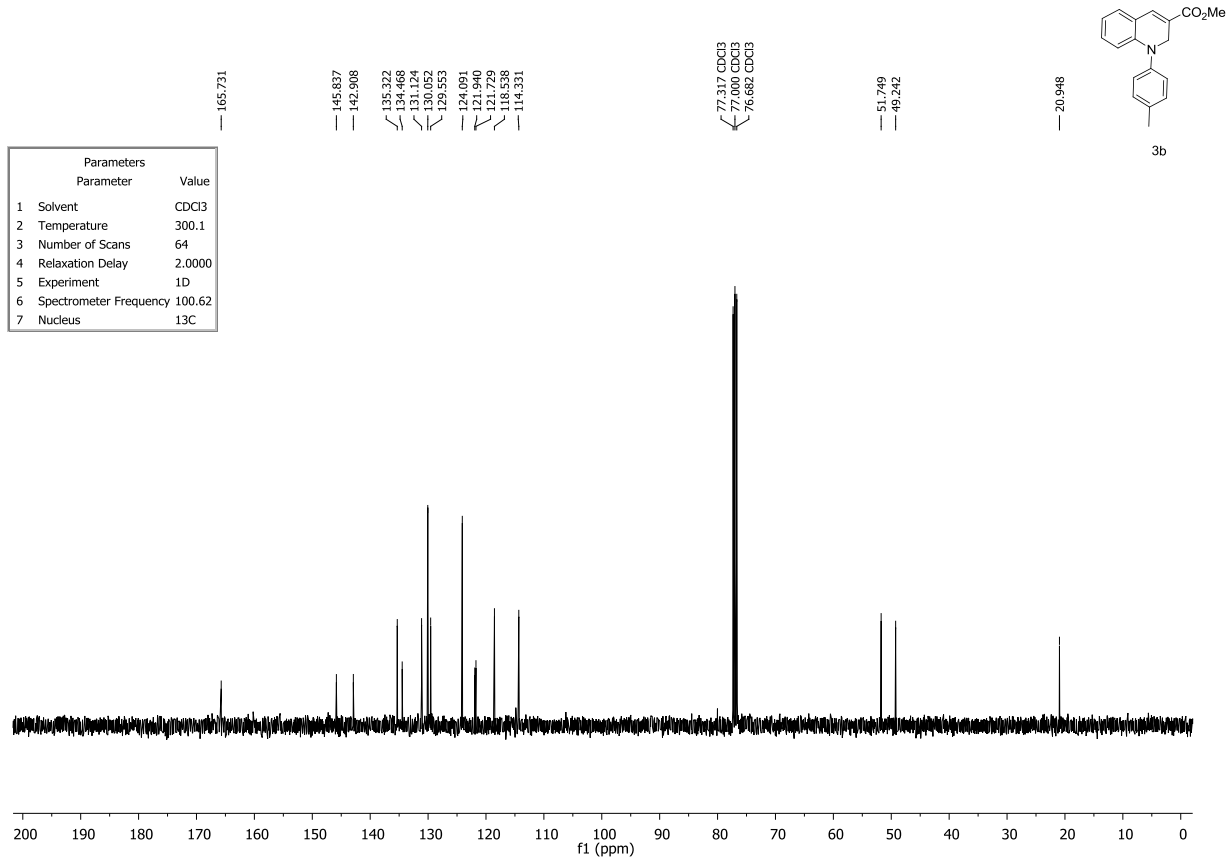

mml084-b-f2
1H routine 8 scans
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Spectrometer Frequency 300.16
6 Nucleus 1H
CO2Me
Br
NHPh
2c

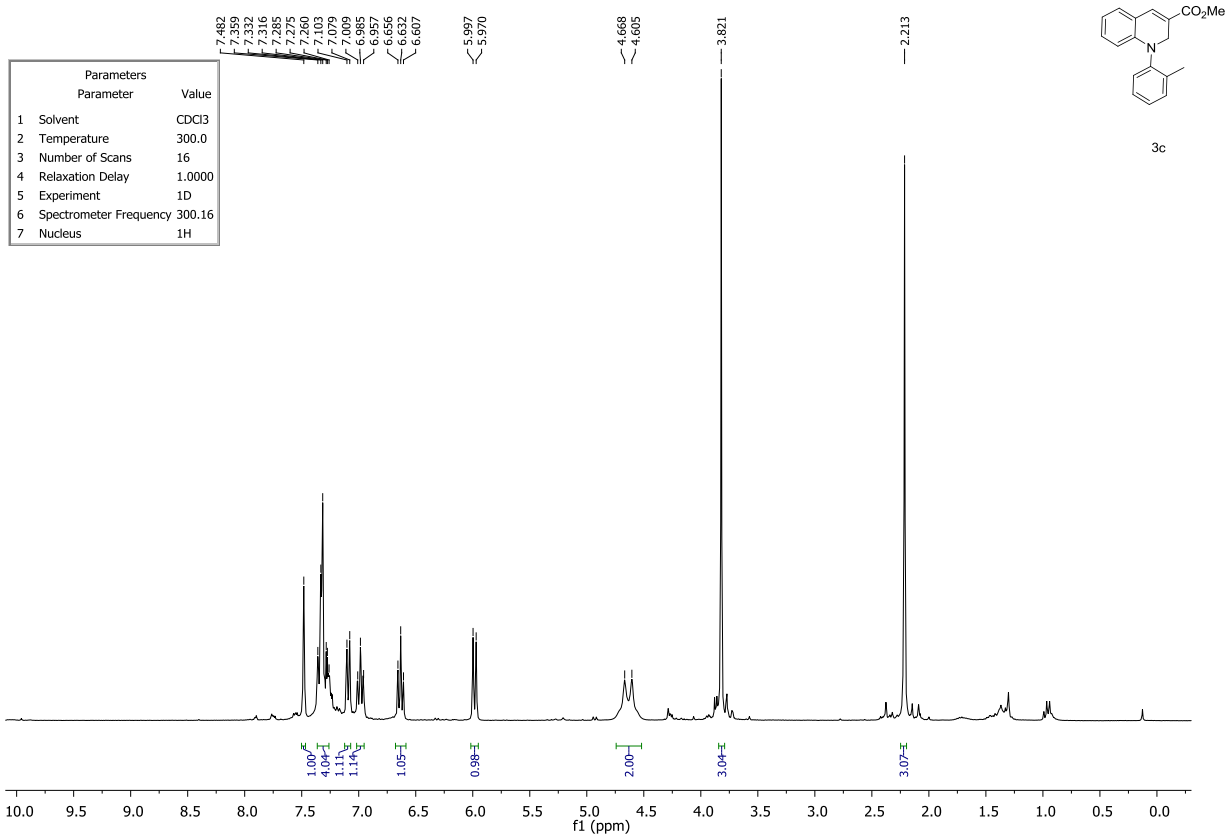

mml084-pf2
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 1000
4 Relaxation Delay 2.0000
5 Spectrometer Frequency 75.48
6 Nucleus 13C
CO2Me
Br
NHPh
2c

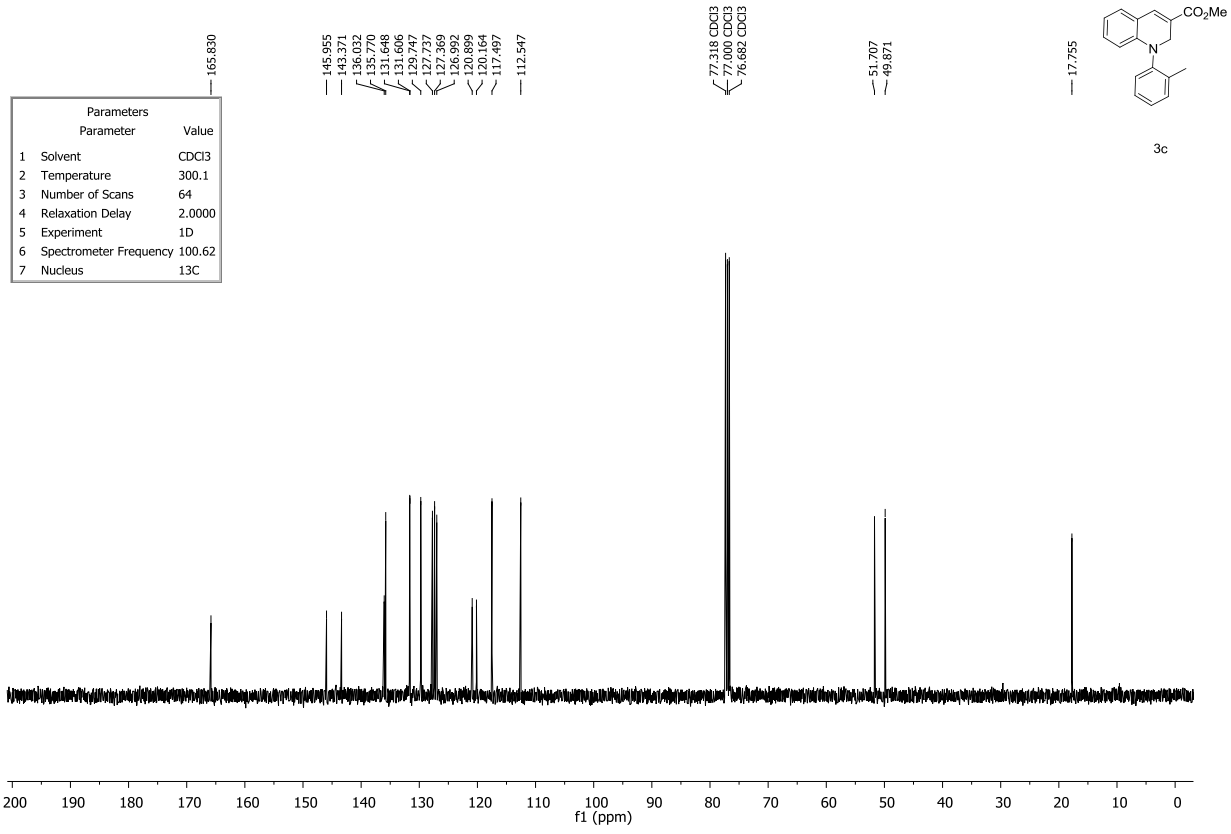

7.479
7.407
7.389
7.373
7.288
7.285
7.263
7.260
7.260
7.176
7.160
7.158
7.141
7.121
7.066
7.042
7.027
6.751
6.731
6.712
4.624
4.621
3.801
CO2Me
N
3a
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 400.13
7 Nucleus 1H
1.04
2.05
2.30
2.09
1.03
2.04
2.00
3.02
10.0 9.5 9.0 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)

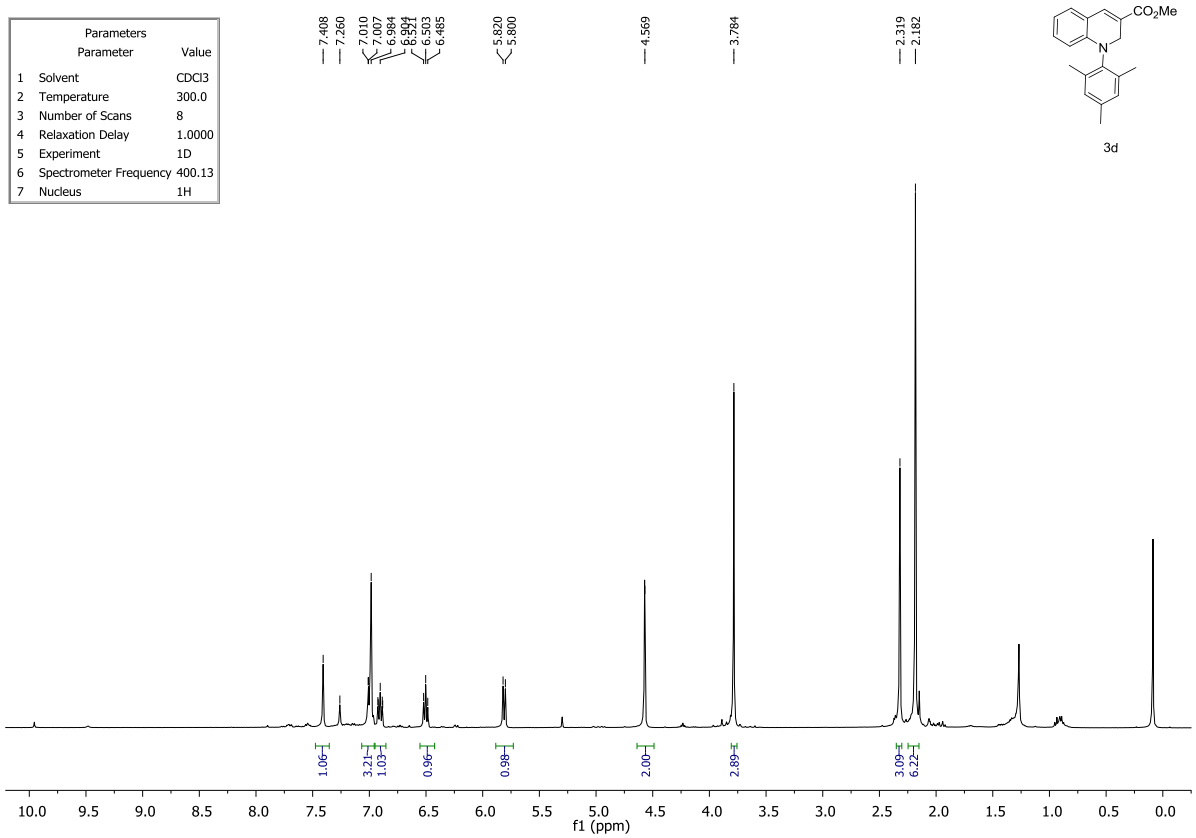

165.679
145.530
145.318
135.223
131.057
129.540
129.380
124.418
123.709
122.401
122.060
119.036
114.767
77.317 CDCl3
77.000 CDCl3
76.682 CDCl3
51.785
48.922
CO2Me
N
3a
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 32
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

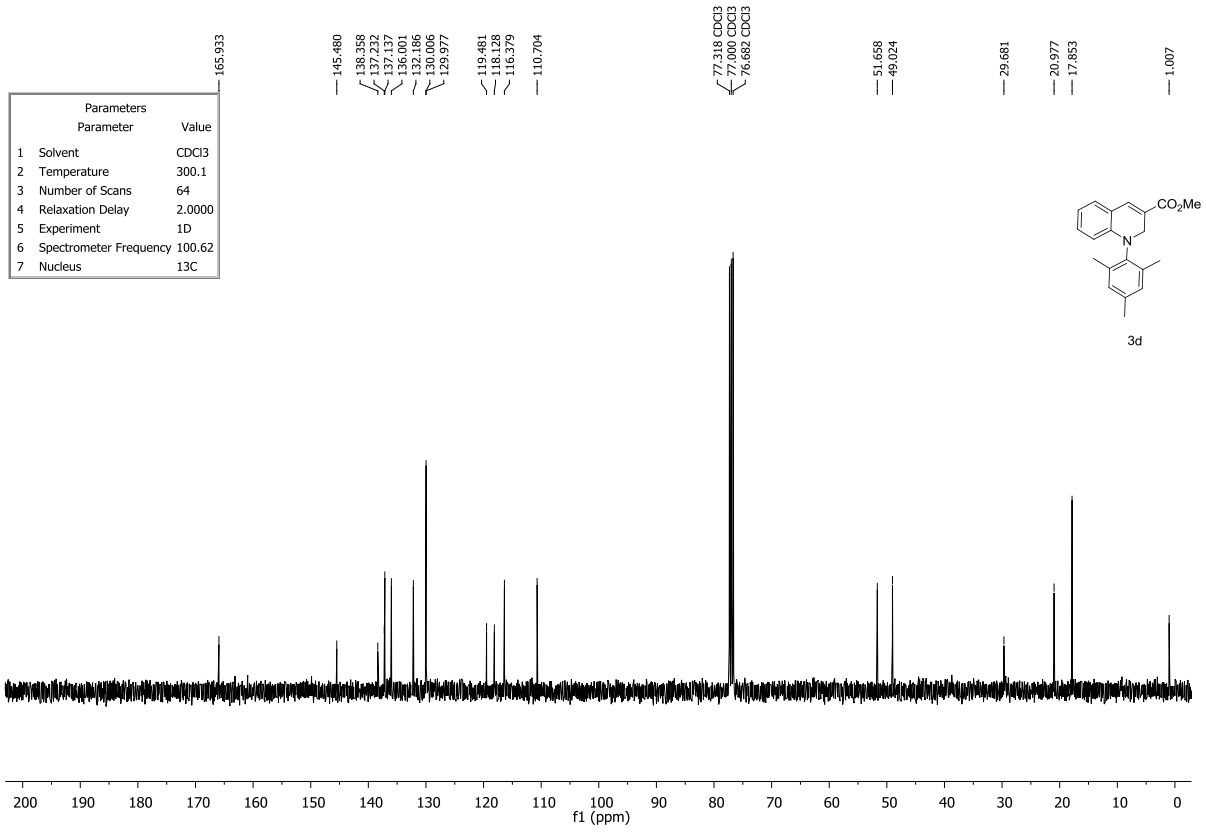

7.4615
7.2605
7.2600
7.2165
7.1954
7.1776
7.1563
7.1157
7.0968
7.0404
7.0193
7.0014
6.7096
6.6912
6.6729
6.6283
6.6075
4.6058
3.7965
2.3682
CO2Me
N
3b
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 400.13
7 Nucleus 1H
1.01
4.10
1.15
1.08
1.04
1.01
2.00
2.99
3.08
10.0 9.5 9.0 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)


165.731
145.837
142.908
135.322
134.468
131.124
130.052
129.553
124.091
121.940
121.729
119.538
114.331
77.317 CDCl3
77.000 CDCl3
76.682 CDCl3
51.749
49.242
20.948
CO2Me
N
3b
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 64
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.482
7.359
7.332
7.316
7.285
7.275
7.260
7.103
7.079
7.009
6.985
6.957
6.656
6.632
6.607
5.997
5.970
4.668
4.605
3.821
2.213
CO2Me
N
3c
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 16
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 300.16
7 Nucleus 1H
1.00
4.04
1.11
1.14
1.05
0.98
2.00
3.04
3.07
10.0 9.5 9.0 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)

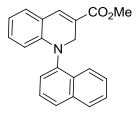

165.830
145.955
143.371
136.032
135.770
131.648
131.606
129.747
127.737
127.369
126.992
120.899
120.164
117.497
112.547
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
51.707
49.871
17.755
CO2Me
N
3c
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 64
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 400.13
7 Nucleus 1H
7.408
7.260
7.010
7.007
6.984
6.904
6.521
6.503
6.485
5.820
5.800
4.569
3.784
2.319
2.182
CO2Me
N
3d
1.06
3.21
1.03
0.96
0.98
2.00
2.89
3.09
6.22
10.0 9.5 9.0 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)

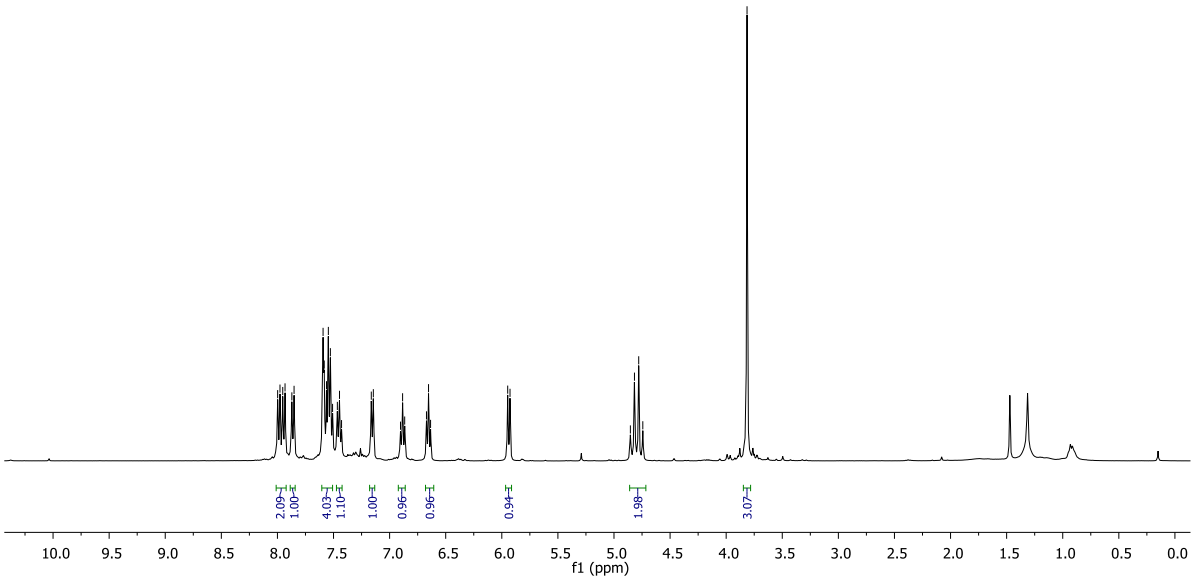

Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 64
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
165.933
145.480
138.358
137.232
137.137
136.001
132.186
130.006
129.977
119.481
118.128
116.379
110.704
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
51.658
49.024
29.681
20.977
17.853
1.007
CO2Me
N
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Parameters		
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	300.0
3	Number of Scans	16
4	Relaxation Delay	1.0000
5	Experiment	1D
6	Spectrometer Frequency	400.13
7	Nucleus	1H

8.00 7.98 7.95 7.93 7.87 7.85 7.59 7.55 7.53 7.18 7.15 6.90 6.88 6.67 6.65 6.63 5.95 5.93 4.85 4.82 4.78 4.74 3.81



3e



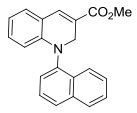
2.09 1.00 4.03 1.10 1.00 0.96 0.96 0.94 1.98 3.07

10.0 9.5 9.0 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

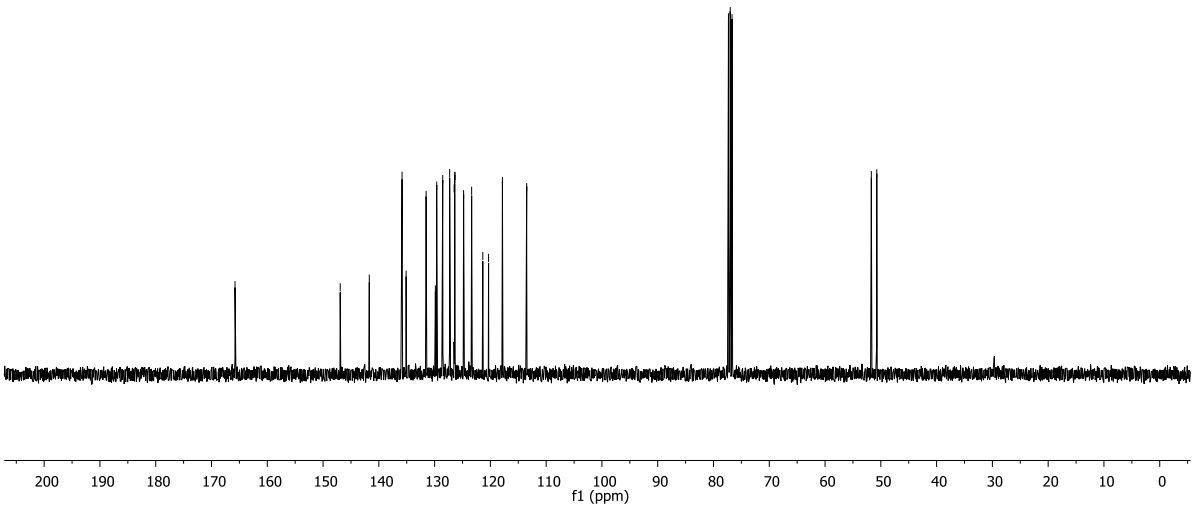
f1 (ppm)

Parameters		
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	300.1
3	Number of Scans	32
4	Relaxation Delay	2.0000
5	Experiment	1D
6	Spectrometer Frequency	100.62
7	Nucleus	13C

165.782 146.926 141.715 135.835 135.109 131.523 129.865 129.623 128.546 127.300 126.500 126.392 126.347 124.801 123.363 121.361 120.323 117.840 113.491 77.318 CDCl3 77.000 CDCl3 76.682 CDCl3 51.705 50.725

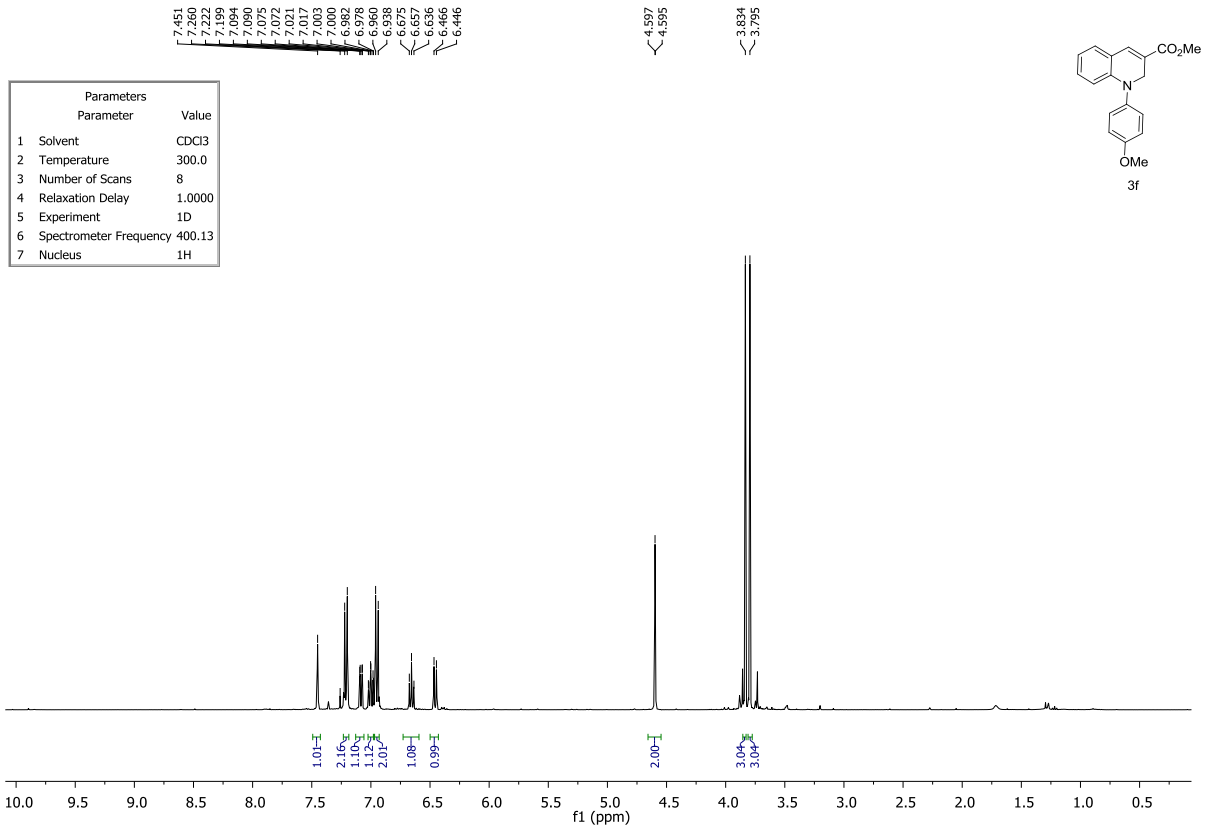


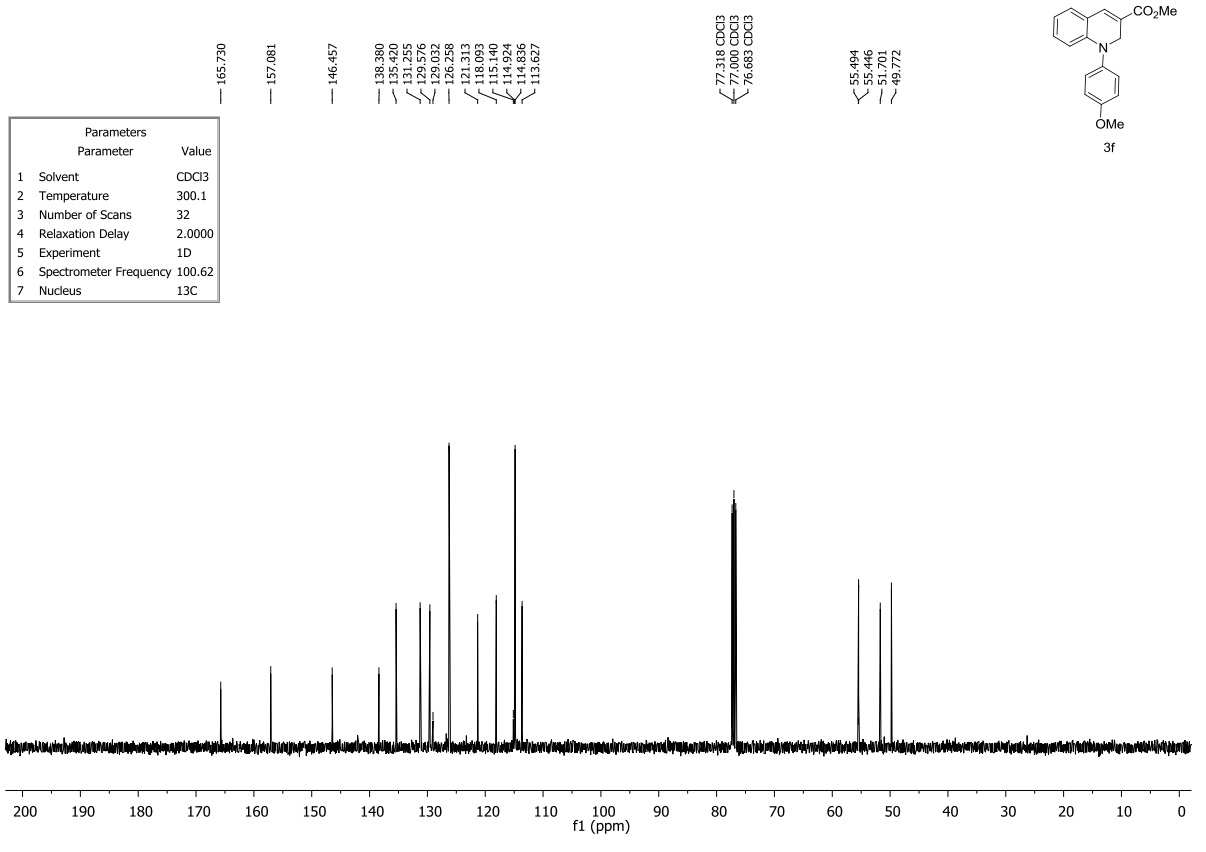
3e



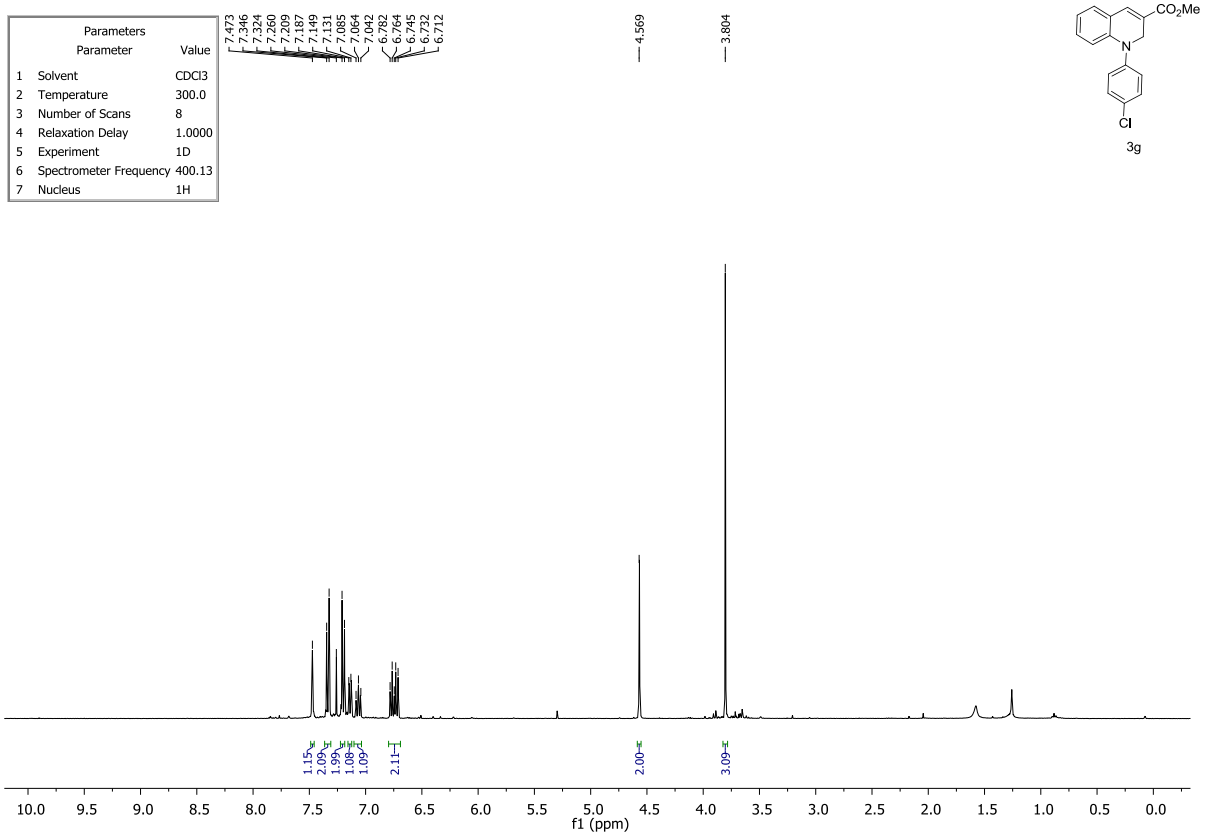
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

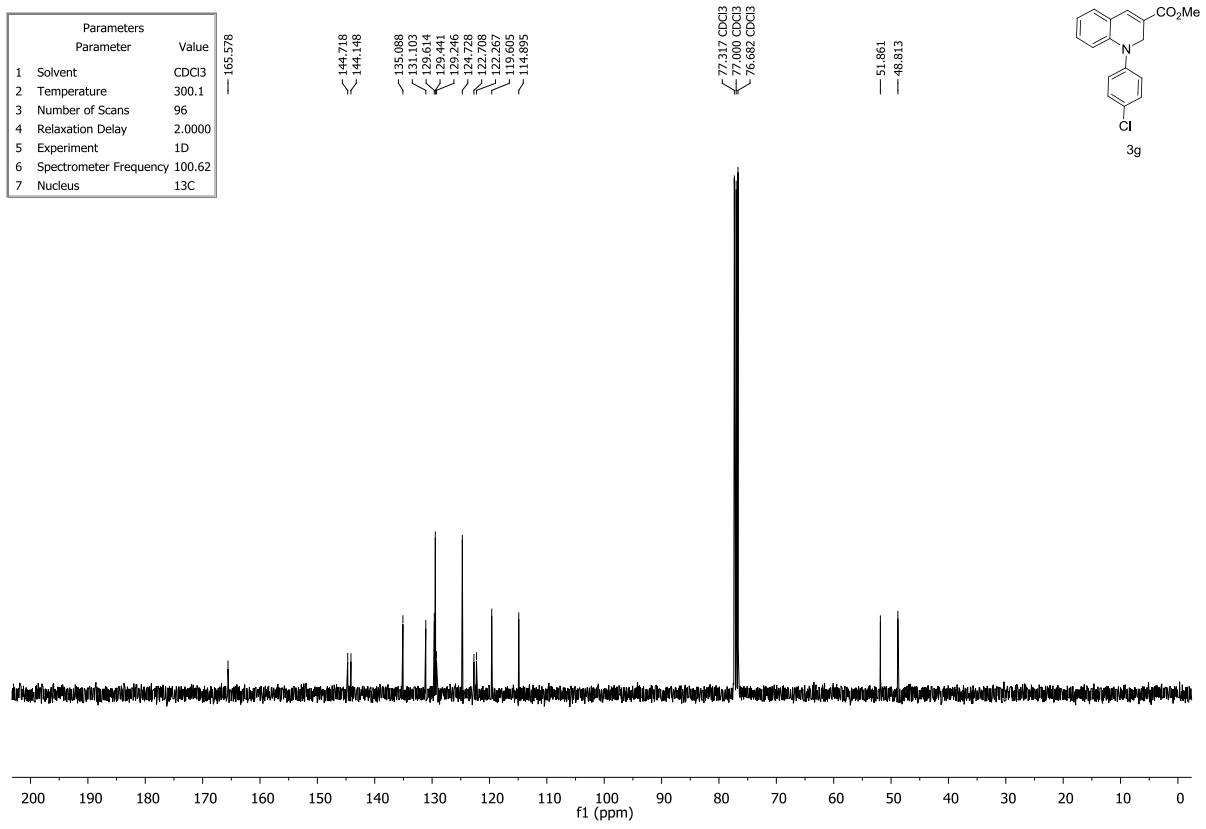

7.451
7.260
7.222
7.199
7.094
7.090
7.075
7.072
7.021
7.017
7.003
7.000
6.982
6.978
6.960
6.938
6.675
6.657
6.636
6.466
6.446
4.597
4.595
3.834
3.795
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 400.13
7 Nucleus 1H
CO2Me
N
OMe
3f
1.01
2.16
1.10
1.12
2.01
1.08
0.99
2.00
3.04
3.04
f1 (ppm)

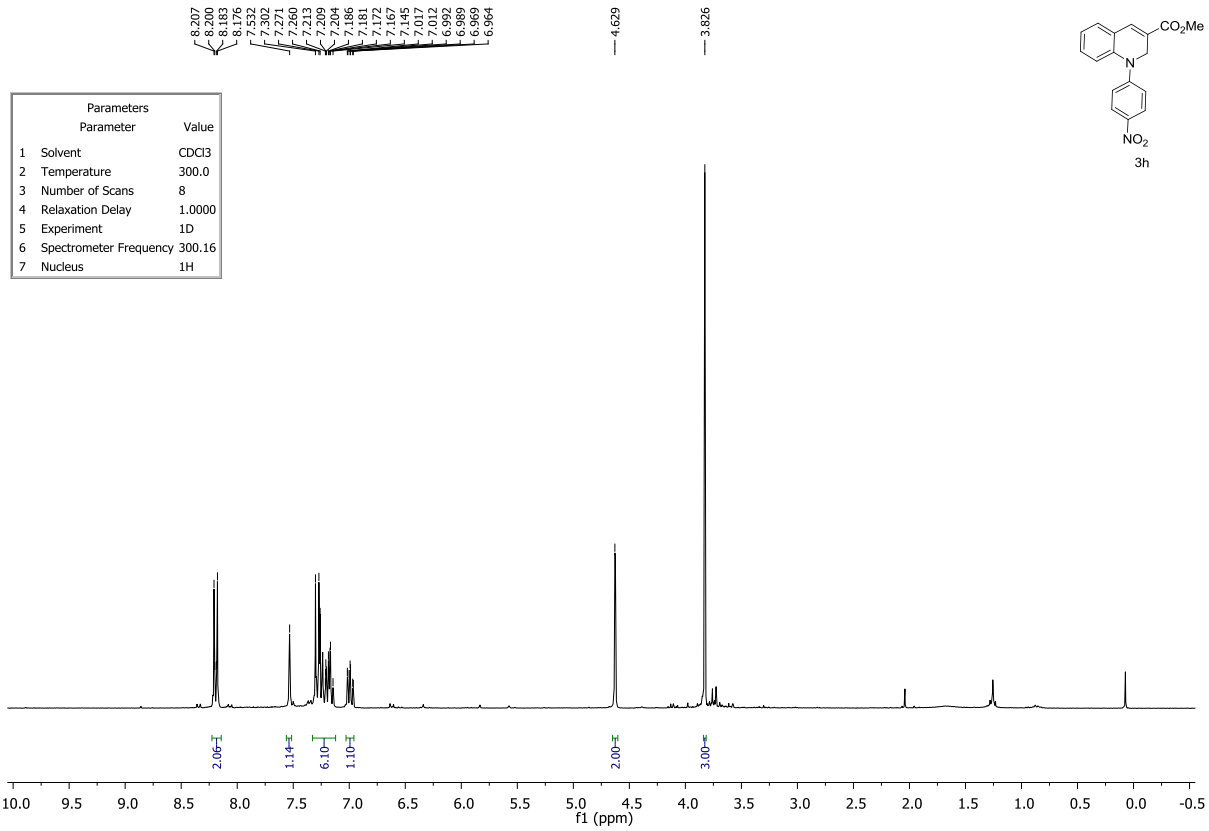

165.730
157.081
146.457
138.380
135.420
131.255
129.576
129.032
126.258
121.313
118.093
115.140
114.924
114.836
113.627
77.318 CDCl3
77.000 CDCl3
76.683 CDCl3
55.494
55.446
51.701
49.772
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 32
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
CO2Me
N
OMe
3f
f1 (ppm)

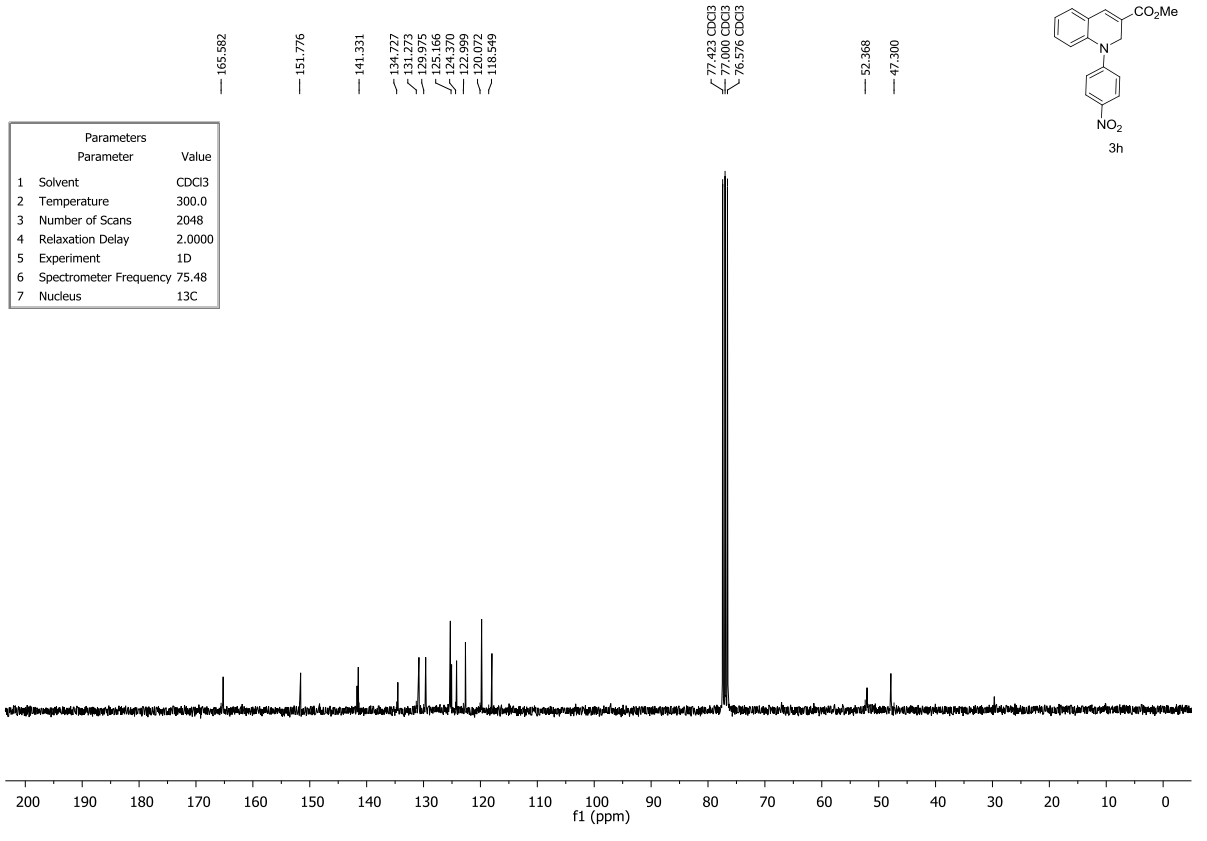
Parameters		
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	300.0
3	Number of Scans	8
4	Relaxation Delay	1.0000
5	Experiment	1D
6	Spectrometer Frequency	400.13
7	Nucleus	1H

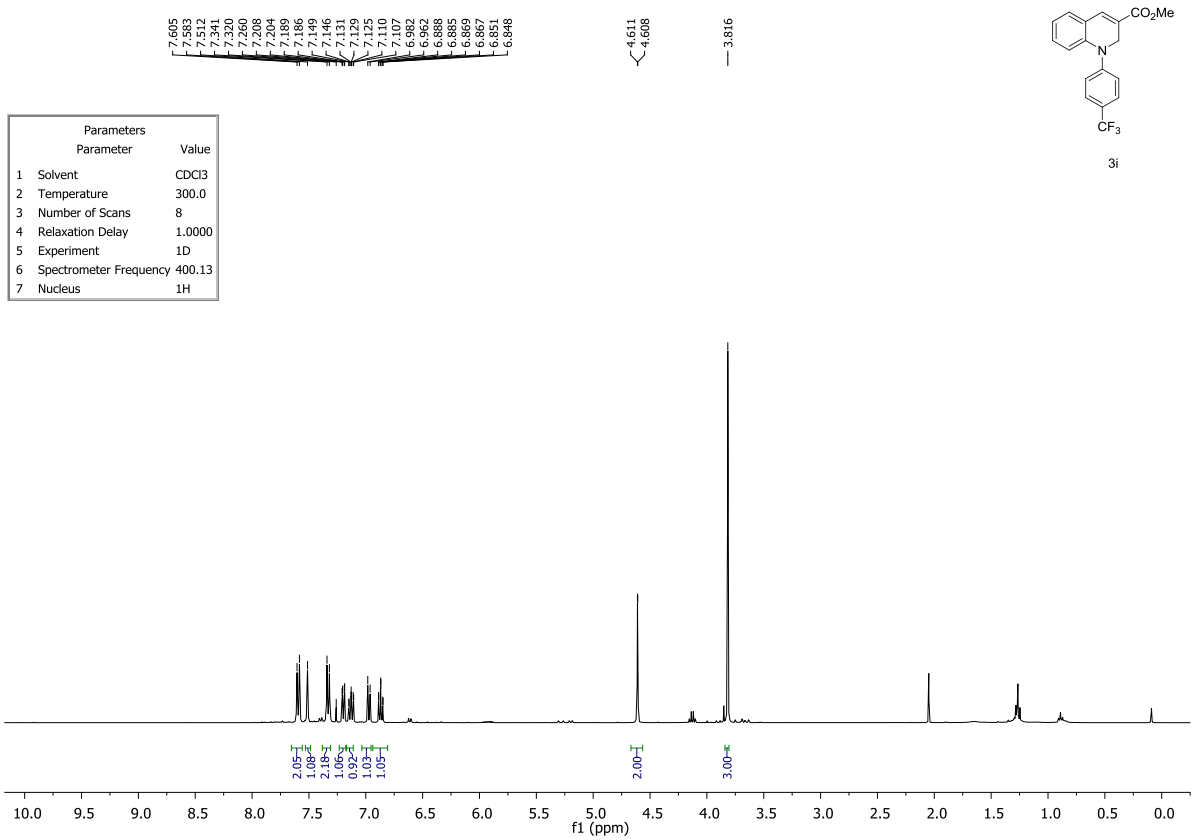


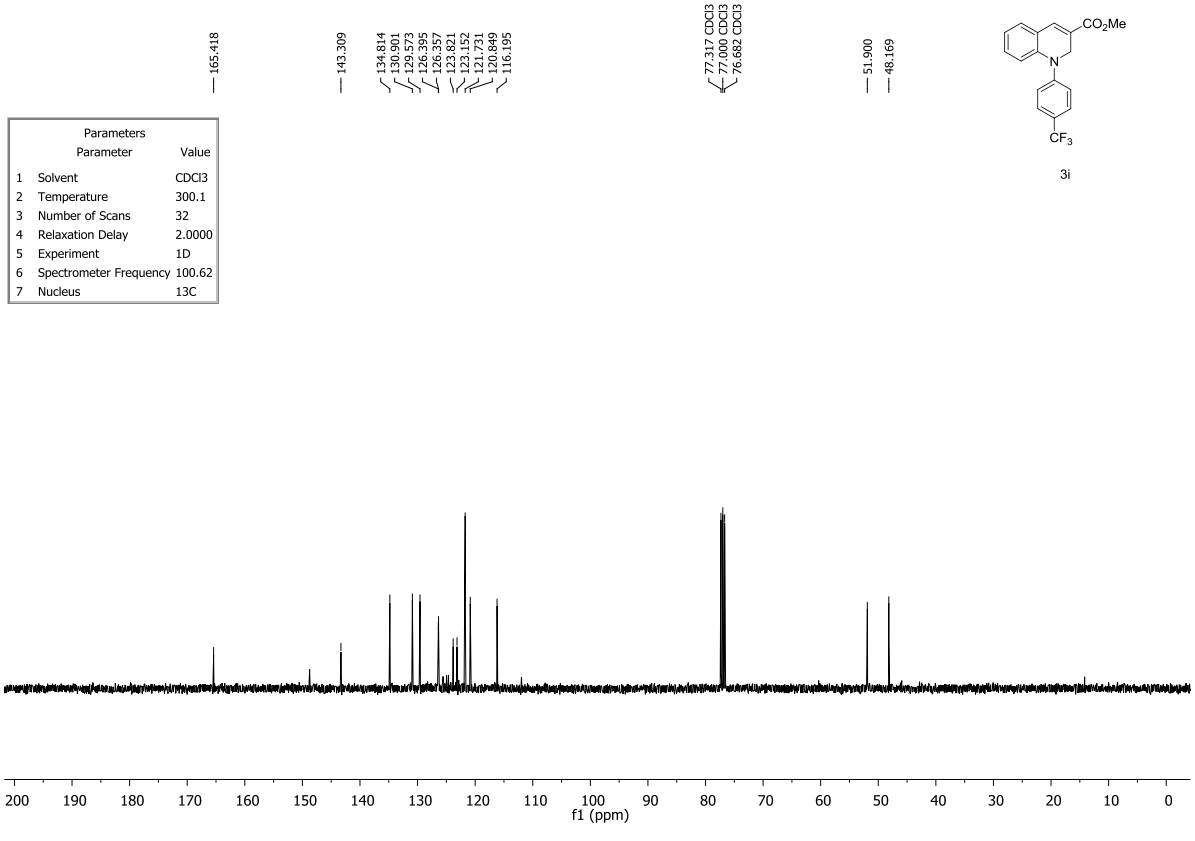
Parameters		
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	300.1
3	Number of Scans	96
4	Relaxation Delay	2.0000
5	Experiment	1D
6	Spectrometer Frequency	100.62
7	Nucleus	13C

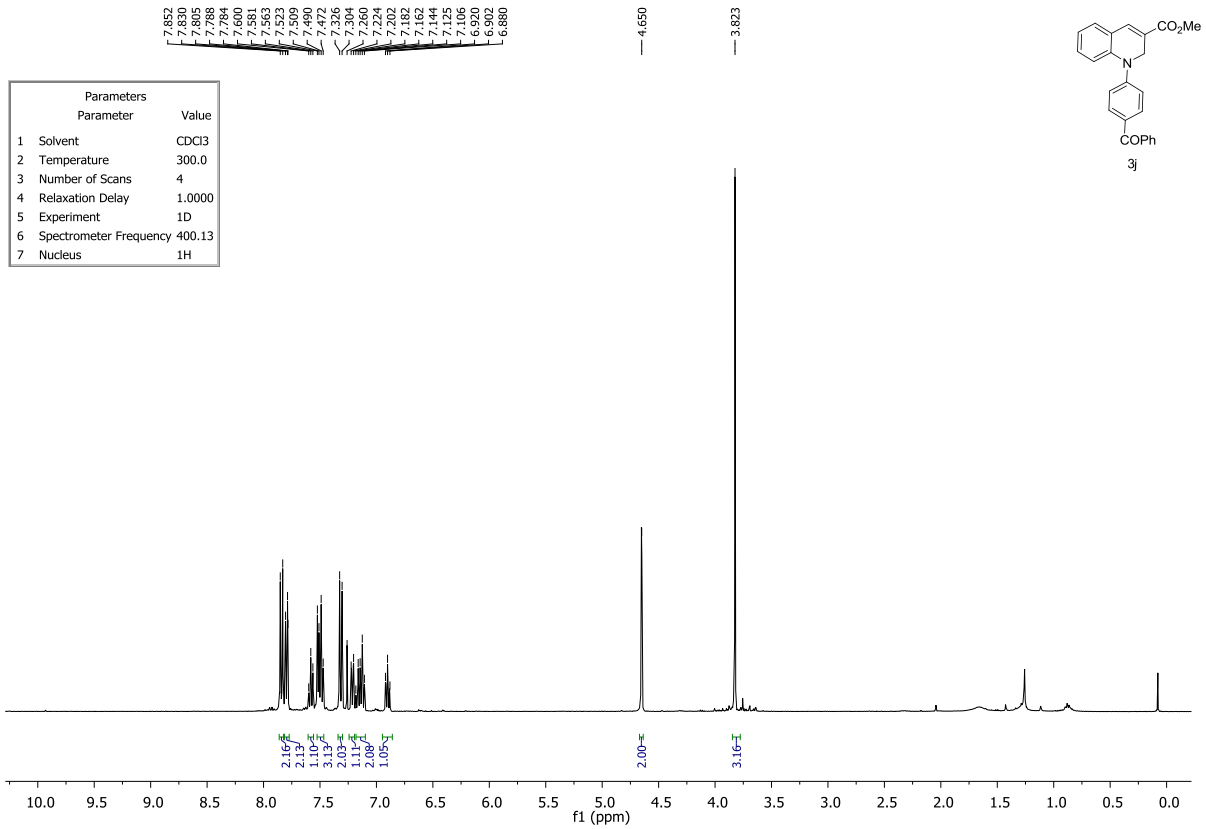


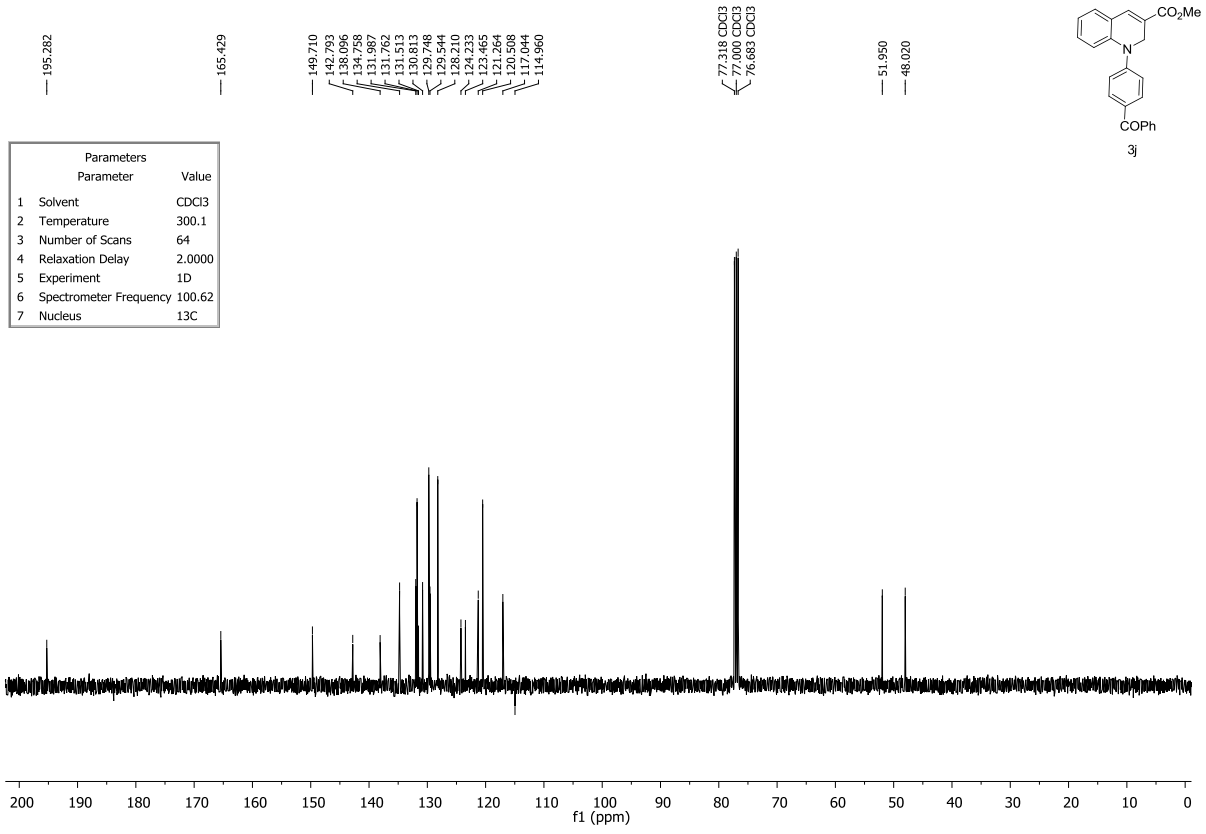

8.207
8.200
8.183
8.176
7.532
7.302
7.271
7.260
7.213
7.209
7.204
7.186
7.181
7.172
7.167
7.145
7.017
7.012
6.992
6.989
6.969
6.964
4.629
3.826
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 300.16
7 Nucleus 1H
CO2Me
N
NO2
3h
2.06
1.14
6.10
1.10
2.00
3.00
10.0 9.5 9.0 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)

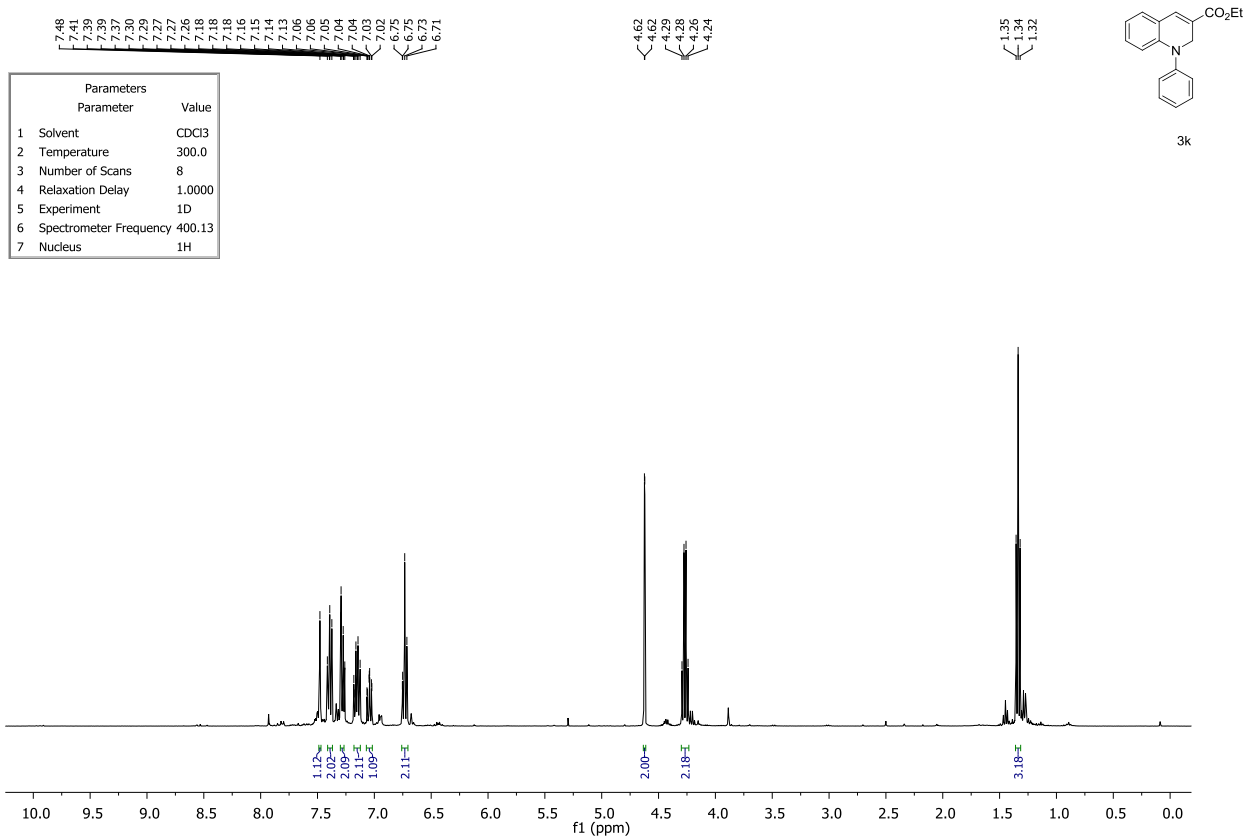

165.582
151.776
141.331
134.727
131.273
129.975
125.166
124.370
122.999
120.072
118.549
77.423 CDCl3
77.000 CDCl3
76.576 CDCl3
52.368
47.300
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 2048
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 75.48
7 Nucleus 13C
CO2Me
N
NO2
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

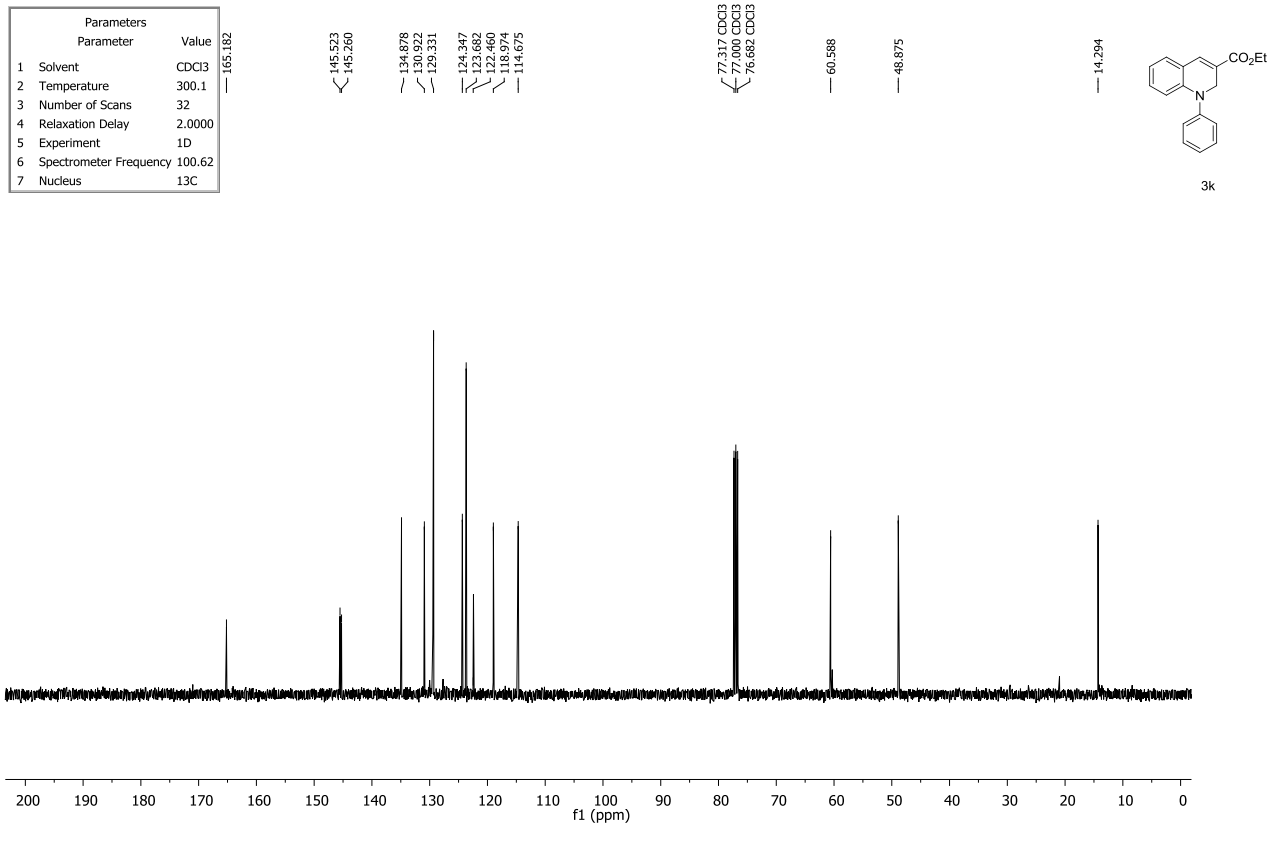

7.605
7.583
7.512
7.341
7.320
7.260
7.208
7.204
7.189
7.186
7.149
7.146
7.131
7.129
7.125
7.110
7.107
6.982
6.962
6.888
6.885
6.869
6.867
6.851
6.848
4.611
4.608
3.816
CO2Me
N
CF3
3i
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 400.13
7 Nucleus 1H
2.05
1.08
2.18
1.06
0.92
1.03
1.05
2.00
3.00
10.0 9.5 9.0 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)


165.418
143.309
134.814
130.901
129.573
126.395
126.357
123.821
123.152
121.731
120.849
116.195
77.317 CDCl3
77.000 CDCl3
76.682 CDCl3
51.900
48.169
CO2Me
N
CF3
3i
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 32
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

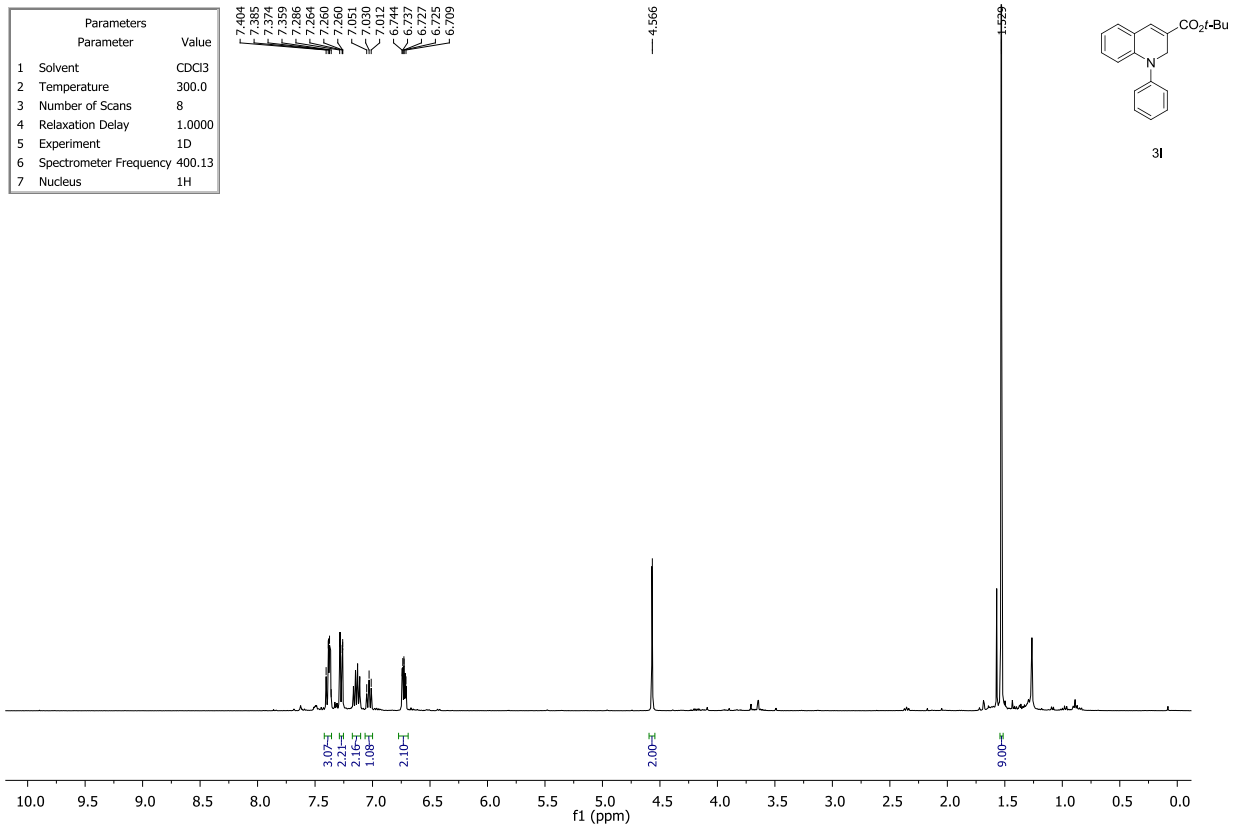

7.852
7.830
7.805
7.798
7.784
7.600
7.581
7.563
7.523
7.509
7.490
7.472
7.326
7.304
7.260
7.224
7.202
7.182
7.162
7.144
7.125
7.106
6.920
6.902
6.880
4.650
3.823
CO2Me
N
COPh
3j
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 4
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 400.13
7 Nucleus 1H
2.16
2.13
1.10
3.13
2.03
1.11
2.08
1.05
2.00
3.16
10.0 9.5 9.0 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)


195.282
165.429
149.710
142.793
138.096
134.758
131.987
131.762
131.513
130.813
129.748
129.544
128.210
124.233
123.465
121.264
120.508
117.044
114.960
77.318 CDCl3
77.000 CDCl3
76.683 CDCl3
51.950
48.020
CO2Me
N
COPh
3j
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 64
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.48
7.41
7.39
7.39
7.37
7.30
7.29
7.27
7.27
7.26
7.18
7.18
7.16
7.15
7.14
7.13
7.06
7.06
7.05
7.04
7.04
7.03
7.02
6.75
6.75
6.73
6.71
4.62
4.62
4.29
4.28
4.26
4.24
1.35
1.34
1.32
CO2Et
N
3k
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 400.13
7 Nucleus 1H
1.12
2.02
2.09
2.11
1.09
2.11
2.00
2.18
3.18
10.0 9.5 9.0 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)

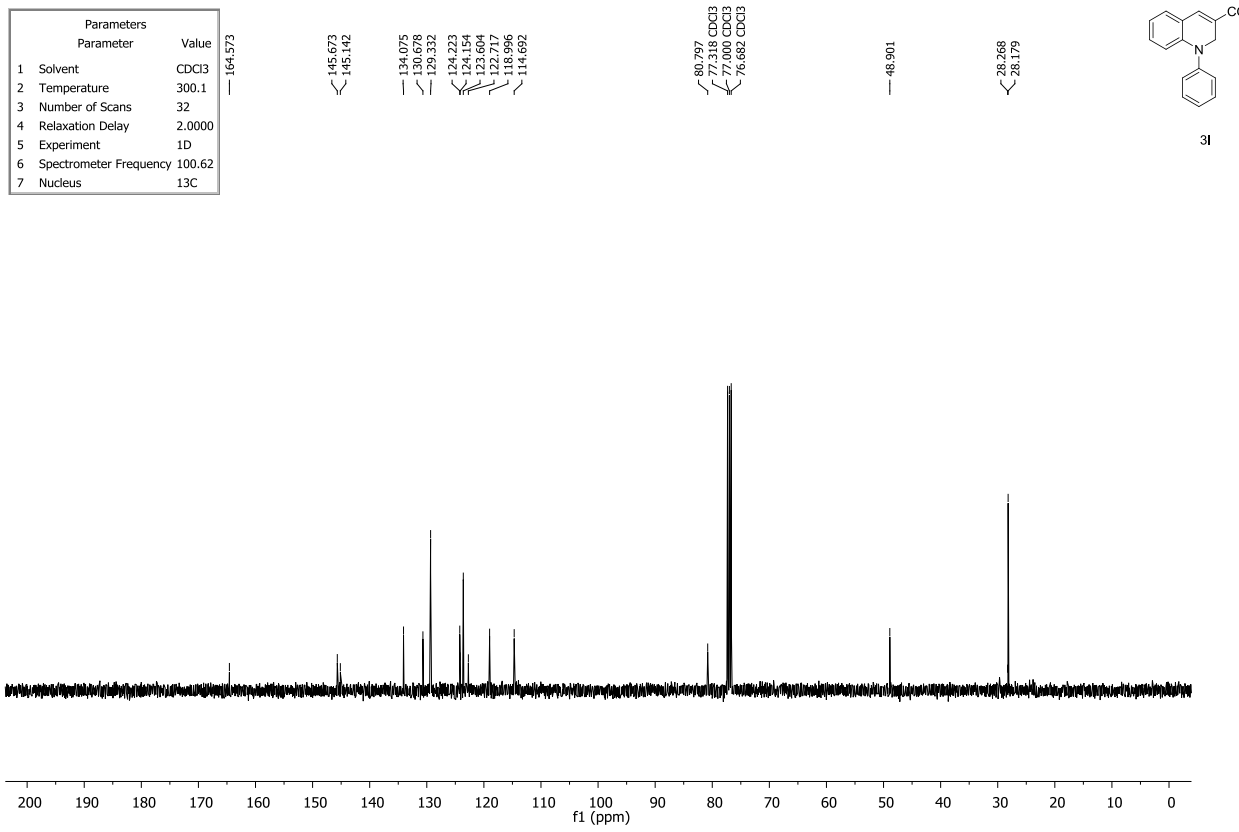

Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 32
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
165.182
145.523
145.260
134.878
130.922
129.331
124.347
123.682
122.460
118.974
114.675
77.317 CDCl3
77.000 CDCl3
76.682 CDCl3
60.588
48.875
14.294
CO2Et
N
3k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Parameters	
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.0
3 Number of Scans	8
4 Relaxation Delay	1.0000
5 Experiment	1D
6 Spectrometer Frequency	400.13
7 Nucleus	1H

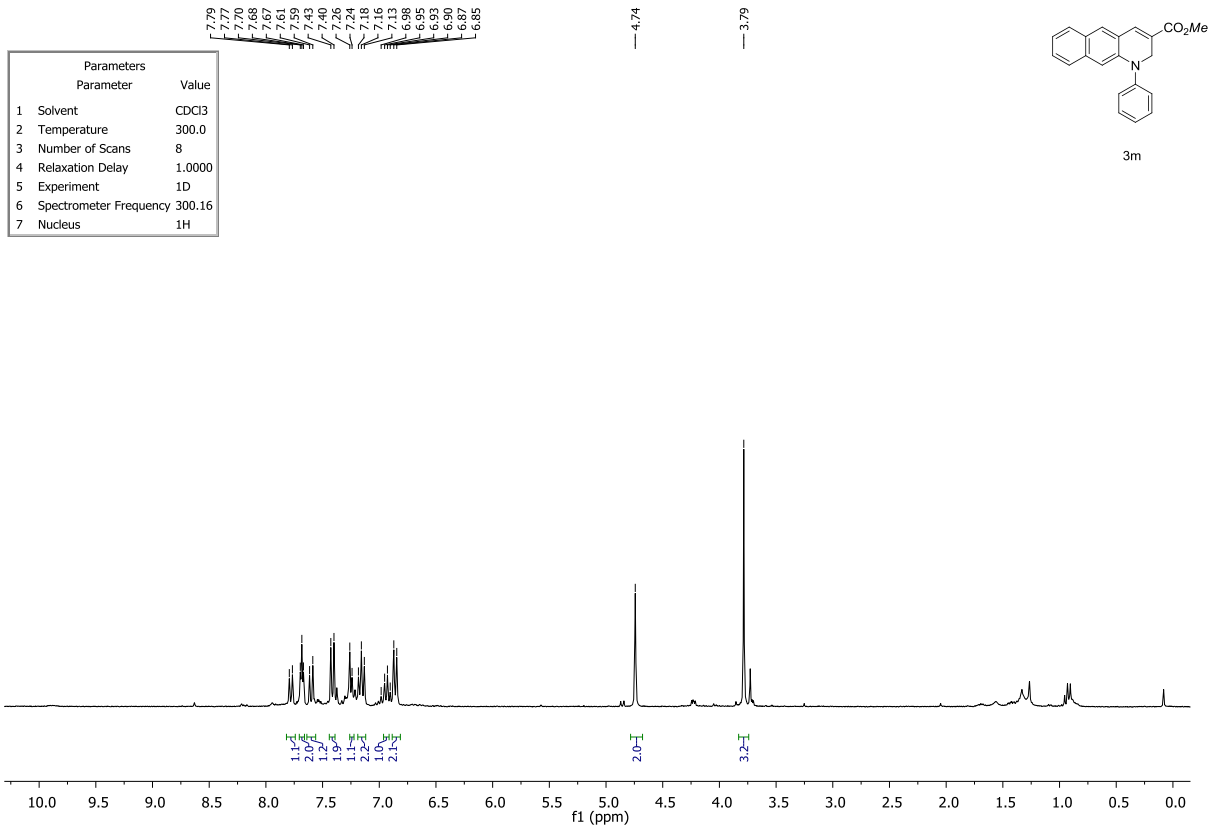


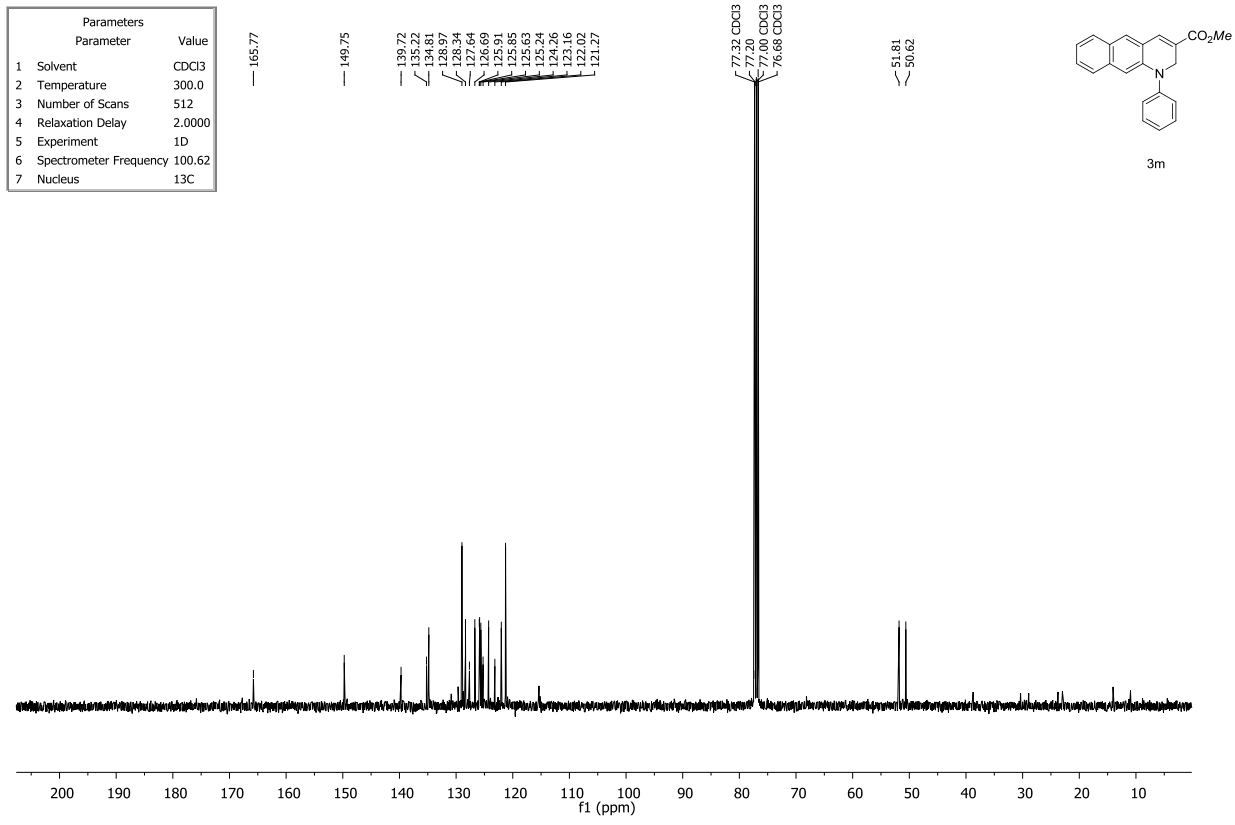
3l

Parameters	
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.1
3 Number of Scans	32
4 Relaxation Delay	2.0000
5 Experiment	1D
6 Spectrometer Frequency	100.62
7 Nucleus	13C



3l


7.79
7.77
7.70
7.68
7.67
7.61
7.59
7.43
7.40
7.26
7.24
7.18
7.16
7.13
6.98
6.95
6.93
6.90
6.87
6.85
4.74
3.79
CO2Me
N
3m
Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 8
4 Relaxation Delay 1.0000
5 Experiment 1D
6 Spectrometer Frequency 300.16
7 Nucleus 1H
1.1
2.0
1.2
1.9
1.1
2.2
1.0
2.1
2.0
3.2
10.0 9.5 9.0 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)


Parameters
Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 512
4 Relaxation Delay 2.0000
5 Experiment 1D
6 Spectrometer Frequency 100.62
7 Nucleus 13C
165.77
149.75
139.72
135.22
134.81
128.97
128.34
127.64
126.69
125.91
125.85
125.63
125.24
124.26
123.16
122.02
121.27
77.32 CDCl3
77.20
77.00 CDCl3
76.68 CDCl3
51.81
50.62
CO2Me
N
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)