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Transition-metal Free Reactions of Boronic Acids: Cascade Addition – Ring-opening of Furans towards Functionalized γ-Ketoaldehydes

Silvia Roscales and Aurelio G. Csákÿ*

Instituto Pluridisciplinar, Universidad Complutense de Madrid. Campus de Excelencia Internacional Moncloa. Paseo de Juan XXIII, 1. 28040-Madrid. Spain. E-mail: csaky@ucm.es

Supporting Information

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1. General Information

All starting materials were commercially available research-grade chemicals, and were used without further purification. All solvents were dried by standard methods and distilled under argon. Silica gel 60 F254 was used for TLC, and the spots were detected with UV light or vanillin solution. Flash column chromatography was carried out on silica gel 60. ^{1}H NMR spectra were recorded at 300, 500 or 700 MHz. ^{13}C NMR spectra were recorded at 75, 125 or 176 MHz, and ^{19}F NMR spectra were recorded at 282 MHz, all of them in $CDCl_3$ solution.

2. Synthesis of the Starting Materials

Compound **1b** was prepared following a previously reported procedure starting from 3-methylfuran-2-carbaldehyde.[1] Compounds **1c**, **1d** and **1e** were prepared following a previously reported procedure starting from 3-bromofuran-2-carbaldehyde.[2] Compound **1f** was prepared following a previously reported procedure starting from 4-bromofuran-2-carbaldehyde.[3] Compound **1g** was prepared following a previously reported procedure starting from 5-methylfuran-2-carbaldehyde.[4] Compound **1h** was prepared following a previously reported procedure starting from 1-(furan-2-yl)ethanone.[5] Compounds **1i** and **1j** were prepared following a previously reported procedure starting from furan-2-carbaldehyde.[6]

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1 Y. Li, C. C. Nawrat, G. Pattenden, J. M. Winne, *Org. Biomol. Chem.* 2009, **7**, 639.

2 (a) J. R. Allen, S. A. Hitchcock, B. Liu and W. W. Turner Jr., *PCT Int. Appl.*, 2005, WO 2005009941; (b) D. Clark, S. M. Cramp, H. J. Dyke, T. D. Pallin and R. Zahler, *PCT Int. Appl.*, 2012, WO 2012012642.

3 (a) A. G. Taveras, J. Zheng, P. J. Biju, Y. Yu, J. Chao, J. Fine, D. Lundell, T. Priestley, A. Reggiani, J. R. Merritt, *et. al.*, *PCT Int. Appl.*, 2005, WO 2005068460; (b) C. Cheng, S. Liu and G. Zhu, *Org Lett.,* 2015, **17**, 1581.

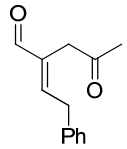
4 A. Hashmi, K. Stephen, M. Ghanbari, M. Rudolph and F. Rominger, *Chem. Eur. J.,* 2012, **18**, 8113.

5 W. –P. Mai, H. –H. Wang, Z. –C. Li, J. –W. Yuan, Y. –M. Xiao, L. –R. Yang, P. Mao and L. –B. Qu, *Chem. Commun*., 2012, **48**, 10117.

6 M. Pawlicki, L. Latos-Grazynski and L. Szterenberg, *J. Org. Chem.*, 2002, **67**, 5644.

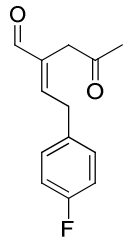
3. Experimental Procedures and Spectroscopic Data of Compounds

(*E*)-4-Oxo-2-(2-phenylethylidene)pentanal (5a)



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2a** (36.2 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 µL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4a** was filtered over $MgSO_4$. To the filtrate was added Et_3N (56 µL, 0.41 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5a** was isolated as a colorless oil (36.6 mg, 89%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 2.23 (s, 3H), 3.51 (s, 2H), 3.65 (d, *J* = 7.4 Hz, 2H), 6.86 (t, *J* = 7.4 Hz, 1H), 7.17-7.38 (m, 5H), 9.44 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 30.3, 35.9, 39.1, 127.4, 129.0 (2C), 129.3 (2C), 137.5, 137.9, 155.5, 194.1, 204.5. Anal. calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.27, H, 6.91.

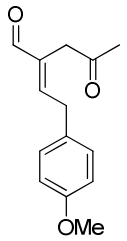
(*E*)-2-(2-(4-Fluorophenyl)ethylidene)-4-oxopentanal (5b)



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2b** (40.6 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 µL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4b** was filtered

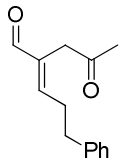
over $MgSO_4$. To the filtrate was added Et_3N (56 μL, 0.41 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5b** was isolated as a colorless oil (40.8 mg, 91%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 2.24 (s, 3H), 3.50 (s, 2H), 3.61 (d, J = 7.4 Hz, 2H), 6.81 (t, J = 7.4 Hz, 1H), 6.97-7.07 (m, 2H), 7.11-7.21 (m, 2H), 9.43 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 28.9, 33.7, 37.6, 114.7 (d, J_{CF} = 22 Hz), 129.1 (d, J_{CF} = 8 Hz), 132.1 (d, J_{CF} = 3 Hz), 136.1, 153.7, 160.9 (d, J_{CF} = 244 Hz), 192.6, 203.0. ^{19}F NMR ($CDCl_3$, 282 MHz): δ (ppm) = -116.1 (s). Anal. calcd. for $C_{13}H_{13}FO_2$: C, 70.90; H, 5.95. Found: C, 70.95, H, 6.01.

(*E*)-2-(2-(4-Methoxyphenyl)ethylidene)-4-oxopentanal (5c)



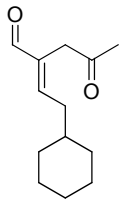
A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2c** (43.5 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4c** was filtered over $MgSO_4$. To the filtrate was added Et_3N (56 μL, 0.41 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5c** was isolated as a yellow oil (33.6 mg, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.23 (s, 3H), 3.50 (s, 2H), 3.58 (d, J = 7.5 Hz, 2H), 3.80 (s, 3H), 6.80-6.89 (m, 3H), 7.09-7.13 (m, 2H), 9.43 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 30.1, 34.8, 38.9, 55.4, 114.5, 129.5, 129.7 (4C), 136.9, 155.8, 158.7, 193.9, 204.4. Anal. calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.42, H, 6.88.

(*E*)-2-(2-Oxopropyl)-5-phenylpent-2-enal (5d)



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2d** (39.6 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4d** was filtered over $MgSO_4$. To the filtrate was added Et_3N (56 μL, 0.41 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5d** was isolated as a colourless oil (35.7 mg, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.15 (s, 3H), 2.69 (dt, *J* = 7.5 Hz, *J* = 7.5 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 3.32 (s, 2H), 6.74 (t, *J* = 7.5 Hz, 1H), 7.15-7.34 (m, 5H), 9.39 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 29.9, 31.3, 34.3, 38.9, 126.6, 128.5 (2C), 128.8 (2C), 137.6, 140.4, 156.3, 193.9, 204.3. Anal. calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.80, H, 7.39.

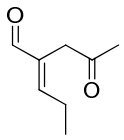
(*E*)-2-(2-Cyclohexylethylidene)-4-oxopentanal (5e)



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2e** (37.6 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4e** was filtered

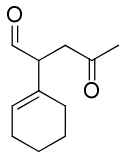
over $MgSO_4$. To the filtrate was added Et_3N (56 µL, 0.41 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5e** was isolated as a colourless oil (36.0 mg, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.53-1.78 (m, 11H), 2.19 (s, 3H), 2.21 (d, *J* = 7.4 Hz, 2H), 3.38 (s, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 9.42 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 26.3 (2C), 26.3, 29.9, 33.4 (2C), 37.2, 37.8, 39.1, 137.7, 156.9, 194.0, 204.5. Anal. calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.03; H, 9.61.

(*E*)-2-(2-Oxopropyl)pent-2-enal (5f)



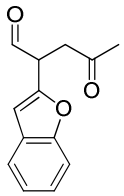
A solution of **1a** (20.0 mg, 0.20 mmol), potassium trifluoroborate **3f** (36.2 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 µL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4f** was filtered over $MgSO_4$. To the filtrate was added Et_3N (56 µL, 0.41 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5f** was isolated as a colourless oil (22.8 mg, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.12 (t, *J* = 7.5 Hz, 3H), 2.20 (s, 3H), 2.32 (dt, *J* = 7.5 Hz, *J* = 7.5 Hz, 2H), 3.39 (s, 2H), 6.71 (t, *J* = 7.5 Hz, 1H), 9.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 12.9, 23.0, 29.9, 38.8, 136.6, 159.2, 194.1, 204.4. Anal. calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.49; H, 8.70.

2-(Cyclohex-1-en-1-yl)-4-oxopentanal (4g):



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2g** (30.8 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The solution was filtered over $MgSO_4$ and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **4g** was isolated as a colourless oil (27.5 mg, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.50-1.67 (m, 6H), 2.01-2.08 (m, 2H), 2.19 (s, 3H), 2.43 (dd, *J* = 17.8 Hz, *J* = 4.4 Hz, 1H), 3.06 (dd, *J* = 17.8 Hz, *J* = 9.4 Hz, 1H), 3.51 (dd, *J* = 9.4 Hz, *J* = 4.4 Hz, 1H), 5.57-5.62 (1H, m), 9.52 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 22.1, 22.8, 25.6, 27.6, 30.3, 41.3, 55.4, 128.3, 131.7, 199.7, 206.7. Anal. calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.23; H, 9.04.

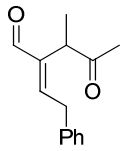
2-(Benzofuran-2-yl)-4-oxopentanal (4h):



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2h** (39.6 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The solution was filtered over $MgSO_4$ and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **4h** was isolated as a colourless oil (38.7 mg, 88%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.26 (s, 3H),

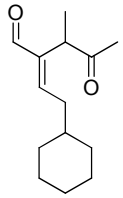
2.89 (dd, *J* = 18.0 Hz, *J* = 4.9 Hz, 1H), 3.42 (dd, *J* = 18.0 Hz, *J* = 8.2 Hz, 1H), 4.45 (dd, *J* = 8.2 Hz, *J* = 4.9 Hz, 1H), 6.63 (s, 1H), 7.19-7.31 (m, 2H), 7.42-7.47 (m, 1H), 7.52-7.58 (m, 1H), 9.79 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 30.1, 41.2, 47.7, 105.6, 111.3, 121.1, 123.2, 124.6, 128.3, 152.1, 155.3, 196.4, 205.2. Anal. calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.29; H, 5.51.

(*E*)-3-Methyl-4-oxo-2-(2-phenylethylidene)ventanal (5j):



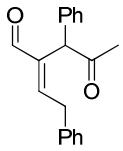
A solution of **1b** (20.0 mg, 0.18 mmol), boronic acid **2a** (39.5 mg, 0.27 mmol, 1.5 equiv), tartaric acid (26.7 mg, 0.18 mmol, 1 equiv) and H_2O (10 μL, 0.54 mmol, 3 equiv) in CH_2Cl_2 (0.7 mL) was stirred at rt for 18 h. The crude product **4j** was filtered over $MgSO_4$. To the filtrate was added Et_3N (49 μL, 0.36 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5j** was isolated as a colorless oil (32.0 mg, 83%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.31 (d, *J* = 7.0 Hz, 3H), 2.08 (s, 3H), 3.67 (t, *J* = 7.5 Hz, 2H), 3.76 (c, *J* = 7.0 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 7.16-7.22 (m, 2H), 7.26-7.38 (m, 3H), 9.42 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 14.6, 28.1, 35.3, 43.8, 127.2, 128.6 (2C), 129.2 (2C), 137.5, 143.3, 155.0, 193.7, 207.4. Anal. calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.81; H, 7.39.

(*E*)-2-(2-Cyclohexylethylidene)-3-methyl-4-oxopentanal (5k)



A solution of **1b** (20.0 mg, 0.18 mmol), boronic acid **2e** (41.2 mg, 0.27 mmol, 1.5 equiv), tartaric acid (26.7 mg, 0.18 mmol, 1 equiv) and H_2O (10 μL, 0.54 mmol, 3 equiv) in CH_2Cl_2 (0.7 mL) was stirred at rt for 18 h. The crude product **4k** was filtered over $MgSO_4$. To the filtrate was added Et_3N (49 μL, 0.36 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5k** was isolated as a colorless oil (31.3 mg, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.14-1.29 (m, 2H), 1.21 (d, *J* = 7.0 Hz, 3H), 1.56-1.79 (m, 9H), 2.02 (s, 3H), 2.18-2.27 (m, 2H), 3.62 (c, *J* = 7.0 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 9.39 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 14.4, 26.3, 28.0, 33.3, 33.4, 36.9, 38.1, 43.9, 143.9, 156.9, 193.8, 207.6. Anal. calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.70; H, 10.01.

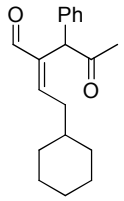
(*E*)-4-Oxo-3-phenyl-2-(2-phenylethylidene)pentanal (5l)



A solution of **1c** (20.0 mg, 0.11 mmol), boronic acid **2a** (25.4 mg, 0.17 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at rt for 18 h. The crude product **4l** was filtered over $MgSO_4$. To the filtrate was added Et_3N (32 μL, 0.23 mmol, 2 equiv) and the mixture

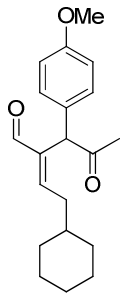
was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5l** was isolated as a colorless oil (25.8 mg, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.22 (s, 3H), 3.57 (d, *J* = 7.5 Hz, 2H), 5.00 (s, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.97-7.04 (m, 2H), 7.20-7.39 (m, 8H), 9.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 29.8, 35.8, 55.8, 127.0, 127.6, 128.7 (2C), 129.0 (2C), 129.1 (2C), 129.3 (2C), 137.3, 137.6, 141.9, 157.1, 194.1, 206.0. Anal. calcd. for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.90; H, 6.59.

(*E*)-2-(2-Cyclohexylethylidene)-4-oxo-3-phenylpentanal (5m)



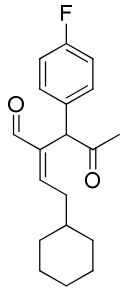
A solution of **1c** (20.0 mg, 0.11 mmol), boronic acid **2e** (26.5 mg, 0.17 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 µL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at rt for 18 h. The crude product **4m** was filtered over $MgSO_4$. To the filtrate was added Et_3N (32 µL, 0.23 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5m** was isolated as a colorless oil (27.1 mg, 83%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.71-0.90 (m, 2H), 0.99-1.24 (m, 4H), 1.25-1.42 (m, 1H), 1.47-1.67 (m, 4H), 2.01-2.20 (m, 2H), 2.09 (s, 3H), 4.70 (s, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 7.09-7.15 (m, 2H), 7.18-7.29 (m, 3H), 9.37 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 26.3, 29.6, 33.2, 33.3, 37.2, 37.9, 59.1, 127.4, 128.8 (2C), 129.3 (2C), 137.4, 142.7, 158.5, 194.1, 206.0. Anal. calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.30; H, 8.57.

(*E*)-2-(2-Cyclohexylethylidene)-3-(4-methoxyphenyl)-4-oxopentanal (5n)



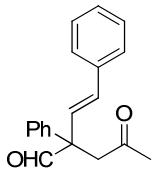
A solution of **1d** (20.0 mg, 0.10 mmol), boronic acid **2e** (22.6 mg, 0.15 mmol, 1.5 equiv), tartaric acid (14.6 mg, 0.10 mmol, 1 equiv) and H_2O (5 μL, 0.29 mmol, 3 equiv) in CH_2Cl_2 (0.4 mL) was stirred at rt for 18 h. The crude product **4n** was filtered over $MgSO_4$. To the filtrate was added Et_3N (27 μL, 0.19 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5n** was isolated as a yellow oil (24.9 mg, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.81-0.97 (m, 2H), 1.06-1.29 (m, 4H), 1.34-1.49 (m, 1H), 1.57-1.72 (m, 4H), 2.09-2.28 (m, 2H), 2.14 (s, 3H), 3.79 (s, 3H), 4.68 (s, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.81-6.88 (m, 2H), 7.07-7.16 (m, 2H), 9.42 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 25.1, 28.2, 32.1, 32.2, 36.0, 36.7, 54.2, 54.3, 113.0 (2C), 128.3, 129.3 (2C), 141.8, 157.0, 157.7, 193.0, 205.2. Anal. calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.33. Found: C, 76.32; H, 8.41.

(*E*)-2-(2-Cyclohexylethylidene)-3-(4-fluorophenyl)-4-oxopentanal (5o)



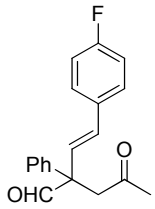
A solution of **1e** (20.0 mg, 0.10 mmol), boronic acid **2e** (24.0 mg, 0.16 mmol, 1.5 equiv), tartaric acid (15.6 mg, 0.10 mmol, 1 equiv) and H_2O (6 μL, 0.31 mmol, 3 equiv) in CH_2Cl_2 (0.4 mL) was stirred at 60ºC for 4 h. The crude product **4o** was filtered over $MgSO_4$. To the filtrate was added Et_3N (29 μL, 0.20 mmol, 2 equiv) and the mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **5o** was isolated as a colourless oil (22.9 mg, 73%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 0.78-0.96 (m, 2H), 1.08-1.24 (m, 4H), 1.38-1.46 (m, 1H), 1.59-1.73 (m, 4H), 2.14 (s, 3H), 2.15-2.24 (m, 2H), 4.72 (s, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.96-7.04 (m, 2H), 7.13-7.20 (m, 2H), 9.44 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 26.5, 33.5, 33.6, 37.6, 38.2, 55.6, 55.3, 115.9 (d, J_{CF} = 21 Hz), 131.2 (d, J_{CF} = 8 Hz), 133.3 (d, J_{CF} = 3 Hz), 142.9, 158.9, 162.4 (d, J_{CF} = 245 Hz), 194.3, 205.8. ^{19}F NMR ($CDCl_3$, 282 MHz): δ (ppm) = -115.5 (s). Anal. calcd. for $C_{19}H_{23}FO_2$: C, 75.47; H, 7.67. Found: C, 75.55; H, 7.59.

(*E*)-4-Oxo-2-phenyl-2-styrylpentanal (4p)



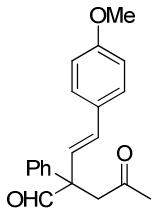
A solution of **1f** (20.0 mg, 0.11 mmol), boronic acid **2a** (25.4 mg, 0.18 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4p** was filtered over a pad of silica gel and $MgSO_4$, and the solvent was evaporated *in vacuo*. The crude reaction product (18.5 mg) was used for the synthesis of **11a** and **12a**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.06 (s, 3H), 3.34 (d, *J* = 3.9 Hz, 2H), 6.27 (d, *J* = 16.7 Hz, 1H), 6.61 (d, *J* = 16.7 Hz, 1H), 7.15-7.45 (m, 10H), 9.65 (s, 1H).

(*E*)-2-(4-Fluorostyryl)-4-oxo-2-phenylpentanal (4q)



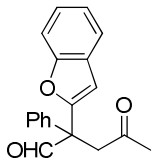
A solution of **1f** (20.0 mg, 0.11 mmol), boronic acid **2b** (28.6 mg, 0.18 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4q** was filtered over a pad of silica gel and $MgSO_4$.and the solvent was evaporated *in vacuo*. The crude reaction product (20.4 mg) was used for the synthesis of **12b**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.14 (s, 3H), 3.40 (d, *J* = 1.6 Hz, 2H), 6.30 (d, *J* = 16.5 Hz, 1H), 6.60 (d, *J* = 16.5 Hz, 1H), 7.18-7.62 (m, 9H), 9.70 (s, 1H).

(*E*)-2-(4-Methoxystyryl)-4-oxo-2-phenylpentanal (4r)



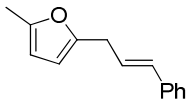
A solution of **1f** (20.0 mg, 0.11 mmol), boronic acid **2c** (30.6 mg, 0.18 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 µL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4r** was filtered over a pad of silica gel and $MgSO_4$.and the solvent was evaporated *in vacuo*. The crude reaction product (25.8 mg) was used for the synthesis of **12c**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.03 (s, 3H), 3.38 (d, *J* = 5.8 Hz, 2H), 3.80 (s, 3H), 6.28 (d, *J* = 16.4 Hz, 1H), 6.50 (d, *J* = 16.4 Hz, 1H), 6.73-7.88 (m, 9H), 9.69 (s, 1H).

2-(Benzofuran-2-yl)-4-oxo-2-phenylpentanal (4s)



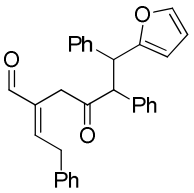
A solution of **1f** (20.0 mg, 0.11 mmol), boronic acid **2h** (27.8 mg, 0.17 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 µL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4s** was filtered over a pad of silica gel and $MgSO_4$.and the solvent was evaporated *in vacuo*. The crude reaction product (20.8 mg) was used for the synthesis of **11b**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.17 (s, 3H), 3.70 (d, *J* = 2.0 Hz, 2H), 6.67 (s, 1H), 7.13-7.64 (m, 9H), 10.1 (s, 1H) ppm.

2-Cinnamyl-5-methylfuran (6)



A solution of **1g** (20.0 mg, 0.18 mmol), potassium trifluoroborate **3a** (44.9 mg, 0.21 mmol, 1.2 equiv), tartaric acid (26.7 mg, 0.18 mmol, 1 equiv) and H_2O (10 μL, 0.54 mmol, 3 equiv) in CH_2Cl_2 (0.7 mL) was stirred at rt for 18 h. The solution was filtered over $MgSO_4$ and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/DCM 9:1). Compound **6** was isolated as a colourless oil (34.6 mg, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.19 (s, 3H), 3.43 (d, *J* = 6.6 Hz, 2H), 5.8 (s, 1H), 5.86 (d, *J* = 3.1 Hz, 1H), 6.23 (dt, *J* = 15.8 Hz, *J* = 6.6 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 7.10-7.32 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 13.7, 32.0, 106.2, 106.4, 126.1, 126.3 (2C), 127.4, 128.6 (2C), 131.8, 137.5, 151.0, 152.0. Anal. calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.90; H, 7.19.

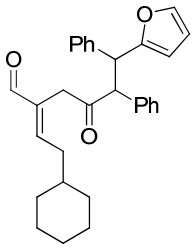
(*E*)-6-(Furan-2-yl)-4-oxo-5,6-diphenyl-2-(2-phenylethylidene)hexanal (7a)



A solution of **1i** (20.0 mg, 0.11 mmol), boronic acid **2a** (20.3 mg, 0.14 mmol, 1.2 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in cyclohexane (0.4 mL) was stirred at rt for 18 h. The mixture was filtered over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (0.8 mL) and Et_3N (32 μL, 0.23 mmol, 2 equiv) was added. The mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **7a** was isolated as a

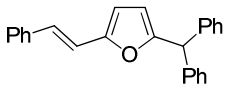
colourless oil (38.9 mg, 78%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.92 (dd, *J* = 16.6 Hz, *J* = 7.1 Hz, 1H), 3.06 (dd, *J* = 16.6 Hz, *J* = 7.1 Hz, 1H), 3.35 (s, 2H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 5.79 (d, *J* = 3.2 Hz, 1H), 6.01 (dd, *J* = 3.2 Hz, *J* = 1.9 Hz, 1H), 6.56 (t, *J* = 7.3 Hz, 1H), 6.91-6.98 (m, 2H), 7.14-7.35 (m, 12H), 7.42-7.46 (m, 2H), 9.26 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 35.2, 38.6, 48.1, 62.6, 107.0, 110.0, 126.8, 127.1, 128.6 (2C), 128.7 (2C), 128.7 (2C), 128.8 (2C), 128.8 (2C), 128.9 (2C), 135.6, 136.3, 137.8, 140.9, 141.5, 154.5, 156.4, 193.3, 204.0. Anal. calcd. for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.89; H, 6.11.

(*E*)-2-(2-Cyclohexylethylidene)-6-(furan-2-yl)-4-oxo-5,6-diphenylhexanal (7b)



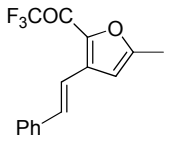
A solution of **1i** (20.0 mg, 0.11 mmol), boronic acid **2e** (21.2 mg, 0.14 mmol, 1.2 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in cyclohexane (0.4 mL) was stirred at rt for 18 h. The mixture was filtered over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (0.8 mL) and Et_3N (32 μL, 0.23 mmol, 2 equiv) was added. The mixture was stirred at rt for 1 h. A saturated solution of $NaHCO_3$ (10 mL) was added. The layers were separated and the aqueous one was extracted with DCM (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **7c** was isolated as a colourless oil (37.4 mg, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.02-1.31 (m, 4H), 1.42-1.71 (m, 9H), 3.22 (s, 2H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 5.76 (d, *J* = 3.1 Hz, 1H), 6.00 (dd, *J* = 3.1 Hz, *J* = 0.6 Hz, 1H), 6.48 (t, *J* = 7.4 Hz, 1H), 7.07-7.48 (m, 11H), 9.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 26.2, 26.2, 26.3, 33.0, 33.1, 36.7, 37.5, 38.6, 48.0, 62.4, 106.9, 110.0, 127.0, 127.7, 128.5 (2C), 128.6 (2C), 128.7 (2C), 128.8 (2C), 136.2, 136.4, 140.9, 141.4, 154.7, 157.9, 193.5, 204.0. Anal. calcd. for $C_{30}H_{32}O_3$: C, 81.78; H, 7.32. Found: C, 81.85; H, 7.28.

(E)-2-Benzhydryl-5-styrylfuran (8)



A solution of **1j** (27.5 mg, 0.11 mmol), boronic acid **2a** (20.3 mg, 0.14 mmol, 1.2 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in DCM (0.4 mL) was stirred at rt for 18 h. The mixture was filtered over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **8** was isolated as a colorless oil (30.3 mg, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 5.42 (s, 1H), 5.84 (d, *J* = 3.6 Hz, 1H), 6.21 (d, *J* = 3.6 Hz, 1H), 7.09-7.38 (m, 15 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 51.2, 109.5, 110.8, 116.7, 126.4, 126.6, 126.9, 127.5, 128.6, 128.8, 128.9, 137.3, 141.9, 152.9, 156.7. Anal. calcd. for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.21; H, 6.05.

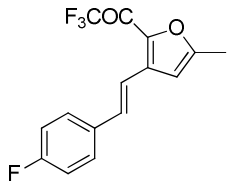
(*E*)-2,2,2-Trifluoro-1-(5-methyl-3-styrylfuran-2-yl)ethanone (9a)



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2a** (36.2 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4a** was filtered over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was redissolved in TFAA (0.8 mL) and TFA (5 μL, 0.061 mmol, 0.3 equiv) was added at 0ºC. The mixture was stirred at rt for 3 h. The solvent was evaporated *in vacuo*. NaOH 1M (10 mL) and AcOEt (10 mL) were added. The layers were separated and the organic one washed with NaOH 1M (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/DCM 8:2). Compound **9a** was isolated as a white solid (35.9 mg, 63%). ^{1}H NMR ($CDCl_3$, 700 MHz): δ (ppm) = 2.44 (s, 3H), 6.62 (s, 1H), 7.18 (d, *J* = 16.4 Hz, 1H), 7.29-7.43 (m, 3H), 7.52-7.58 (m, 3H), 7.79 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 176 MHz): δ (ppm) = 14.2, 107.5, 116.4 (q, J_{CF} = 294 Hz), 118.8, 127.3, 128.8, 129.1, 136.0, 136.9, 140.5, 142.0, 159.9,

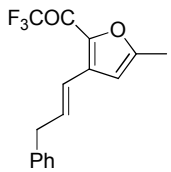
168.9 (q, J_{CF} = 37 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ (ppm) = -74.7 (s). Anal. calcd. for $C_{15}H_{11}F_3O_2$: C, 64.29; H, 3.96. Found: C, 64.34; H, 3.87.

(*E*)-2,2,2-Trifluoro-1-[3-(4-fluorostyryl)-5-methylfuran-2-yl]ethanone (9b)



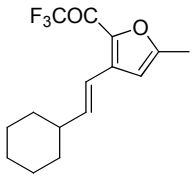
A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2b** (40.6 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4b** was filtered over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was redissolved in TFAA (0.8 mL) and TFA (5 μL, 0.061 mmol, 0.3 equiv) was added at 0ºC. The mixture was stirred at rt for 3 h. The solvent was evaporated *in vacuo*. NaOH 1M (10 mL) and AcOEt (10 mL) were added. The layers were separated and the organic one washed with NaOH 1M (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/DCM 8:2). Compound **9b** was isolated as a white solid (39.5 mg, 65%). ^{1}H NMR ($CDCl_3$, 700 MHz): δ (ppm) = 2.44 (s, 3H), 6.60 (s, 1H), 7.04-7.17 (m, 3H), 7.49-7.57 (m, 2H), 7.70 (d, J = 16.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 176 MHz): δ (ppm) = 14.3, 107.4, 115.6, 116.3 (q, J_{CF} = 292 Hz), 117.7, 128.9, 132.3, 135.6, 140.3, 142.0, 160.0, 163.2 (d, J_{CF} = 250 Hz), 169.0 (q, J_{CF} = 36.5 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ (ppm) = -74.7 (s, 3F), -111.8 (s, 1F). Anal. calcd. for $C_{15}H_{10}F_4O_2$: C, 60.41; H, 3.38. Found: C, 60.50; H, 3.29.

(*E*)-2,2,2-Trifluoro-1-[5-methyl-3-(3-phenylprop-1-en-1-yl)furan-2-yl]ethanone (9c)



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2d** (39.6 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4d** was filtered over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was redissolved in TFAA (0.8 mL) and TFA (5 μL, 0.061 mmol, 0.3 equiv) was added at 0ºC. The mixture was stirred at rt for 3 h. The solvent was evaporated *in vacuo*. NaOH 1M (10 mL) and AcOEt (10 mL) were added. The layers were separated and the organic one washed with NaOH 1M (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/DCM 8:2). Compound **9c** was isolated as a white solid (36.5 mg, 61%). ^{1}H NMR ($CDCl_3$, 700 MHz): δ (ppm) = 2.39 (s, 3H), 3.60 (d, *J* = 7.1 Hz, 2H), 6.43 (s, 1H), 6.49 (dt, *J* = 15.9 Hz, *J* = 7.1 Hz, 1H), 7.12-7.34 (m, 6H). ^{13}C NMR ($CDCl_3$, 126.5 MHz): δ (ppm) = 14.2, 39.6, 107.9, 116.3 (q, J_{CF} = 290 Hz), 120.7, 126.5, 128.5, 128.6, 138.7, 138.9, 140.3, 141.5, 159.8, 168.9 (q, J_{CF} = 36 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ (ppm) = -74.7 (s). Anal. calcd. for $C_{16}H_{13}F_3O_2$: C, 65.30; H, 4.45. Found: C, 65.21; H, 4.38.

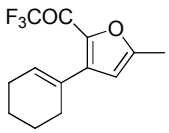
(*E*)-1-[3-(2-Cyclohexylvinyl)-5-methylfuran-2-yl]-2,2,2-trifluoroethanone (9d)



A solution of **1a** (20.0 mg, 0.20 mmol), boronic acid **2e** (37.6 mg, 0.24 mmol, 1.2 equiv), tartaric acid (30.5 mg, 0.20 mmol, 1 equiv) and H_2O (11 μL, 0.61 mmol, 3 equiv) in CH_2Cl_2 (0.8 mL) was stirred at rt for 18 h. The crude product **4e** was filtered over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was redissolved in TFAA (0.8 mL) and TFA (5 μL, 0.061 mmol, 0.3 equiv) was added at 0ºC. The mixture was stirred at rt for 3 h. The solvent was evaporated *in vacuo*. NaOH 1M (10 mL) and AcOEt (10 mL) were added. The layers were separated and the organic one washed with NaOH 1M (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/DCM 8:2). Compound **9d** was isolated as a white solid (37.3 mg, 64%). ^{1}H NMR ($CDCl_3$, 700 MHz): δ (ppm) = 1.48-1.80 (m, 11H), 2.39 (s, 3H), 3.33 (dd, *J* = 15.9 Hz, *J* = 6.1 Hz, 1H), 6.45 (s, 1H),

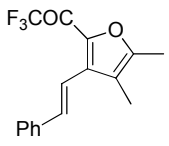
7.01 (d, J = 15.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 176 MHz): δ (ppm) = 14.2, 25.8, 26.0, 32.4, 41.4, 107.8, 116.4 (q, J_{CF} = 292 Hz), 117.4, 141.2, 141.3, 146.3, 159.7, 168.7 (q, J_{CF} = 38 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): -74.7 (s). Anal. calcd. for $C_{15}H_{17}F_3O_2$: C, 62.93; H, 5.99. Found: C, 63.02; H, 6.07.

1-[3-(Cyclohex-1-en-1-yl)-5-methylfuran-2-yl]-2,2,2-trifluoroethanone (9e)



To a solution of **4g** (20.0 mg, 0.11 mmol) in TFAA (0.4 mL) and TFA (3 μL, 0.033 mmol, 0.3 equiv) was added at 0ºC. The mixture was stirred at rt for 3 h. The solvent was evaporated *in vacuo*. NaOH 1M (10 mL) and AcOEt (10 mL) were added. The layers were separated and the organic one washed with NaOH 1M (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/DCM 8:2). Compound **9e** was isolated as a white solid (16.9 mg, 59%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.63-1.79 (m, 4H), 2.17 (s, 3H), 2.18-2.25 (m, 2H), 2.26-2.34 (m, 2H), 6.24 (s, 1H), 6.35 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 14.2, 21.6, 22.5, 25.7, 27.7, 111.8, 116.7 (q, J_{CF} = 286 Hz), 128.5, 131.9, 145.6, 159.4, 167.8 (q, J_{CF} = 36 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): -73.9 (s). Anal. calcd. for $C_{13}H_{13}F_3O_2$: C, 60.46; H, 5.07. Found: C, 60.51; H, 5.11.

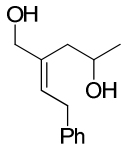
(*E*)-1-(4,5-Dimethyl-3-styrylfuran-2-yl)-2,2,2-trifluoroethanone (9f)



A solution of **1b** (20.0 mg, 0.18 mmol), boronic acid **2a** (39.5 mg, 0.27 mmol, 1.5 equiv), tartaric acid (26.7 mg, 0.18 mmol, 1 equiv) and H_2O (10 μL, 0.54 mmol, 3 equiv) in CH_2Cl_2 (0.7 mL) was stirred at rt for 18 h. The crude product **4j** was filtered over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was redissolved in

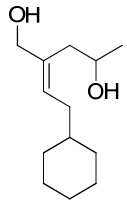
TFAA (0.7 mL) and TFA (4 μL, 0.054 mmol, 0.3 equiv) was added at 0ºC. The mixture was stirred at rt for 3 h. The solvent was evaporated *in vacuo*. NaOH 1M (10 mL) and AcOEt (10 mL) were added. The layers were separated and the organic one washed with NaOH 1M (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/DCM 8:2). Compound **9f** was isolated as a white solid (35.6 mg, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.16 (s, 3H), 2.31 (s, 3H), 7.17-7.35 (m, 4H), 7.46-7.53 (m, 2H), 7.68 (d, J = 16.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 8.6, 12.4, 114.7, 116.9 (q, J_{CF} = 35 Hz), 127.4, 128.4, 136.7, 137.1, 138.9, 141.9, 156.9, 168.5 (q, J_{CF} = 290 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ (ppm) = -74.2 (s). Anal. calcd. for $C_{16}H_{13}F_3O_2$: C, 65.30; H, 4.45. Found: C, 65.39; H, 4.39.

(*E*)-2-(2-Phenylethylidene)pentane-1,4-diol (10a)



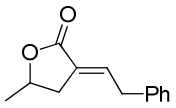
To a solution of **5a** (20.0 mg, 0.10 mmol) in EtOH/THF 1:2 (1.5 mL) at 0ºC was added $NaBH_4$ (3.7 mg, 0.10 mmol, 1 equiv). The mixture was stirred for 10 min. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/AcOEt 4:6). Compound **10a** was isolated as a colourless oil (20.1 mg, 99%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.19 (d, J = 6.2 Hz, 3H), 2.23 (dd, J = 14.2 Hz, J = 8.8 Hz, 1H), 2.45 (dd, J = 14.2 Hz, J = 2.1 Hz, 1H), 2.56 (t, J = 7.3 Hz, 1H), 2.62 (bs, 1H), 3.34 (d, J = 7.3 Hz, 2H), 3.86-3.97 (m, 1H), 4.01 (s, 2H), 5.69 (t, J = 7.3 Hz, 1H), 7.05-7.16 (m, 3H), 7.16-7.26 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 23.8, 34.2, 39.1, 67.5, 68.8, 126.3, 128.5 (2C), 128.7 (2C), 130.1, 136.9, 140.5. Anal. calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.77; H, 8.71.

(*E*)-2-(2-Cyclohexylethylidene)pentane-1,4-diol (10b)



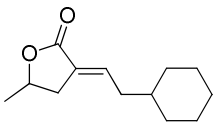
To a solution of **5e** (20.0 mg, 0.10 mmol) in EtOH/THF 1:2 (1.5 mL) at 0ºC $NaBH_4$ (3.7 mg, 0.10 mmol, 1 equiv) was added. The mixture was stirred for 10 min. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/AcOEt 4:6). Compound **10b** was isolated as a colourless oil (20.1 mg, 99%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.12-1.27 (m, 4H), 1.23 (d, *J* = 6.2 Hz, 3H), 1.59-1.73 (m, 7H), 1.93 (t, *J* = 7.2 Hz, 2H), 2.17 (dd, *J* = 14.1 Hz, *J* = 9.0 Hz, 1H), 2.40 (dd, *J* = 14.1 Hz, *J* = 3.0 Hz, 1H), 2.60 (bs, 2H), 3.86-3.99 (m, 1H), 4.05 (s, 2H), 5.90 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 23.7, 26.5 (2C), 26.6, 33.3, 33.4, 35.8, 38.4, 39.2, 67.5, 69.2, 131.0, 136.4. Anal. calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.60; H, 11.31.

(*E*)-5-Methyl-3-(2-phenylethylidene)dihydrofuran-2(3*H*)-one (11a)



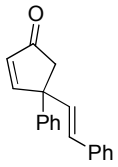
MnO_2 (229.2 mg, 2.63 mmol, 27.2 equiv) was added to a solution of **10a** (20.0 mg, 0.10 mmol) in DCM (1.3 mL). The mixture was stirred at rt for 4 h and then was filtered over a pad of celite. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **11a** was isolated as a colourless oil (14.3 mg, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.44 (d, *J* = 6.2 Hz, 3H), 2.47 (m, 1H), 3.06 (m, 1H), 3.52 (d, *J* = 7.4 Hz, 2H), 4.64-4.75 (m, 1H), 6.87-6.95 (m, 1H), 7.13-7.36 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 22.4, 33.1, 36.4, 74.2, 126.9, 127.6, 128.6 (2C), 129.0 (2C), 137.8, 138.4, 170.9. Anal. calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.29; H, 6.91.

(*E*)-3-(2-Cyclohexylethylidene)-5-methyldihydrofuran-2(3H)-one (11b)



MnO_2 (229.2 mg, 2.63 mmol, 27.2 equiv) was added to a solution of **10b** (20.0 mg, 0.10 mmol) in DCM (1.3 mL). The mixture was stirred at rt for 4 h and then was filtered over a pad of celite. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **11b** was isolated as a colourless oil (13.7 mg, 70%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 0.77-1.04 (m, 2H), 1.16-1.30 (m, 2H), 1.41 (d, *J* = 6.2 Hz, 3H), 1.51-1.77 (m, 6H), 2.01-2.10 (m, 2H), 2.16-2.24 (m, 1H), 2.38 (m, 1H), 2.99 (m, 1H), 4.60-4.72 (m, 1H), 6.81-6.81 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) = 21.3, 25.1, 25.2, 28.7, 32.0, 32.2, 36.8, 72.9, 126.0, 138.8, 169.9. Anal. calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.04; H, 9.74.

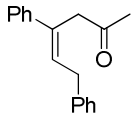
(*E*)-4-Phenyl-4-styrylcyclopent-2-enone (12)



A solution of **1f** (20.0 mg, 0.11 mmol), boronic acid **2a** (25.4 mg, 0.18 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4p** was filtered over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue (18.5 mg) was redissolved in ^{t}BuOH (1.4 mL) and K_2CO_3 (79.3 mg, 0.57 mmol, 5 equiv) was added at rt. The mixture was stirred at reflux for 2 h, then was cooled at rt, diluted with Et_2O and was filtered over a pad of celite. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **12** was isolated as a colourless oil (14.3 mg, 48%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.82 (d, *J* = 18.6 Hz, 1H), 2.96 (d, *J* = 18.6 Hz, 1H), 6.31 (d, *J* = 5.7 Hz, 1H), 6.34 (d, *J* = 16.3 Hz, 1H), 6.54 (d, *J* = 16.3 Hz, 1H), 7.23-7.43 (m, 10H), 7.82 (d, *J* = 5.7 Hz, 1H).

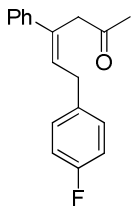
^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 50.1, 54.7, 126.5 (2C), 126.8 (2C), 127.3, 128.0, 128.8 (2C), 129.0 (2C), 130.2, 132.4, 133.8, 136.6, 144.0, 167.9, 208.8. Anal. calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.58; H, 6.27.

(*E*)-4,6-Diphenylhex-4-en-2-one (13a)



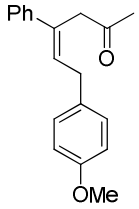
A solution of **1f** (20.0 mg, 0.11 mmol), boronic acid **2a** (25.4 mg, 0.18 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4p** was filtered over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue (18.5 mg) was redissolved in THF:MeOH 2:1 (0.6 mL) and KOH 10% (90 μL) was added. The mixture was stirred at rt for 2 h, then was added brine (10 mL) and Et_2O (10 mL). Layers were separated, and the organic one was washed with brine and dried over $MgSO_4$. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **13a** was isolated as a colourless oil (15.8 mg, 55%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.12 (s, 3H), 3.55 (d, *J* = 7.5 Hz, 2H), 3.71 (s, 2H), 6.17 (t, *J* = 7.5 Hz, 1H), 7.18-7.38 (m, 10H). ^{13}C NMR ($CDCl_3$, 176 MHz): δ (ppm) = 29.9, 35.3, 46.0, 126.2 (2C), 126.4, 127.4, 128.5, (2C), 128.6 (2C), 128.8 (2C), 131.0, 133.9, 140.1, 142.1, 206.4. Anal. calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.44; H, 7.17.

(*E*)-6-(4-Fluorophenyl)-4-phenylhex-4-en-2-one (13b)



A solution of **1f** (20.0 mg, 0.11 mmol), boronic acid **2b** (28.6 mg, 0.18 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4q** was filtered over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue (20.4 mg) was redissolved in THF:MeOH 2:1 (0.6 mL) and KOH 10% (90 μL) was added. The mixture was stirred at rt for 2 h, then was added brine (10 mL) and Et_2O (10 mL). Layers were separated, and the organic one was washed with brine and dried over $MgSO_4$. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **13b** was isolated as a colourless oil (12.9 mg, 42%). ^{1}H NMR ($CDCl_3$, 700 MHz): δ (ppm) = 2.12 (s, 3H), 3.50 (d, *J* = 7.5 Hz, 2H), 3.69 (s, 2H), 6.11 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 8.6 Hz, 2H), 7.19 (dd, *J* = 8.6 Hz, *J* = 5.5 Hz, 2H), 7.29-7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, 175 MHz): δ (ppm) = 31.2, 31.7, 45.9, 115.4, 115.6, 126.2 (2C), 127.5, 128.7 (2C), 129.9, 130.0, 130.8, 134.0, 142.0, 207.2. ^{19}F NMR ($CDCl_3$, 282 MHz): δ (ppm) = -116.4 (s). Anal. calcd. for $C_{18}H_{17}FO$: C, 80.57; H, 6.39. Found: C, 80.66; H, 6.47.

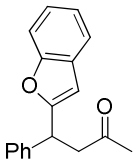
(*E*)-6-(4-Methoxyphenyl)-4-phenylhex-4-en-2-one (13c)



A solution of **1f** (20.0 mg, 0.11 mmol), boronic acid **2c** (30.6 mg, 0.18 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4r** was filtered over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue (25.8 mg) was redissolved in THF:MeOH 2:1 (0.6 mL) and KOH 10% (90 μL) was added. The mixture was stirred at rt for 2 h, then was added brine (10 mL) and Et_2O (10 mL). Layers were separated, and the organic one was washed with brine and dried over $MgSO_4$. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **13c** was isolated as a yellow oil (19.3 mg, 60%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.11 (s, 3H), 3.48

(d, J = 7.3 Hz, 2H), 3.69 (s, 2H), 3.79 (s, 3H), 6.14 (t, J = 7.3 Hz, 1H), 6.83-6.89 (m, 2H), 7.11-7.36 (m, 7H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 29.7, 34.3, 45.8, 55.3, 114.0 (2C), 126.0 (2C), 127.2, 127.3, 127.6, (2C), 128.4, 128.6 (2C), 129.3, 132.0, 157.9, 207.0. Anal. calcd. for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.49; H, 7.10.

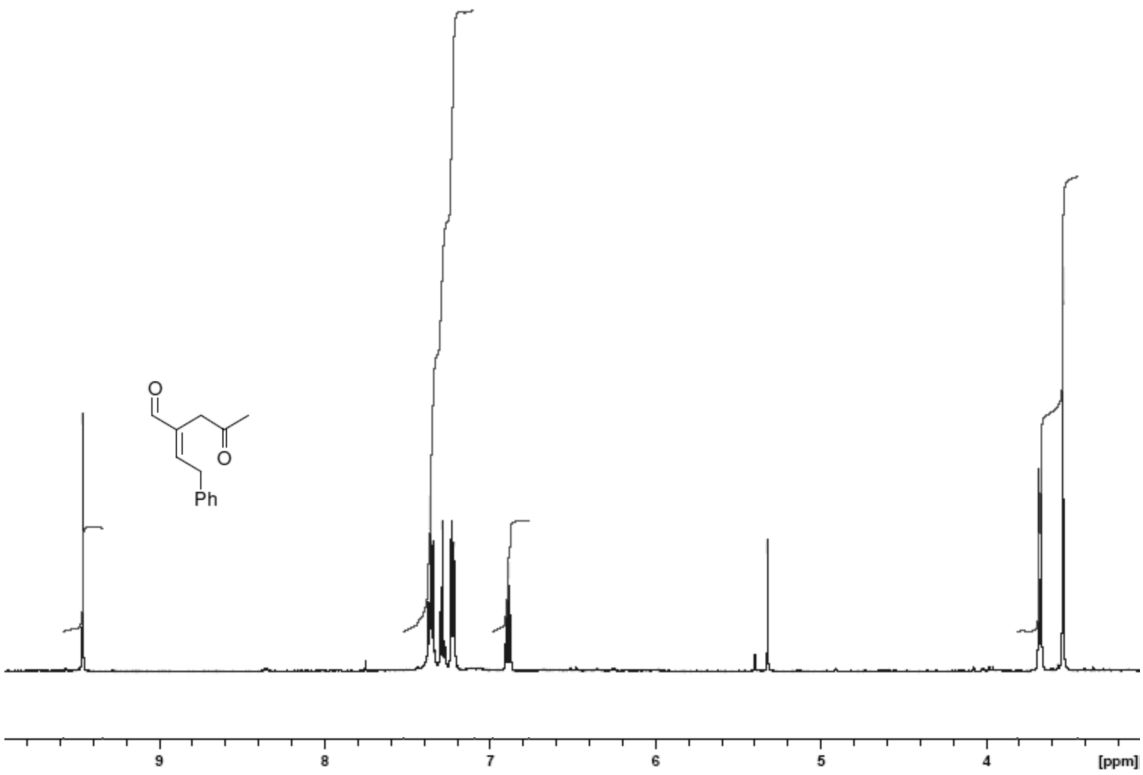
4-(Benzofuran-2-yl)-4-phenylbutan-2-one (14)



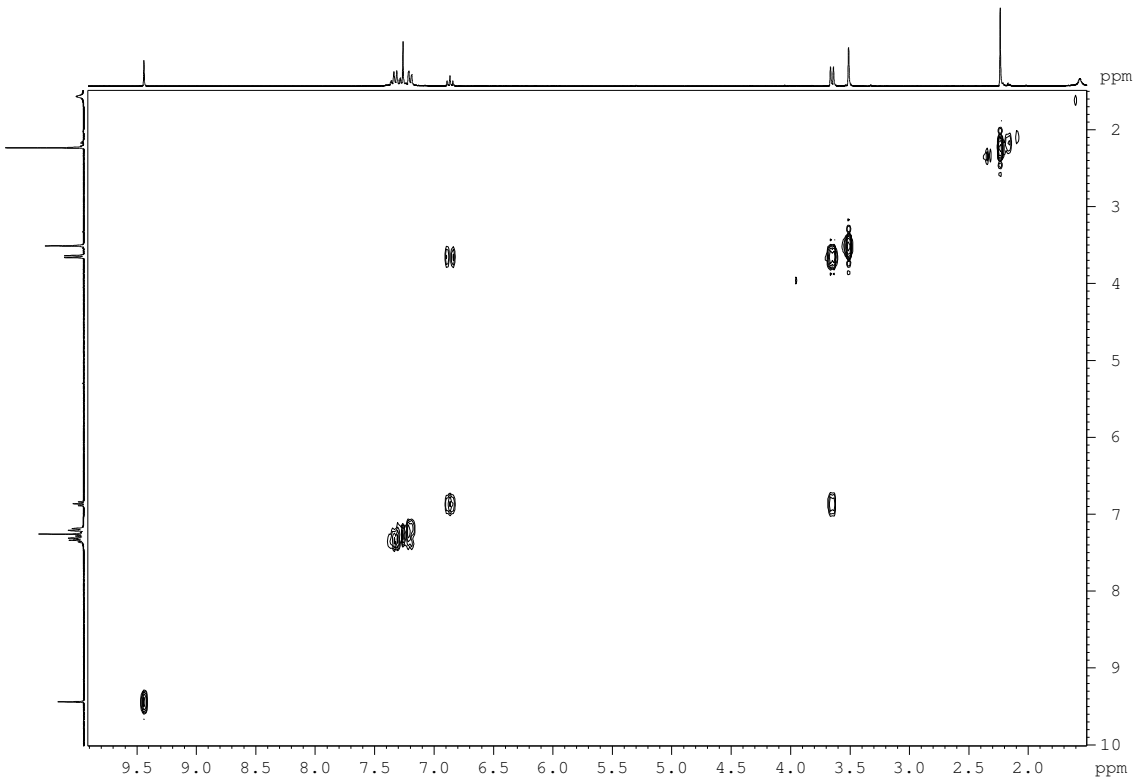
A solution of **1f** (20.0 mg, 0.11 mmol), benzofuran-2-ylboronic acid (29.2 mg, 0.18 mmol, 1.5 equiv), tartaric acid (17.2 mg, 0.11 mmol, 1 equiv) and H_2O (6 μL, 0.34 mmol, 3 equiv) in CH_2Cl_2 (0.5 mL) was stirred at 60ºC for 6 h. The crude product **4s** was filtered over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue (25.8 mg) was redissolved in THF:MeOH 2:1 (0.6 mL) and KOH 10% (90 μL) was added. The mixture was stirred at rt for 2 h, then was added brine (10 mL) and Et_2O (10 mL). Layers were separated, and the organic one was washed with brine and dried over $MgSO_4$. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/AcOEt 8:2). Compound **14** was isolated as a colorless oil (18.2 mg, 63%). Characterization data are in agreement with those previously reported for **14**.[7] ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.17 (s, 3H), 3.15 (dd, J = 17.1 Hz, 7.5 Hz, 1H), 3.39 (dd, J = 17.1 Hz, 7.5 Hz, 1H), 4.77 (t, J = 7.5 Hz, 1H), 6.41 (s, 1H), 7.13-7.59 (m, 9H).^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 30.5, 40.5, 48.1, 102.9, 111.0, 120.6, 122.6, 123.6, 127.2, 127.9, 128.5, 128.7, 140.9, 154.8, 159.6, 205.9. Anal. calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.94; H, 6.23.

[7] S. Dhiman and S. S. V. Ramasastry, *J. Org. Chem.*, 2013, **78**, 10427.

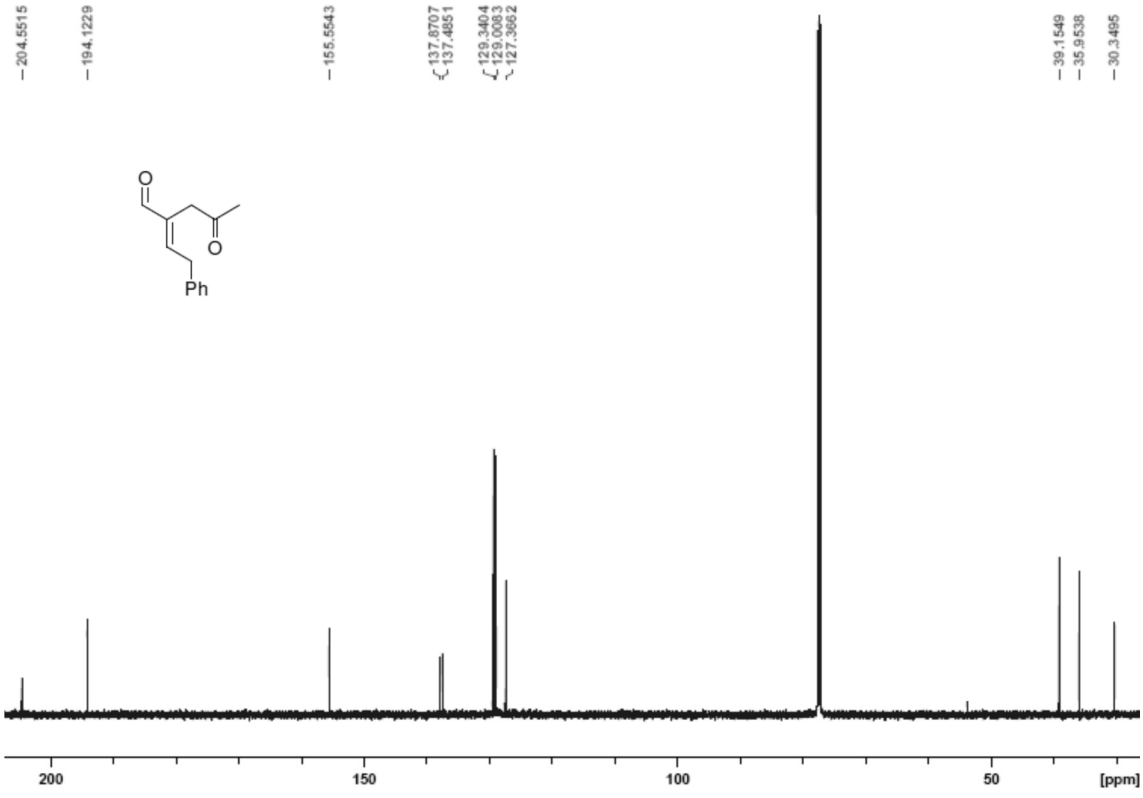
5a: ^{1}H-NMR ($CDCl_3$, 500 MHz)



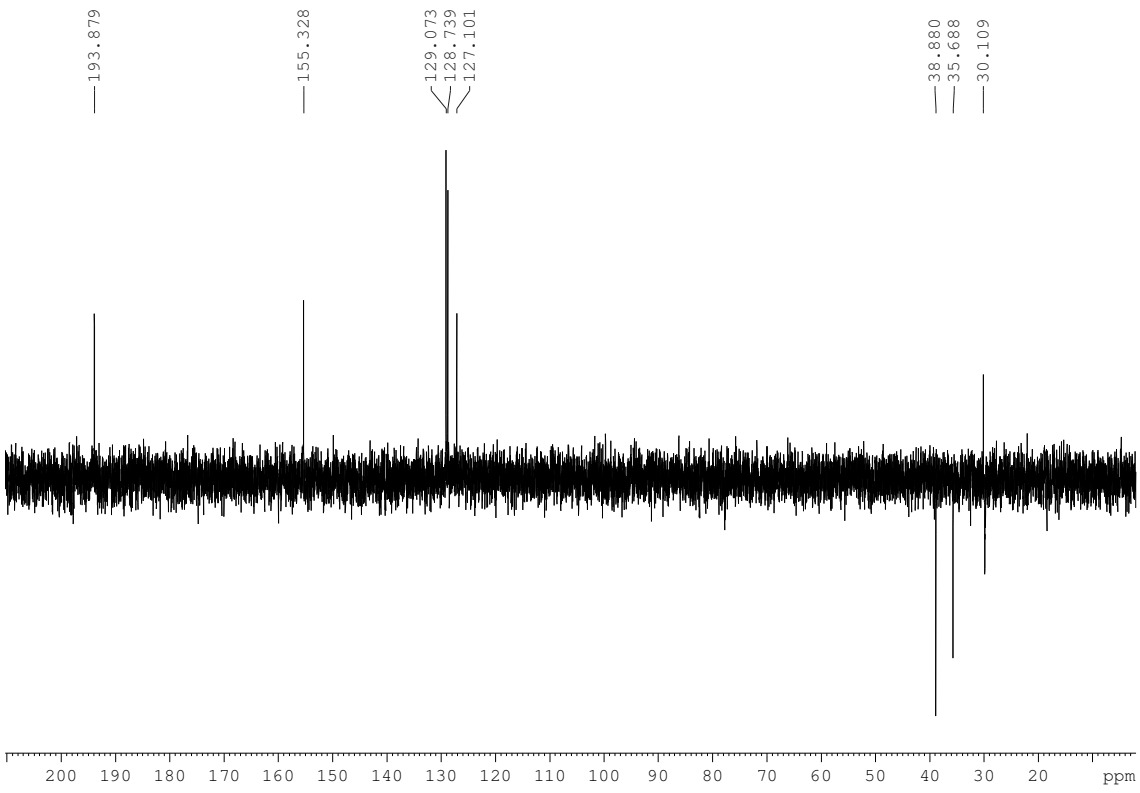
5a: COSY ($CDCl_3$, 300 MHz)



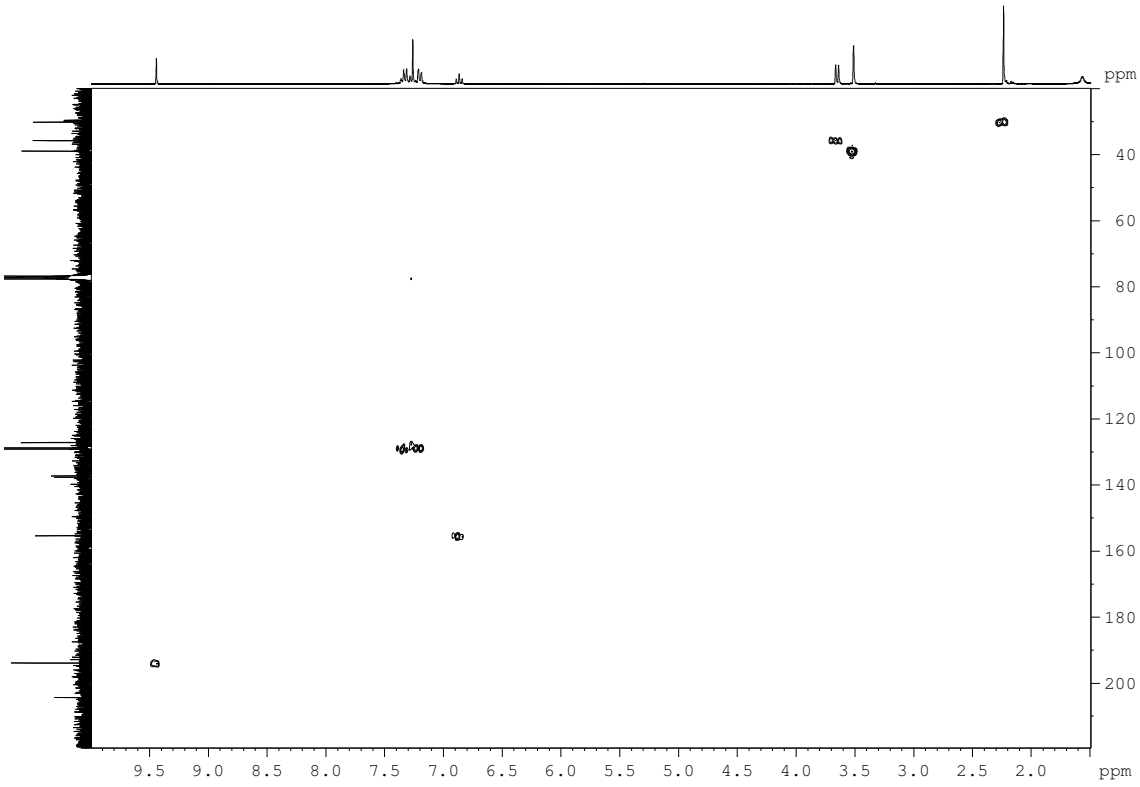
5a: ^{13}C-NMR ($CDCl_3$, 125 MHz)



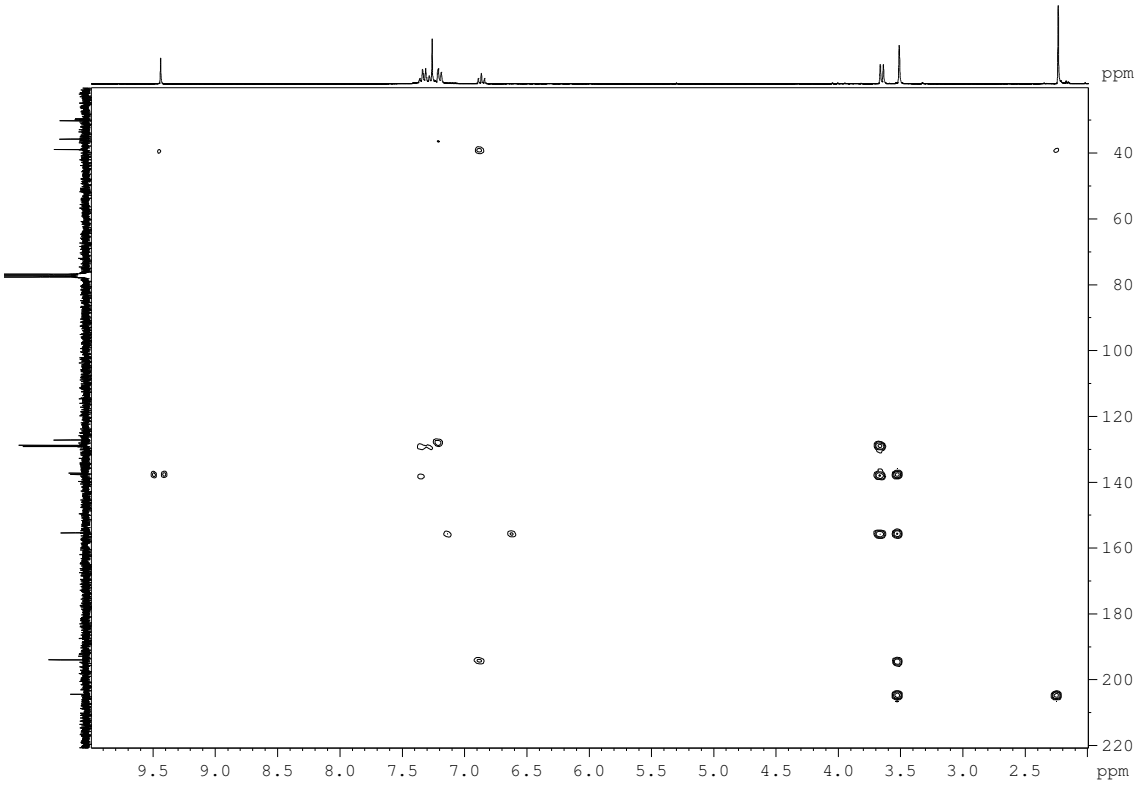
5a: DEPT-135 ($CDCl_3$, 75 MHz)



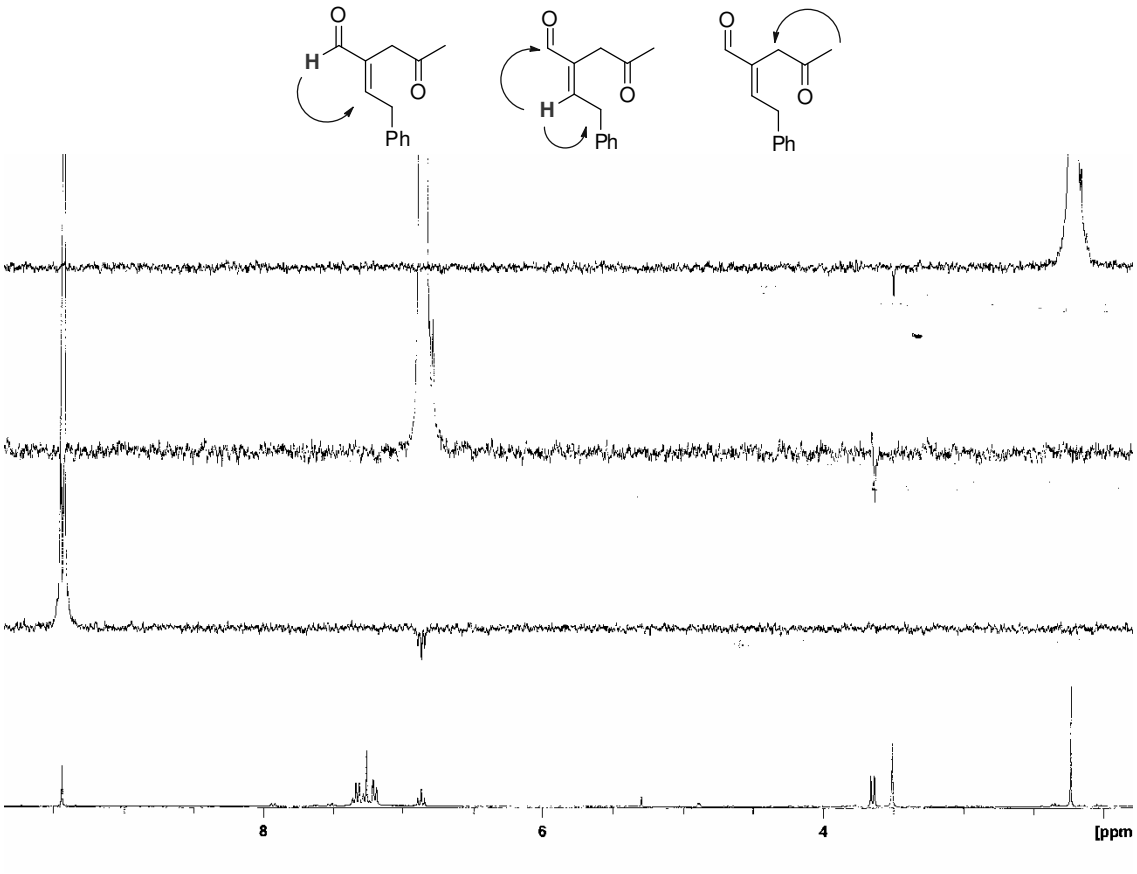
5a: HMQC ($CDCl_3$, 75 MHz)



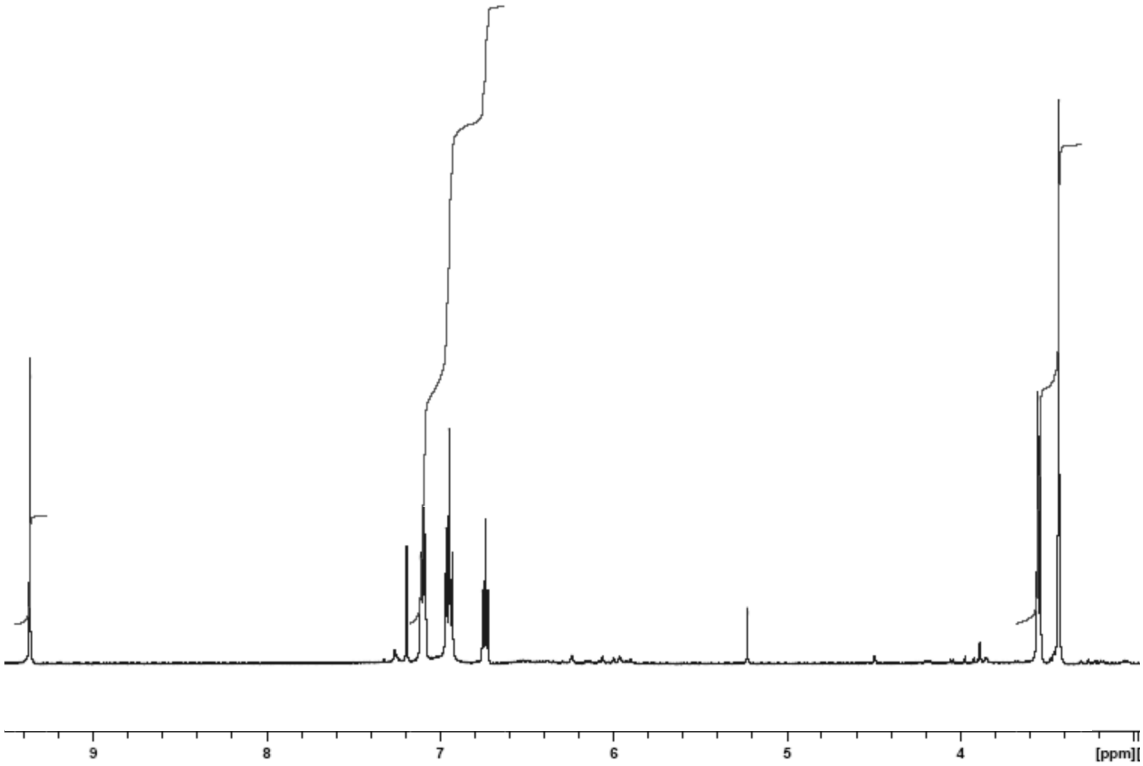
5a: HMBC ($CDCl_3$, 75 MHz)



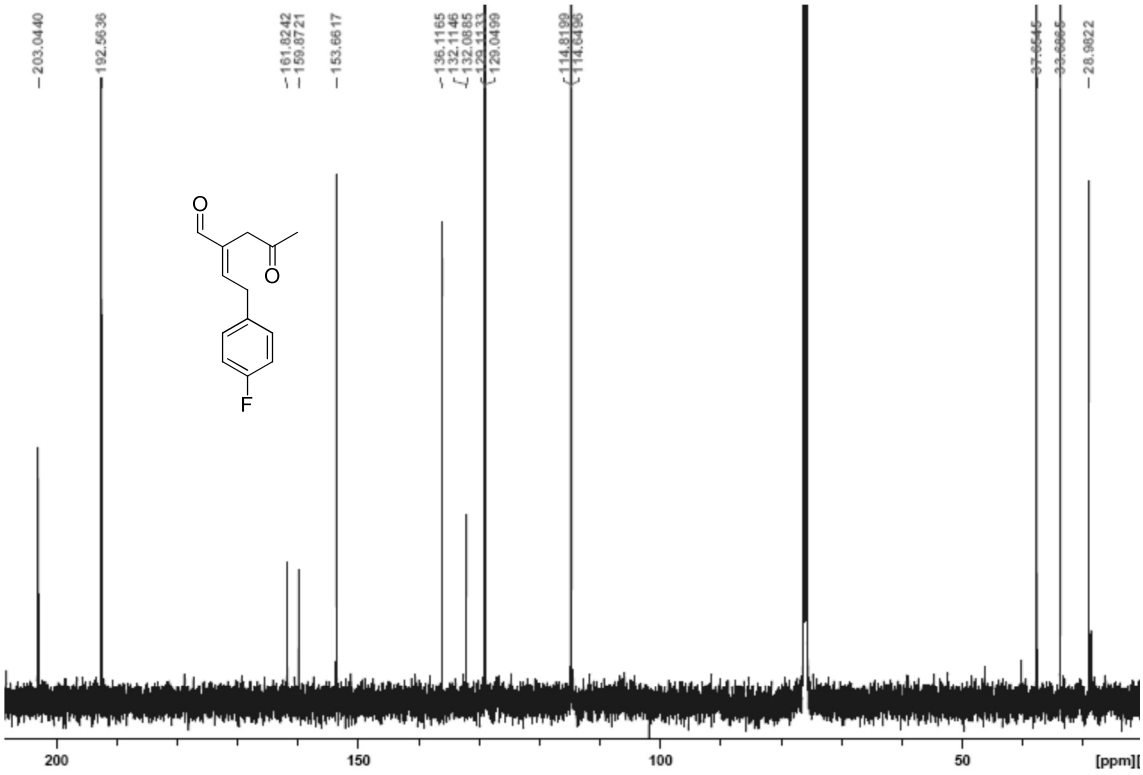
5a: NOE measurements, ($CDCl_3$, 300 MHz)



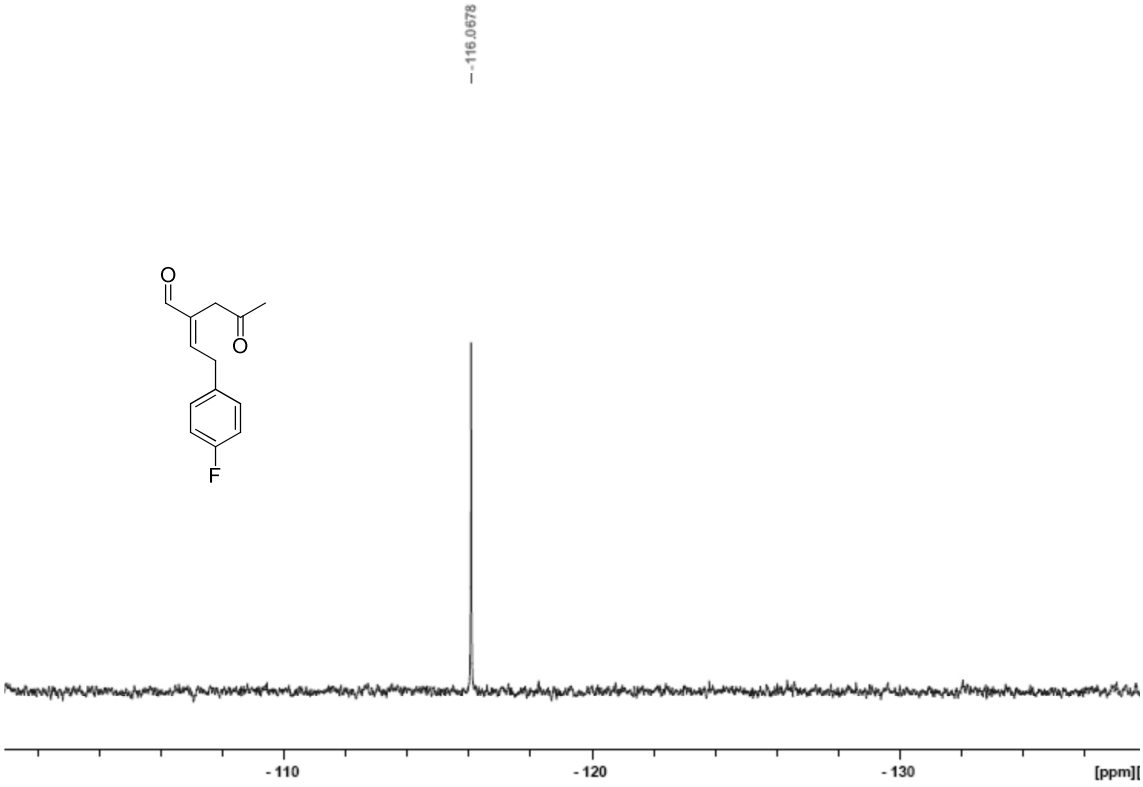
5b: ^{1}H-NMR ($CDCl_3$, 500 MHz)



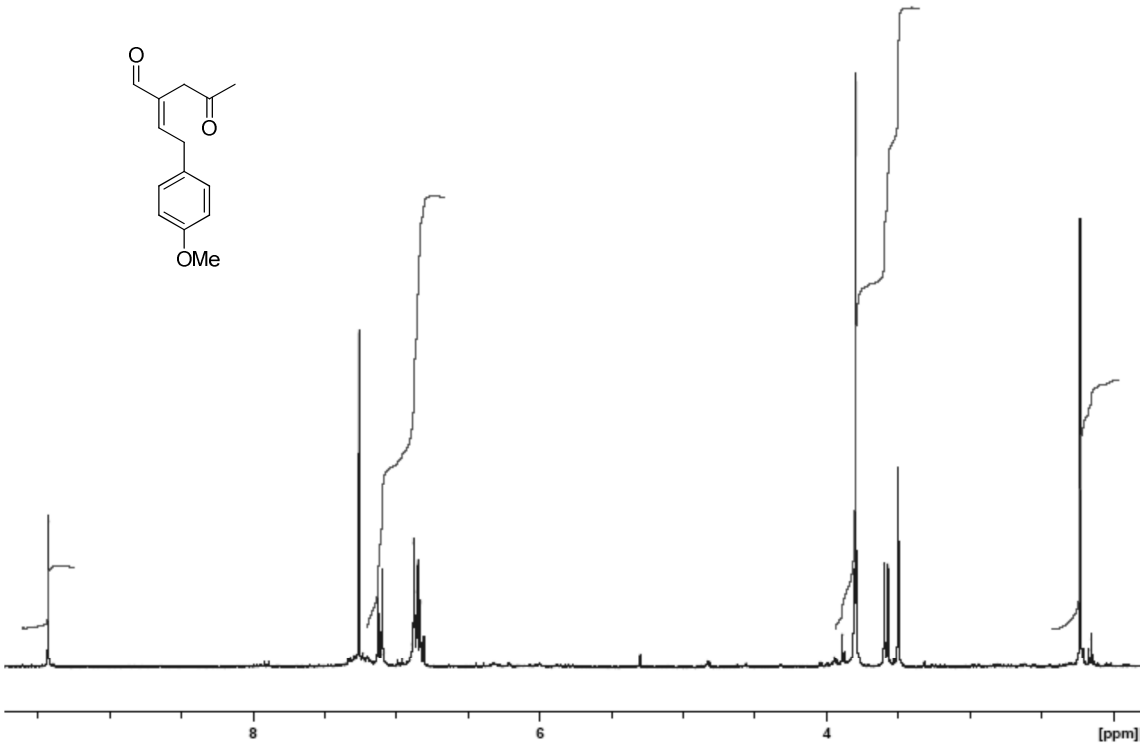
5b: ^{13}C-NMR ($CDCl_3$, 125 MHz)



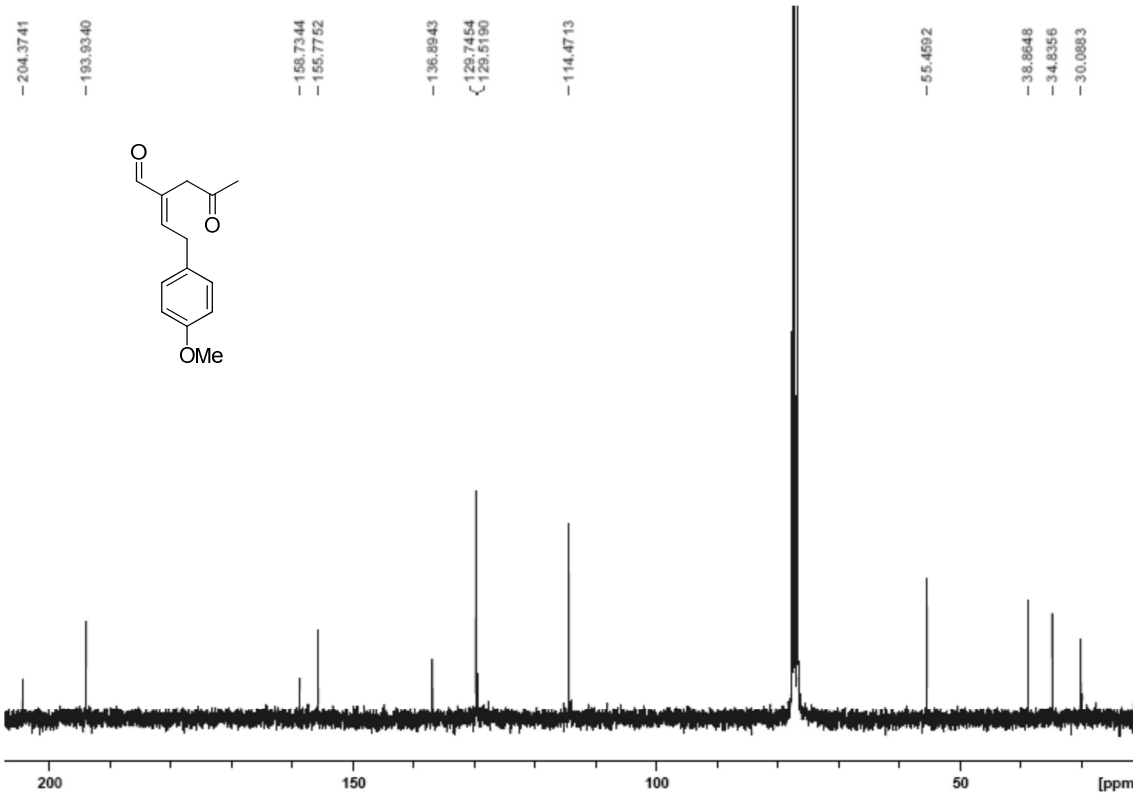
5b: ^{19}F-NMR ($CDCl_3$, 282 MHz)



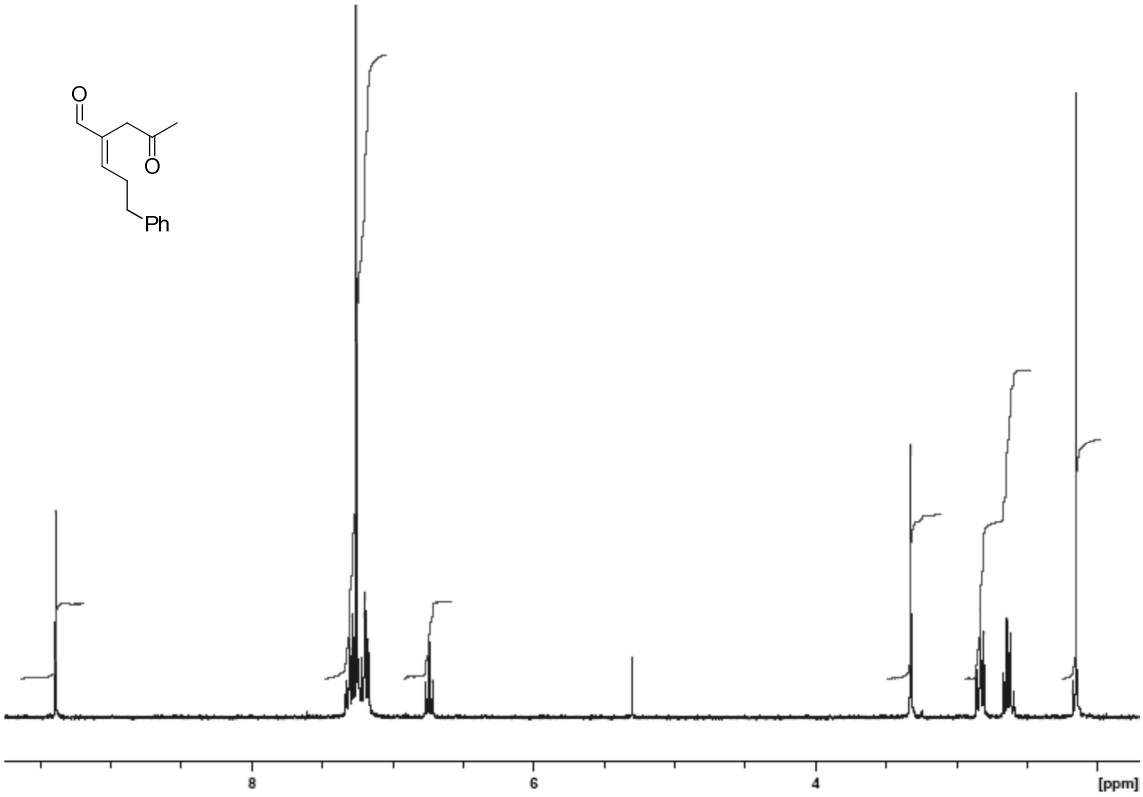
5c: ^{1}H-NMR ($CDCl_3$, 300 MHz)



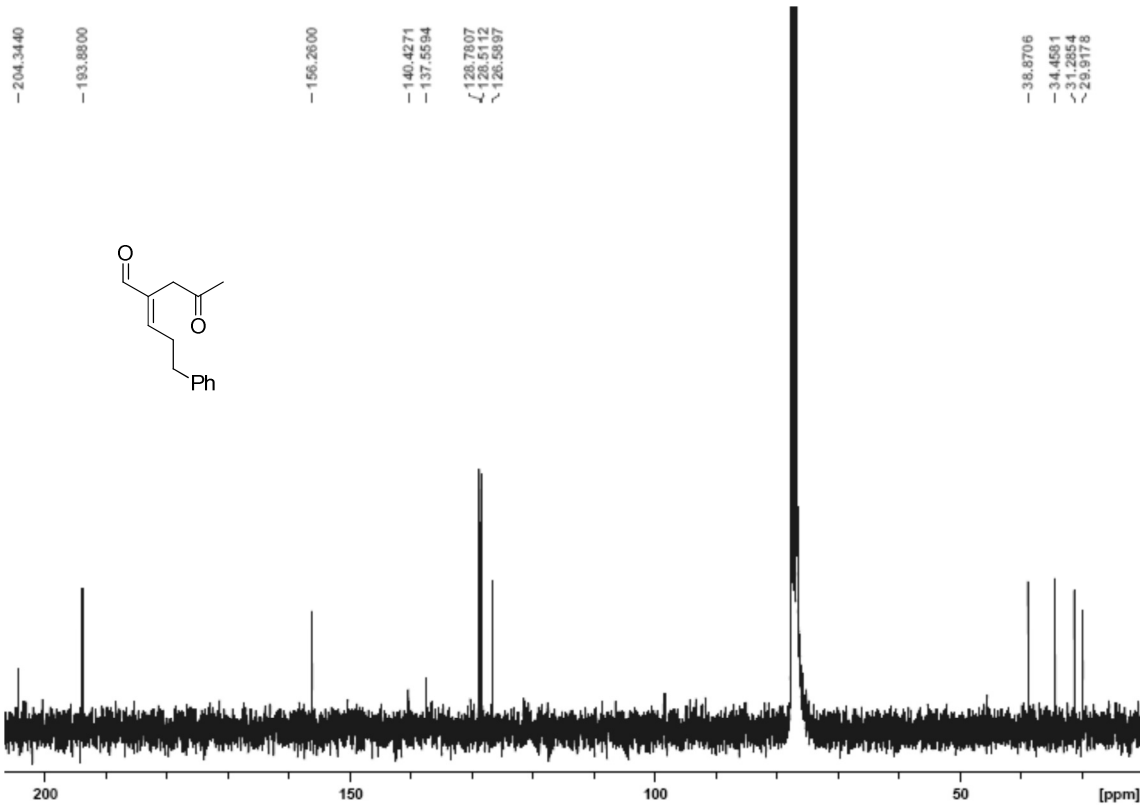
5c: ^{13}C-NMR ($CDCl_3$, 75 MHz)



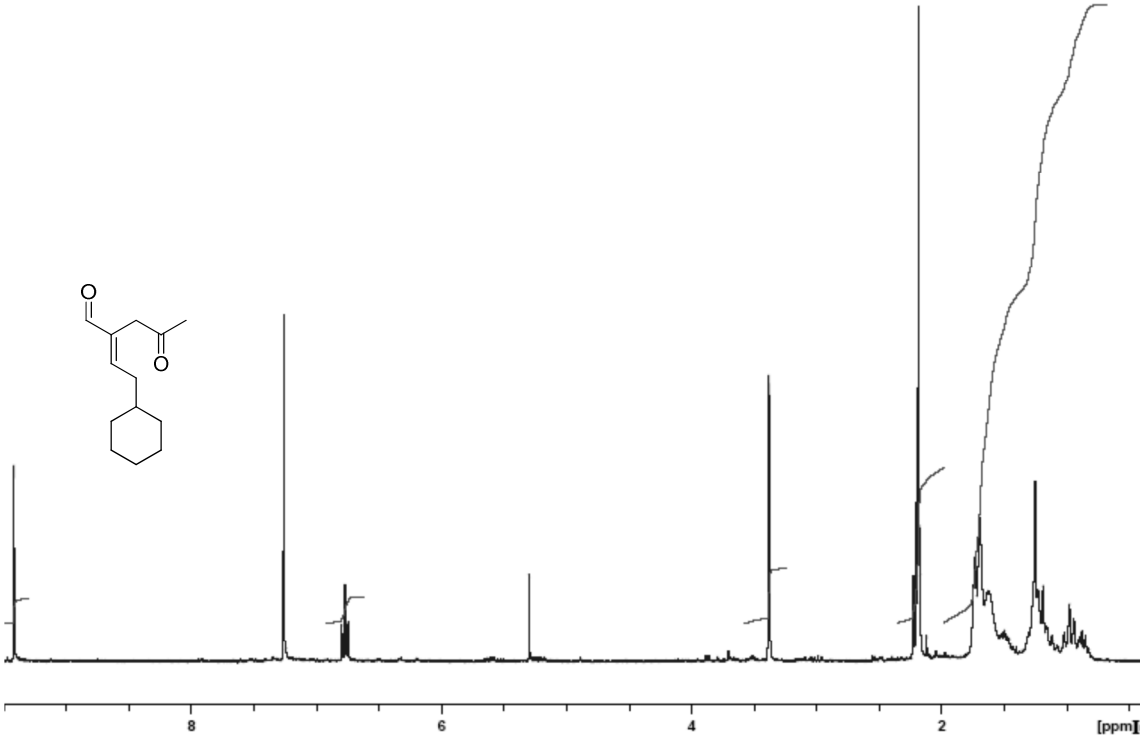
5d: ^{1}H-NMR ($CDCl_3$, 300 MHz)



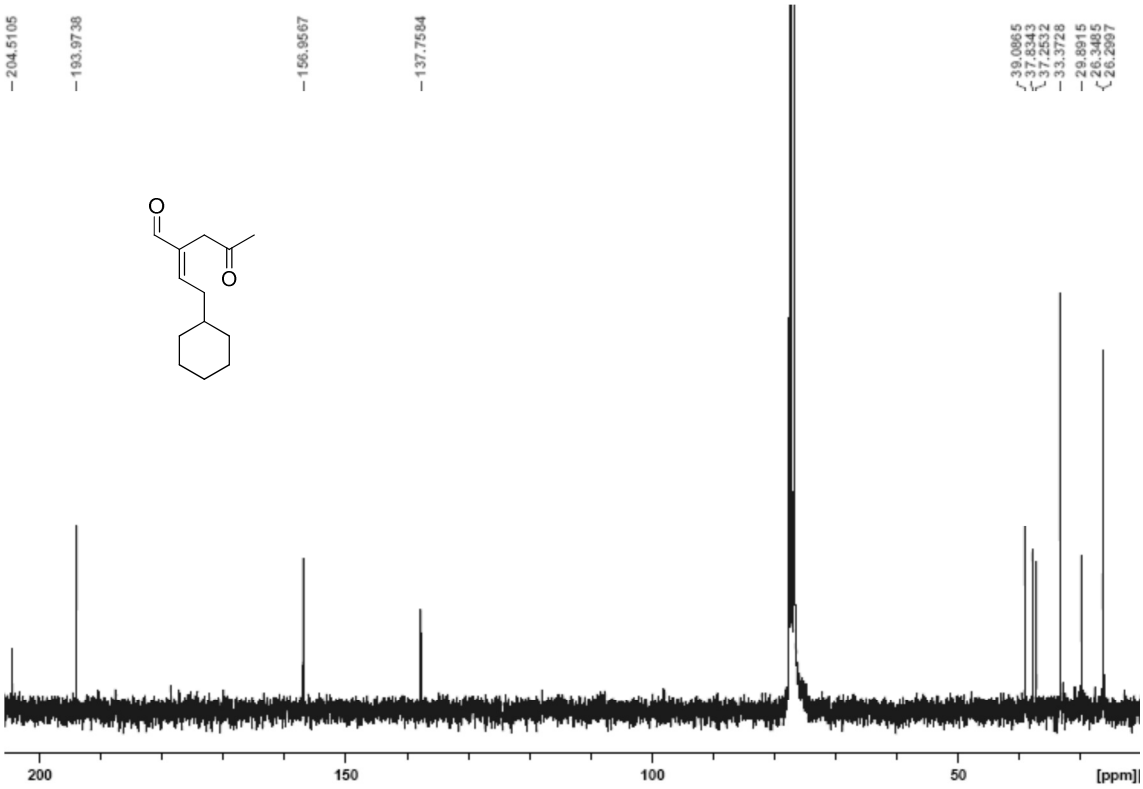
5d: ^{13}C-NMR ($CDCl_3$, 75 MHz)



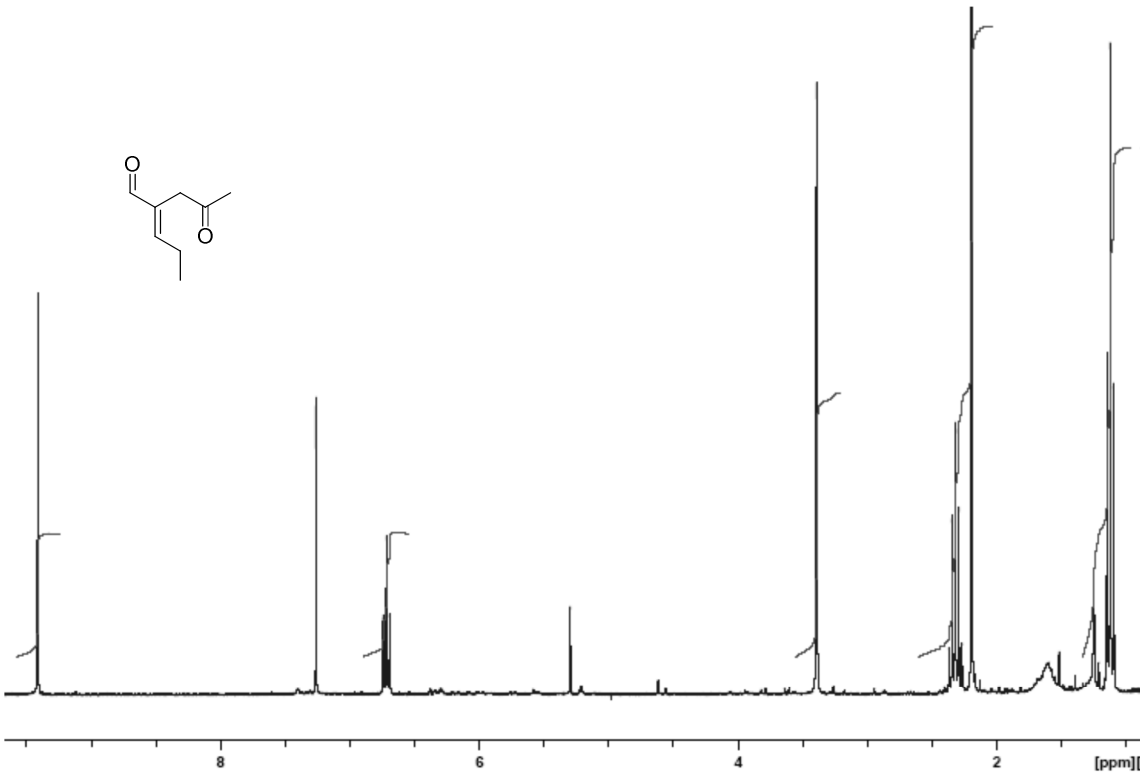
5e: ^{1}H-NMR ($CDCl_3$, 300 MHz)



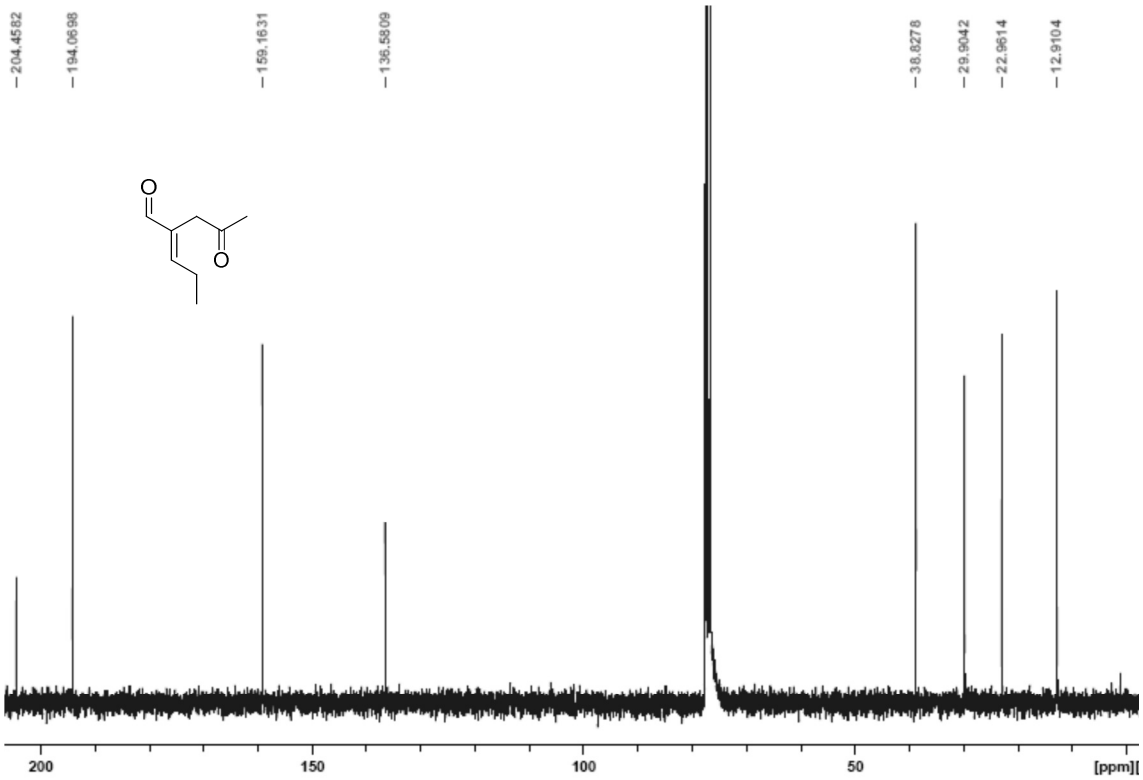
5e: ^{13}C-NMR ($CDCl_3$, 75 MHz)



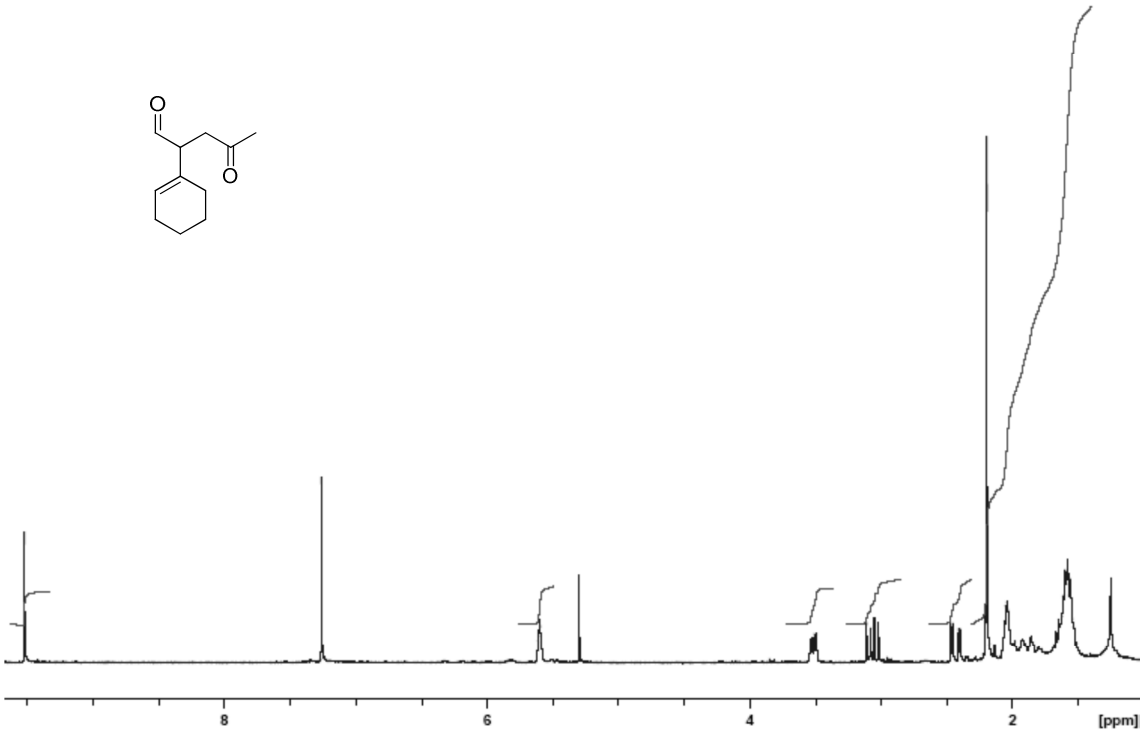
5f: ^{1}H-NMR ($CDCl_3$, 300 MHz)



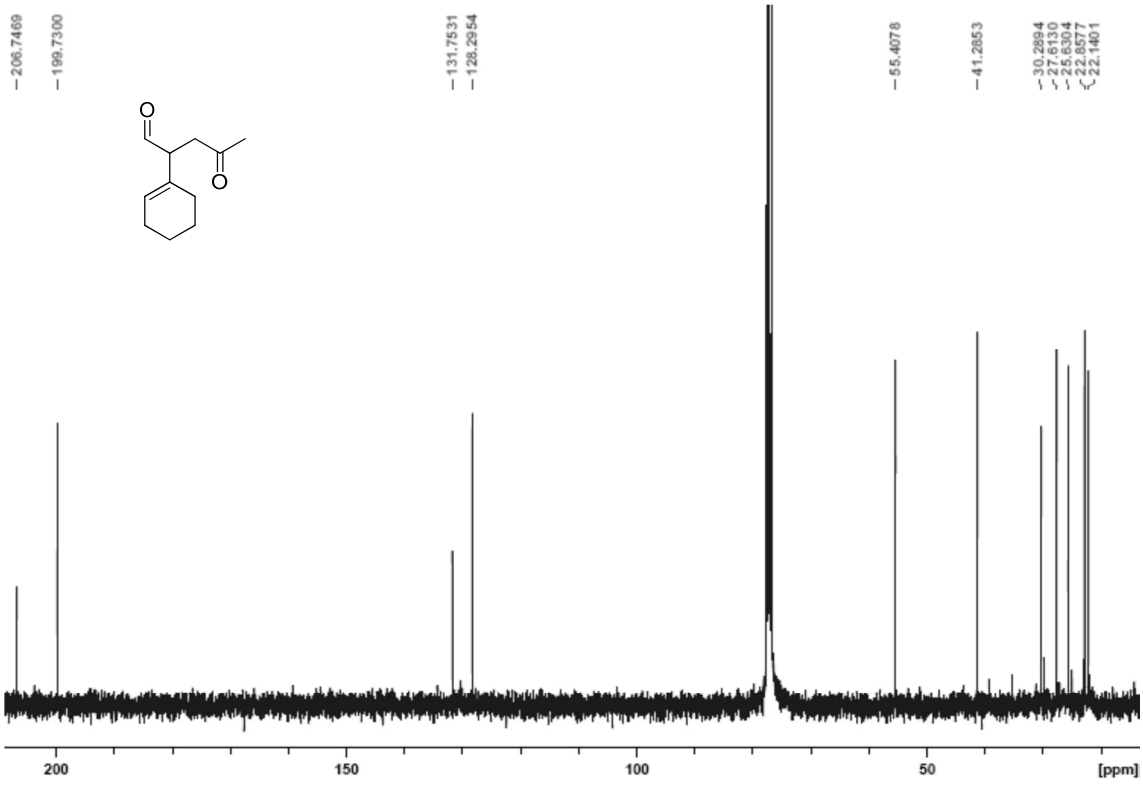
5f: ^{13}C-NMR ($CDCl_3$, 75 MHz)



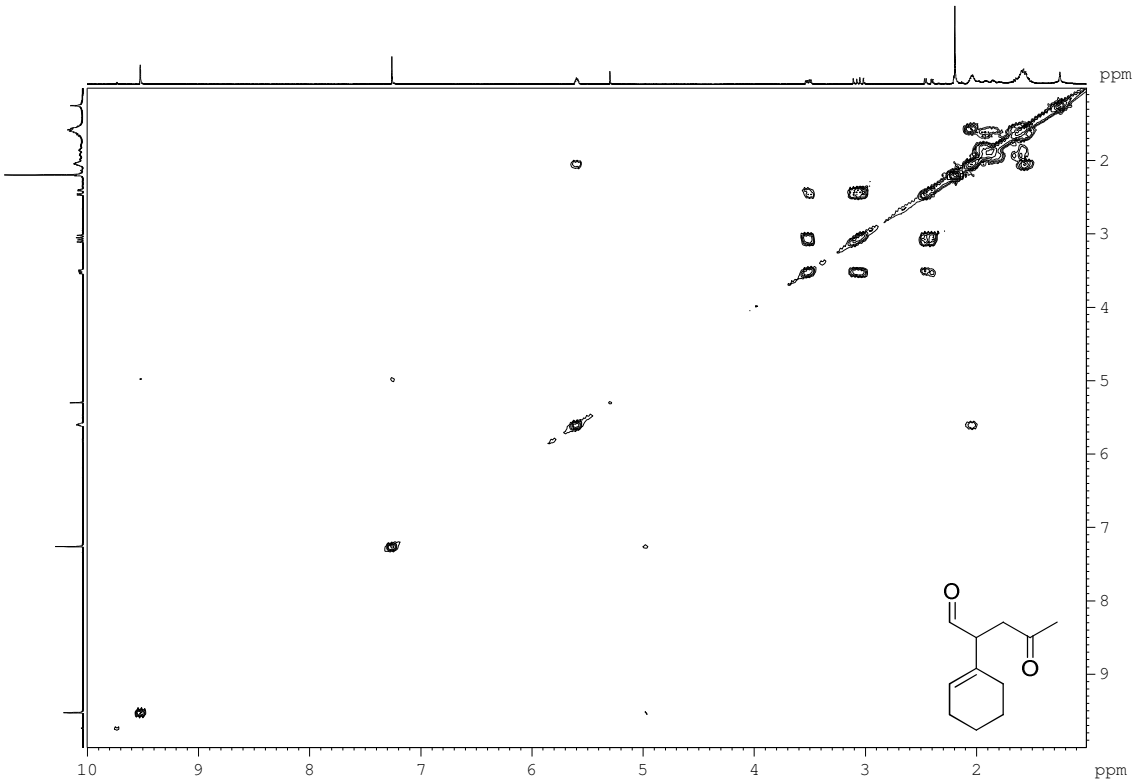
4g: ^{1}H-NMR ($CDCl_3$, 300 MHz)



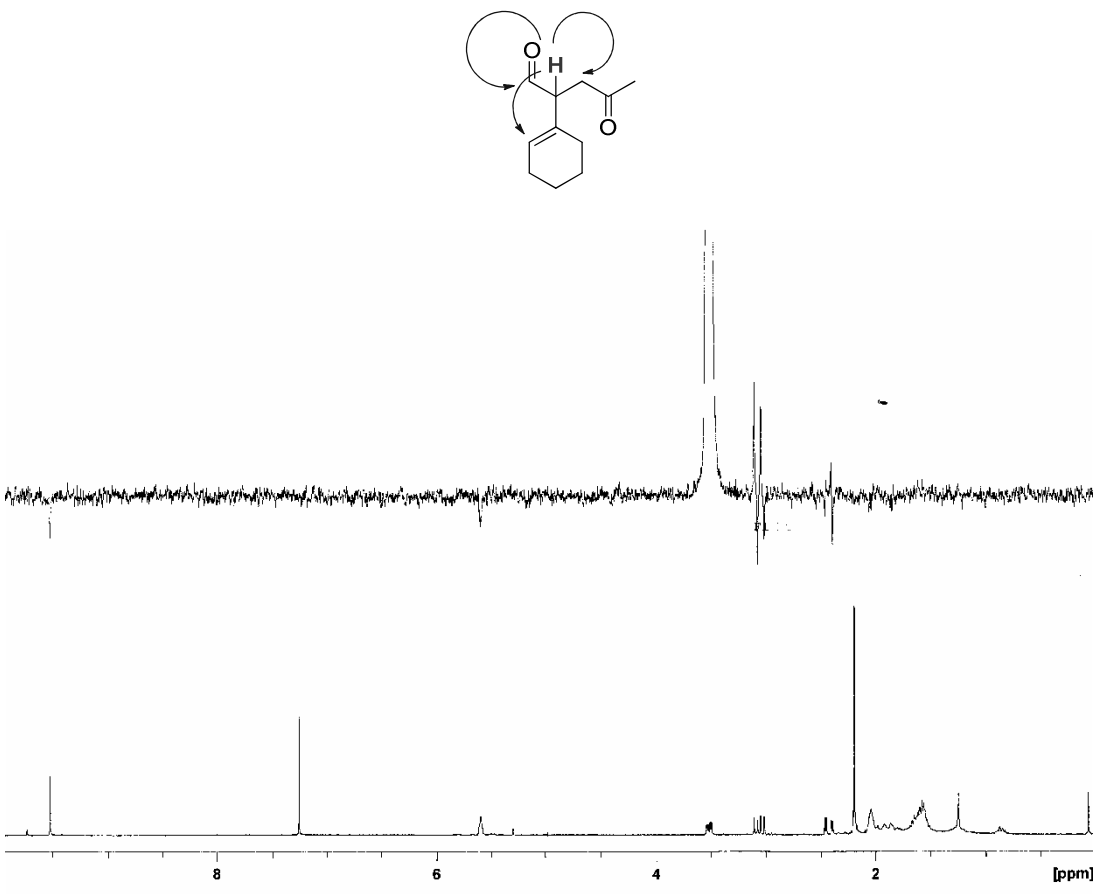
4g: ^{13}C-NMR ($CDCl_3$, 75 MHz)



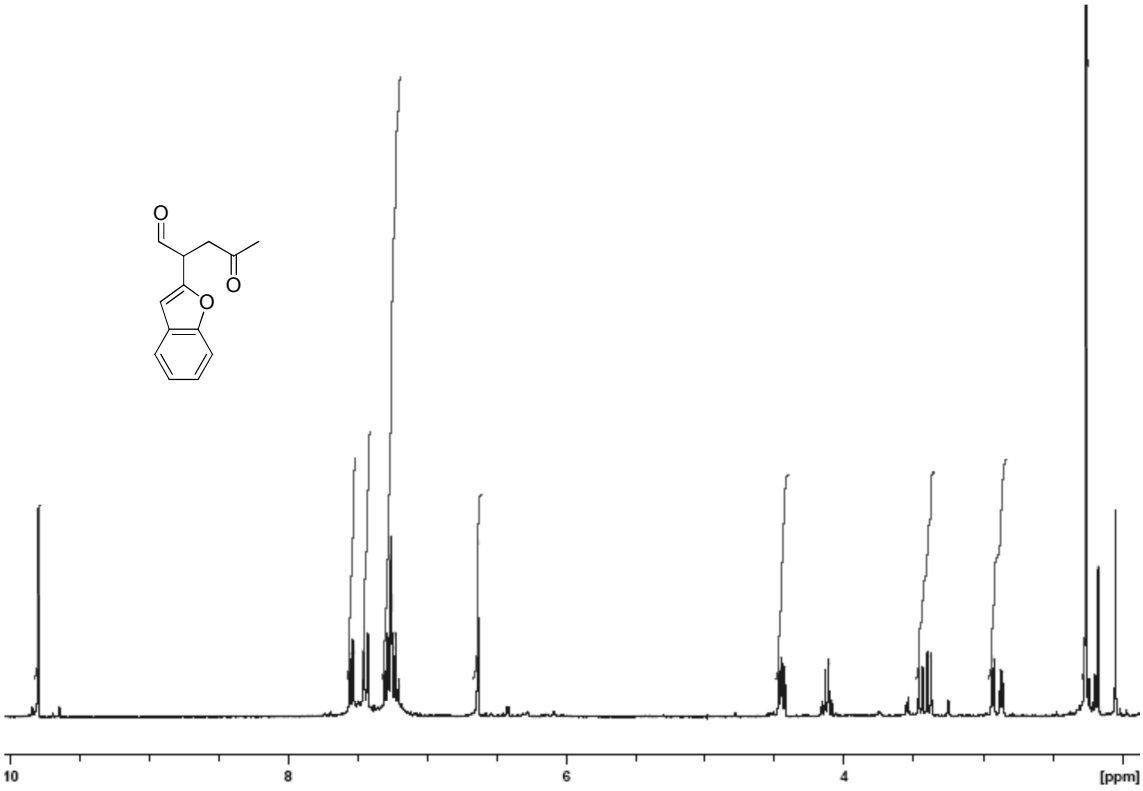
4g: COSY ($CDCl_3$, 300 MHz)



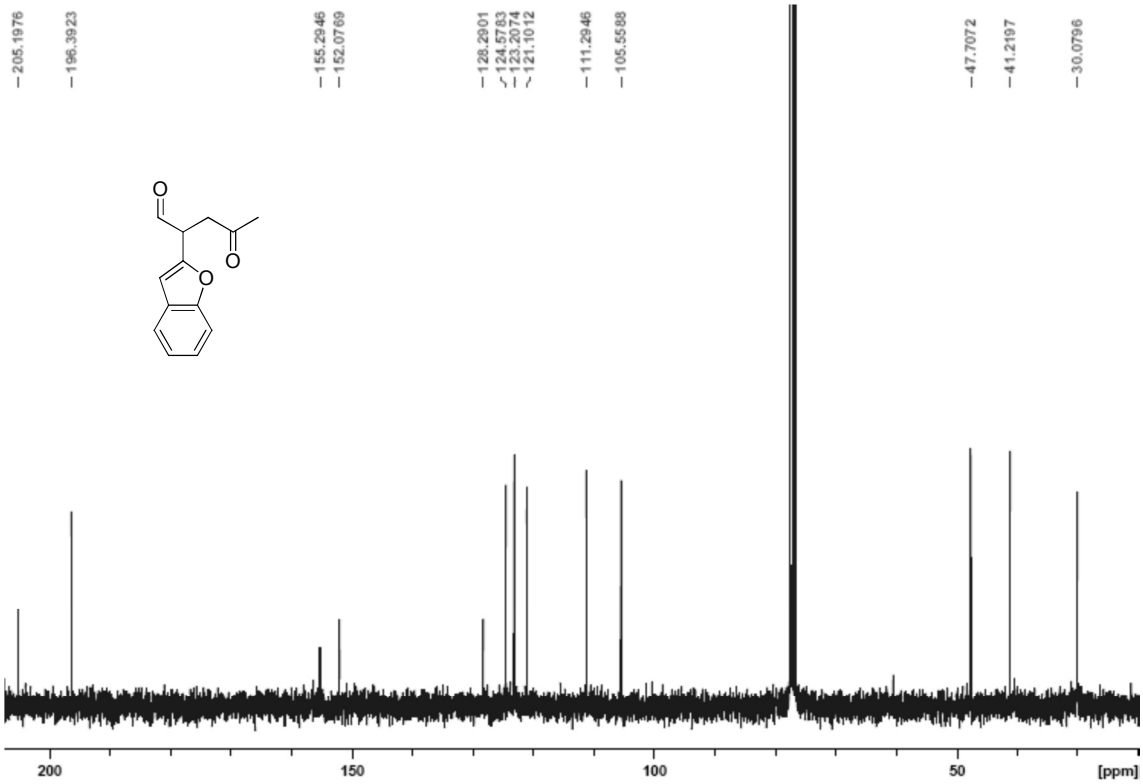
.4g: NOE measurements, ($CDCl_3$, 300 MHz)



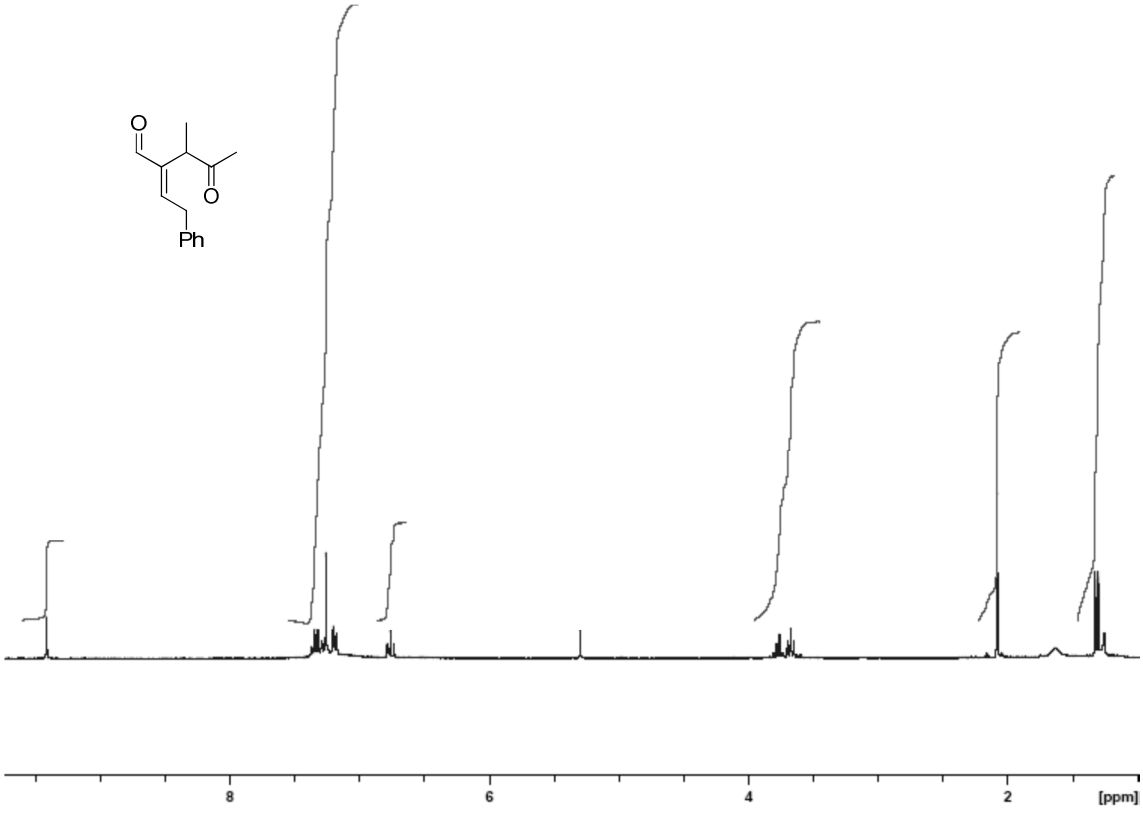
4h: ^{1}H-NMR ($CDCl_3$, 300 MHz)



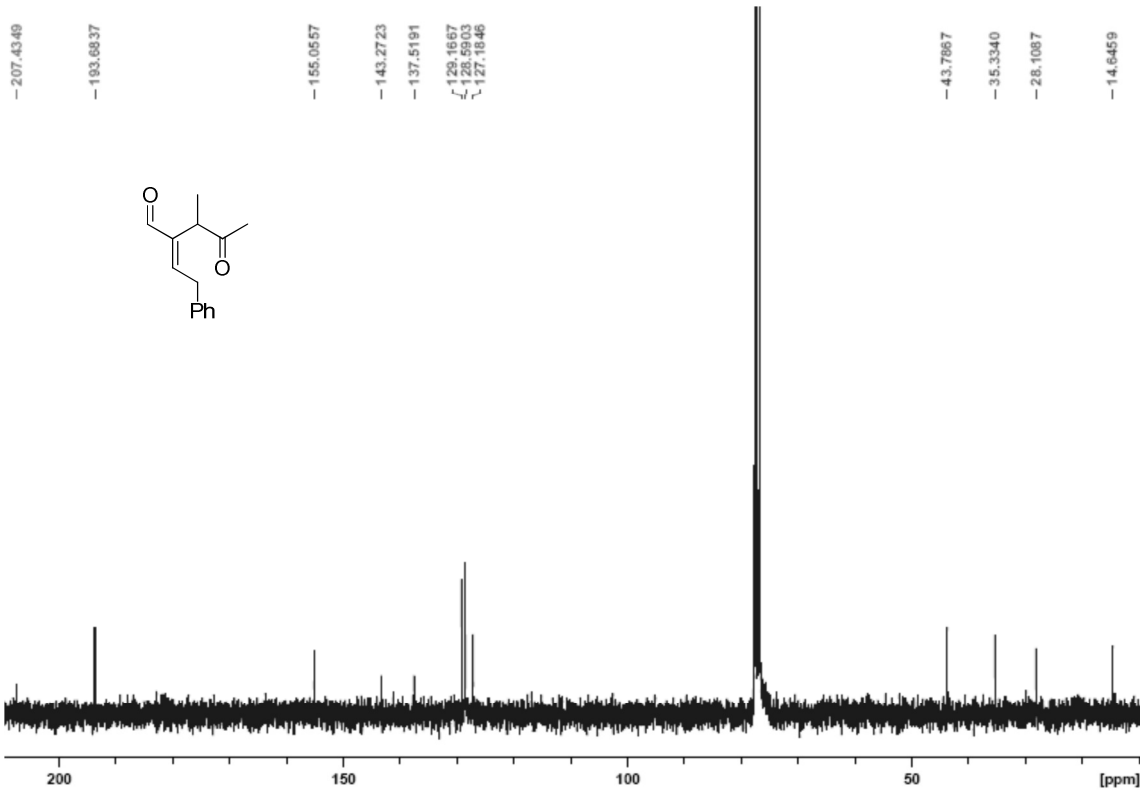
4h: ^{13}C-NMR ($CDCl_3$, 75 MHz)



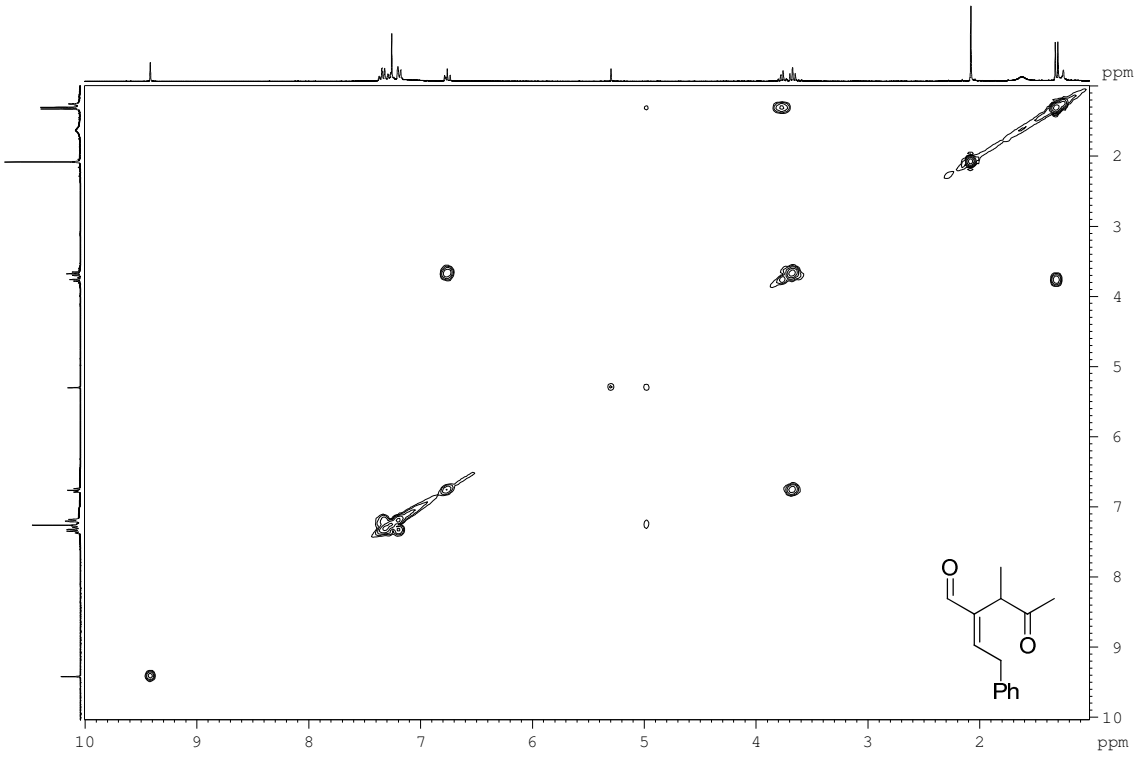
5j: ^{1}H-NMR ($CDCl_3$, 300 MHz)



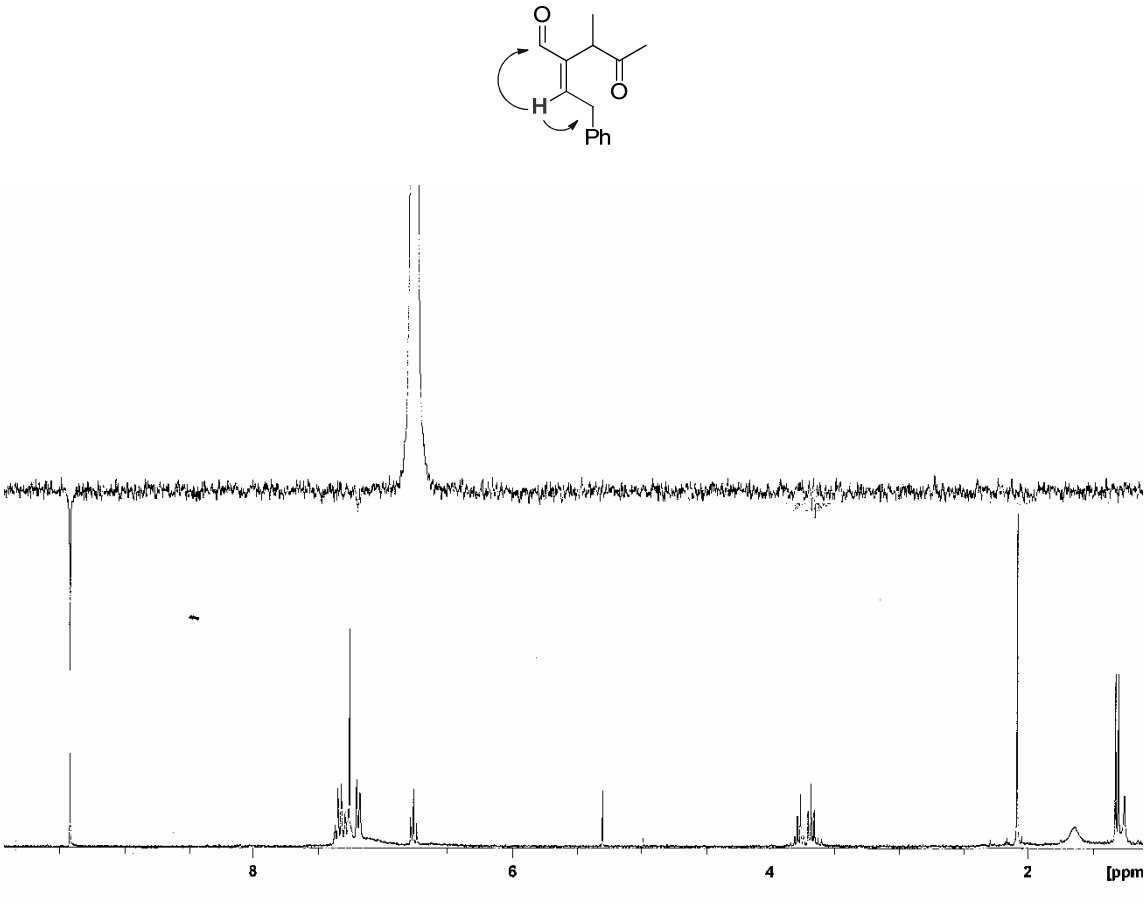
5j: ^{13}C-NMR ($CDCl_3$, 75 MHz)



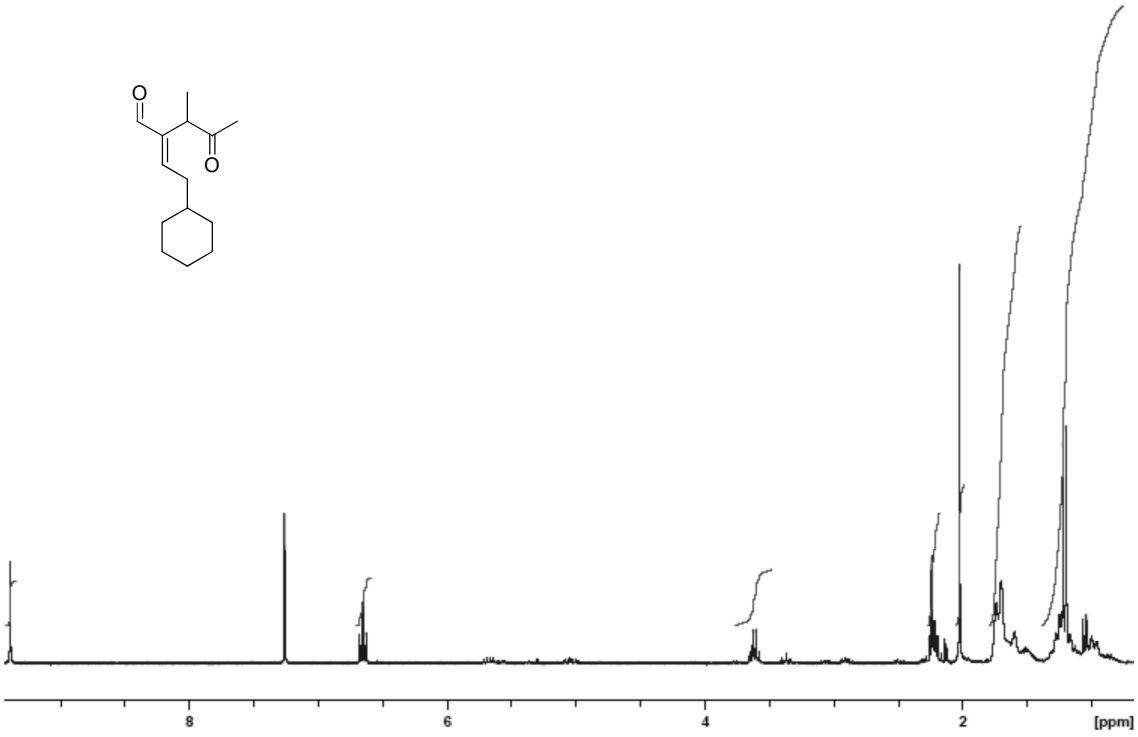
5j: COSY ($CDCl_3$, 300 MHz)



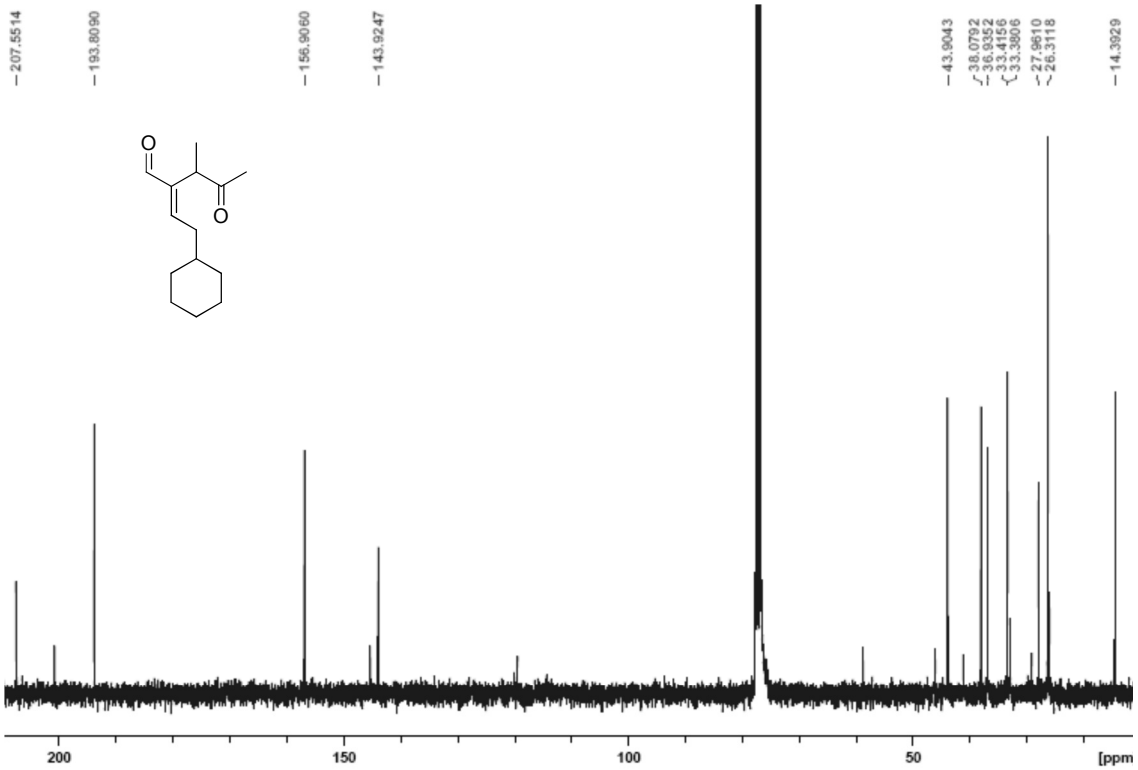
5j: NOE measurements ($CDCl_3$, 300 MHz)



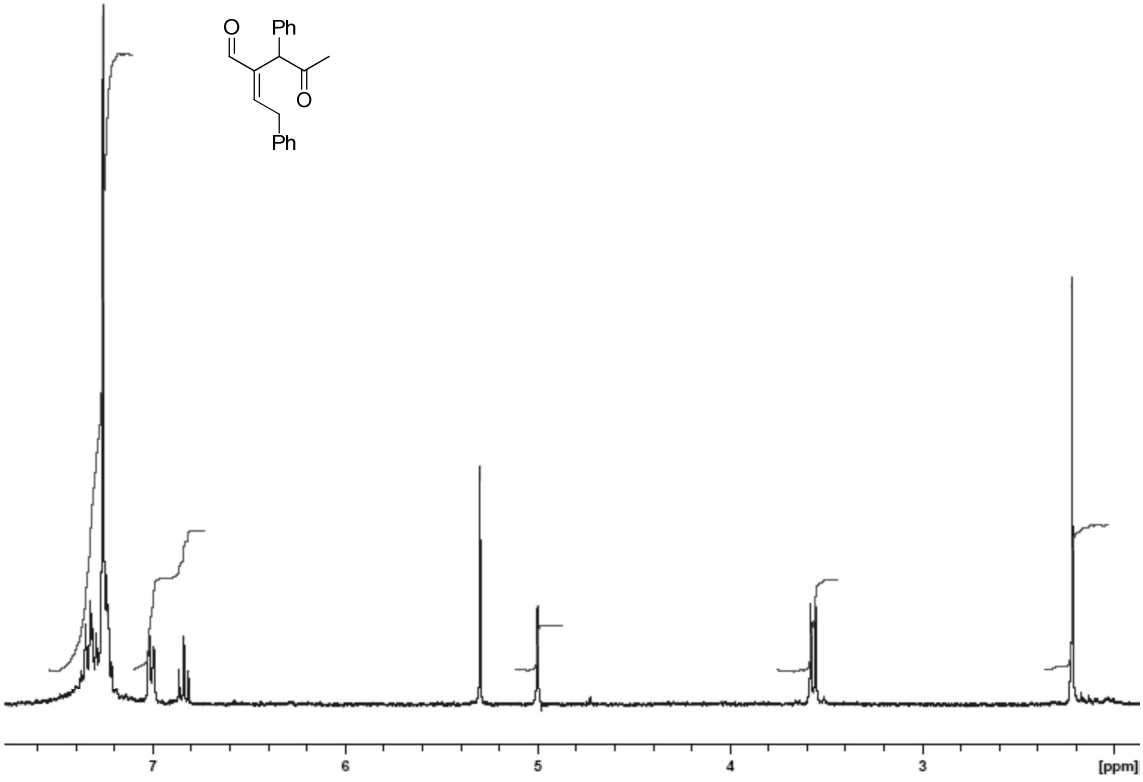
5k: ^{1}H-NMR ($CDCl_3$, 300 MHz)



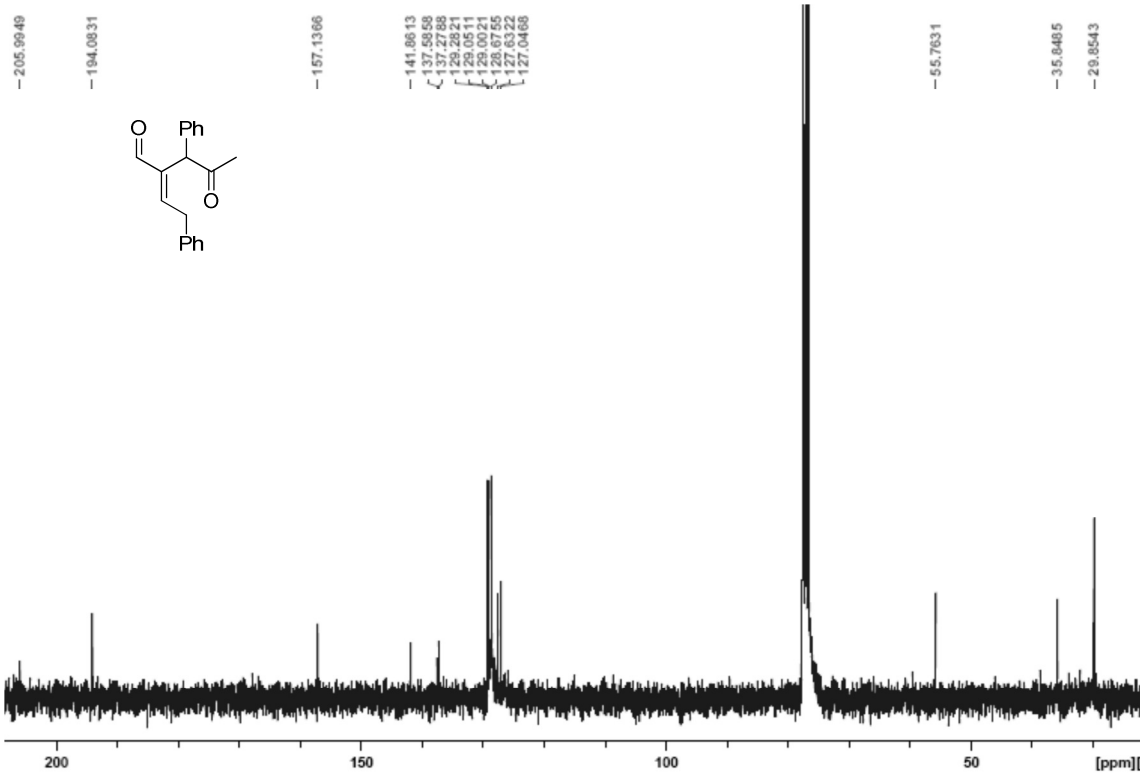
5k: ^{13}C-NMR ($CDCl_3$, 75 MHz)



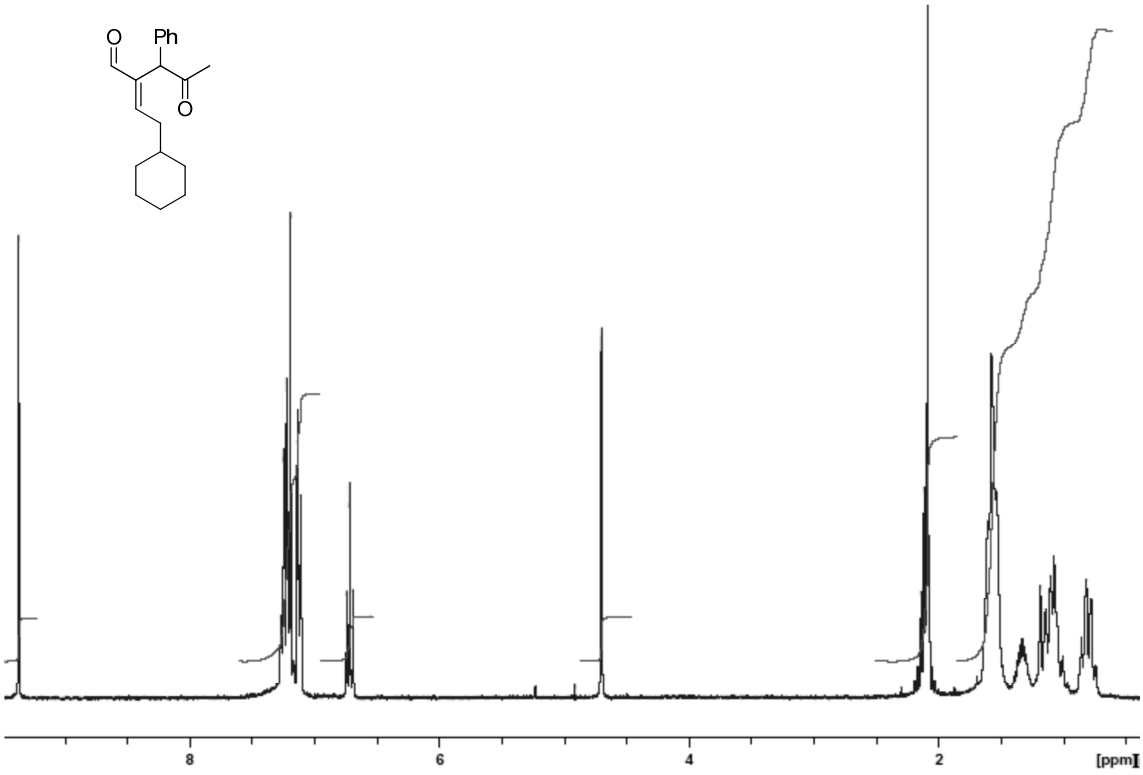
5l: ^{1}H-NMR ($CDCl_3$, 300 MHz)



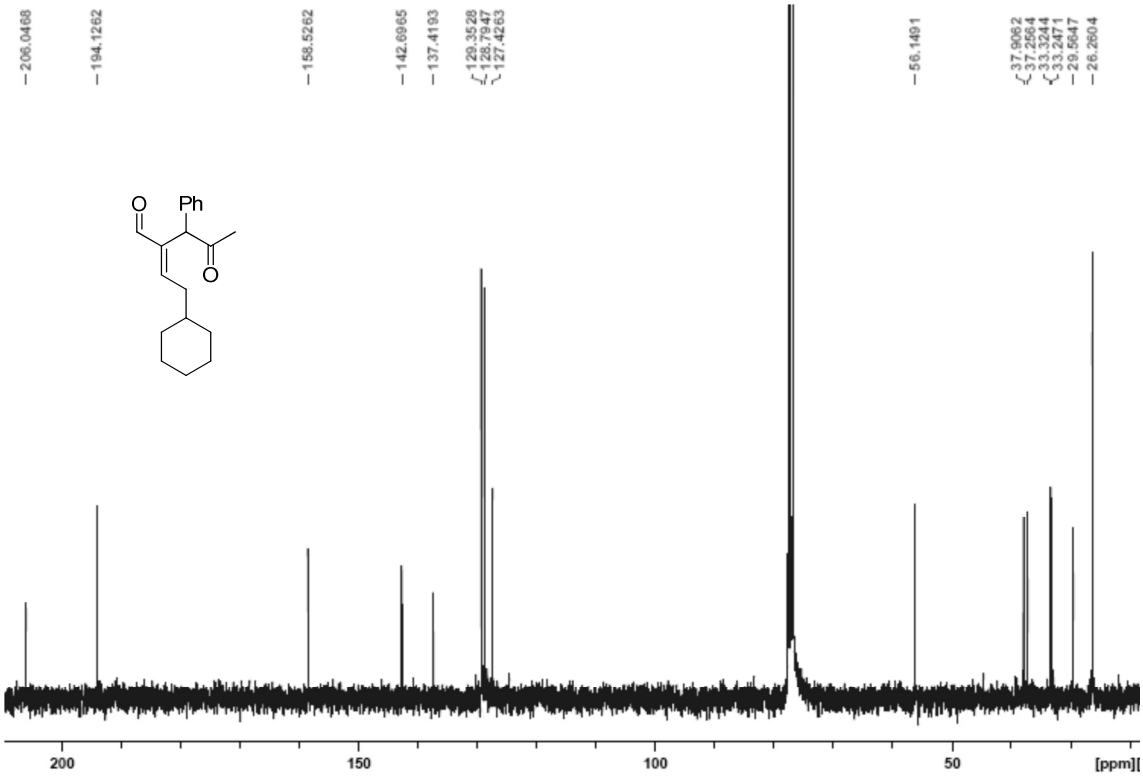
5l: ^{13}C-NMR ($CDCl_3$, 75 MHz)



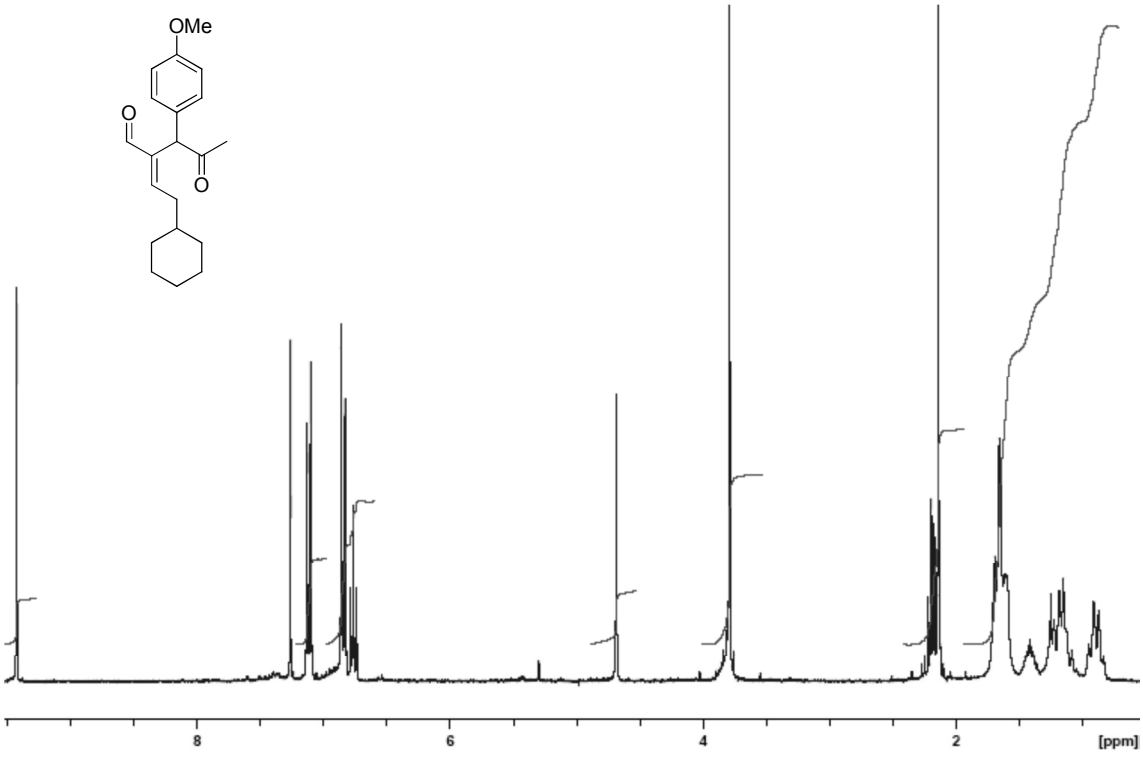
5m: ^{1}H-NMR ($CDCl_3$, 300 MHz)



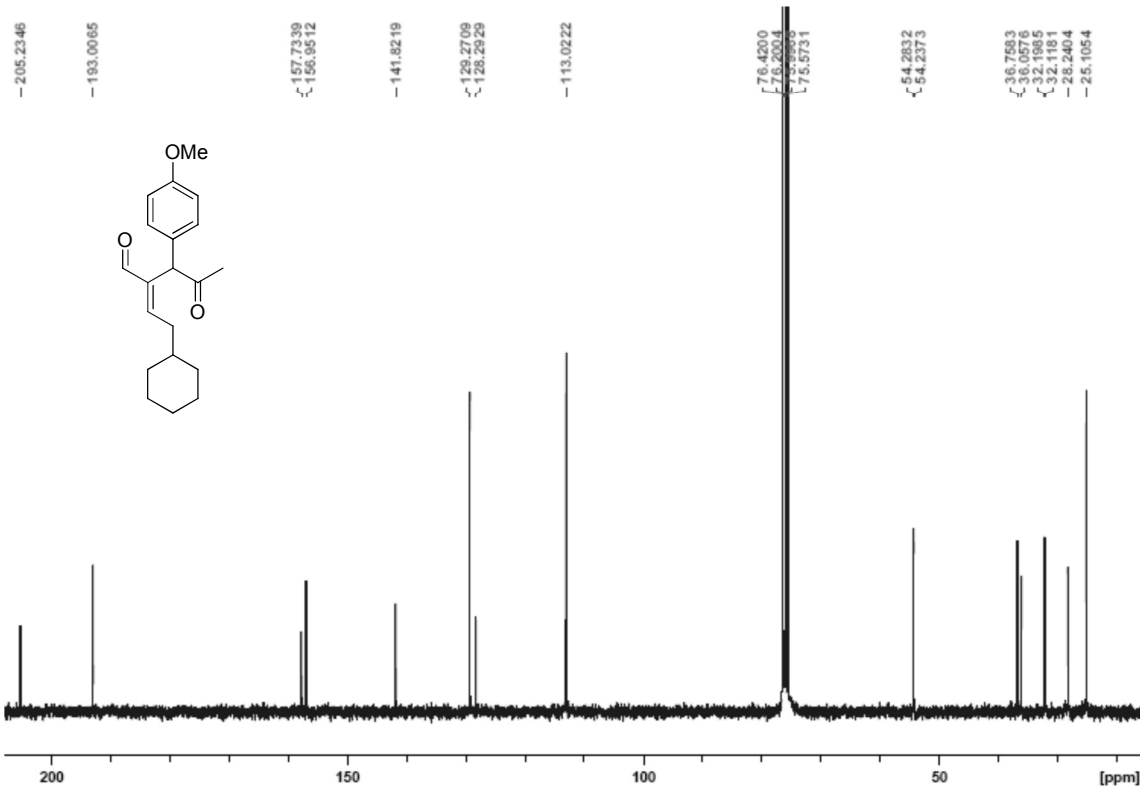
5m: ^{13}C-NMR ($CDCl_3$, 75 MHz)



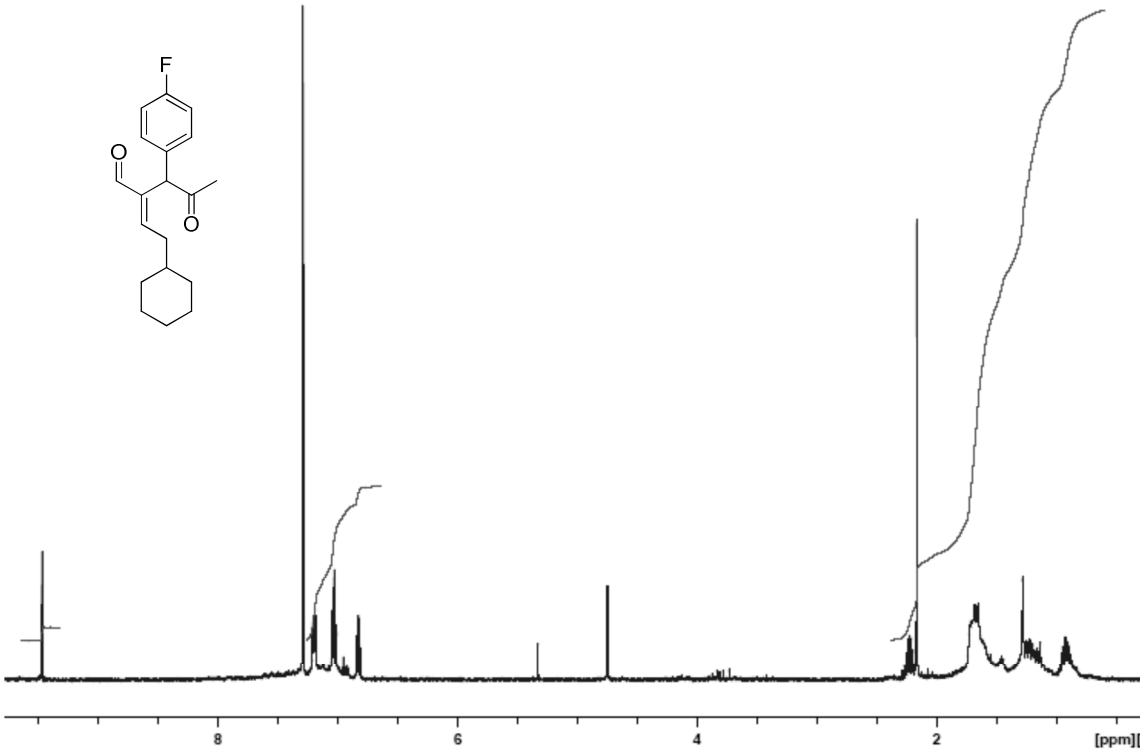
5n: ^{1}H-NMR ($CDCl_3$, 300 MHz)



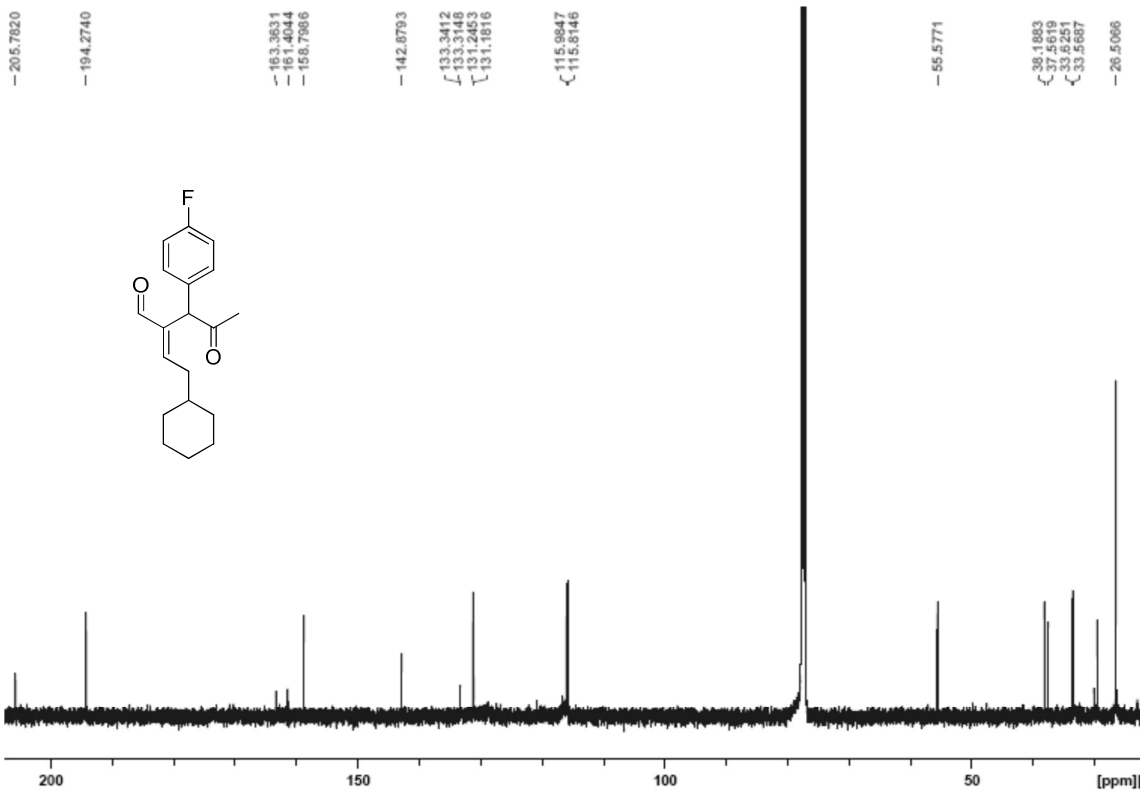
5n: ^{13}C-NMR ($CDCl_3$, 75 MHz)



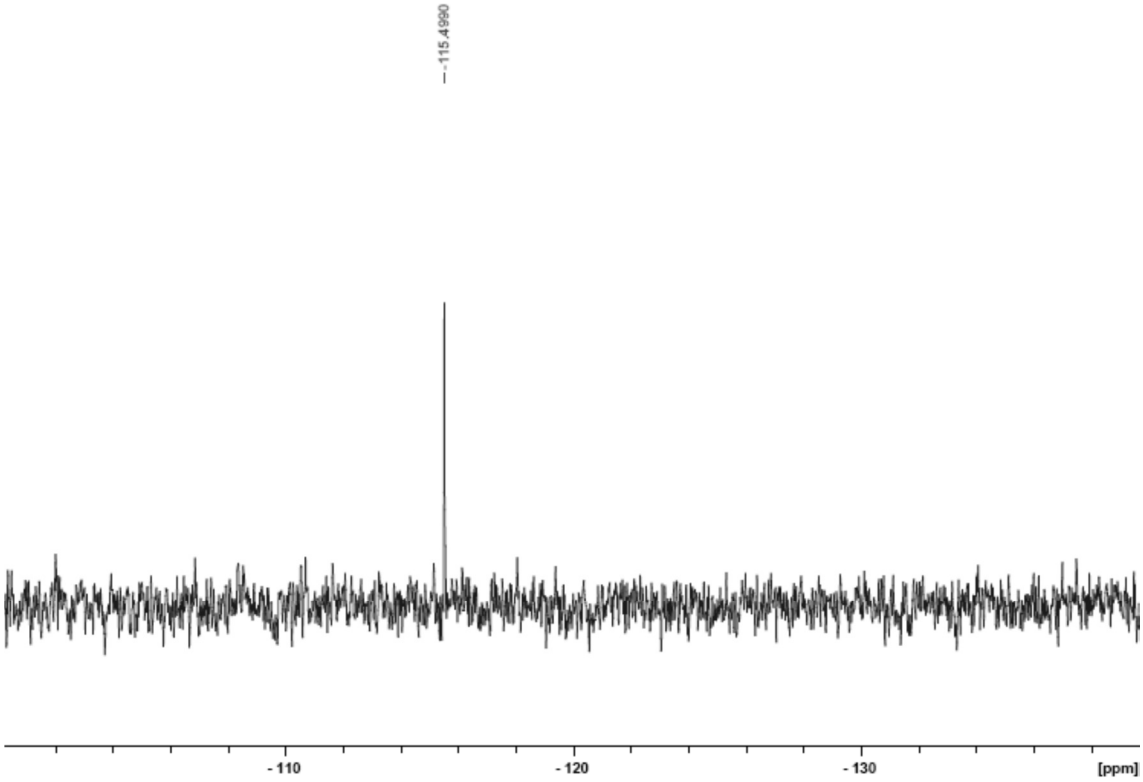
5o: ^{1}H-NMR ($CDCl_3$, 500 MHz)



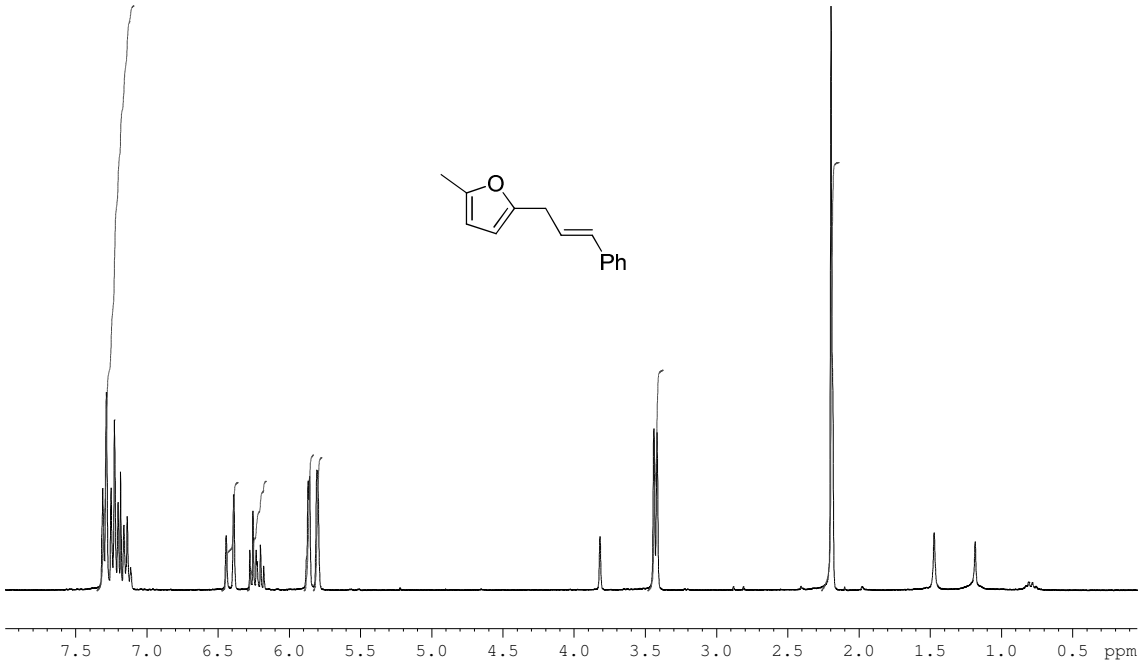
5o: ^{13}C-NMR ($CDCl_3$, 125 MHz)



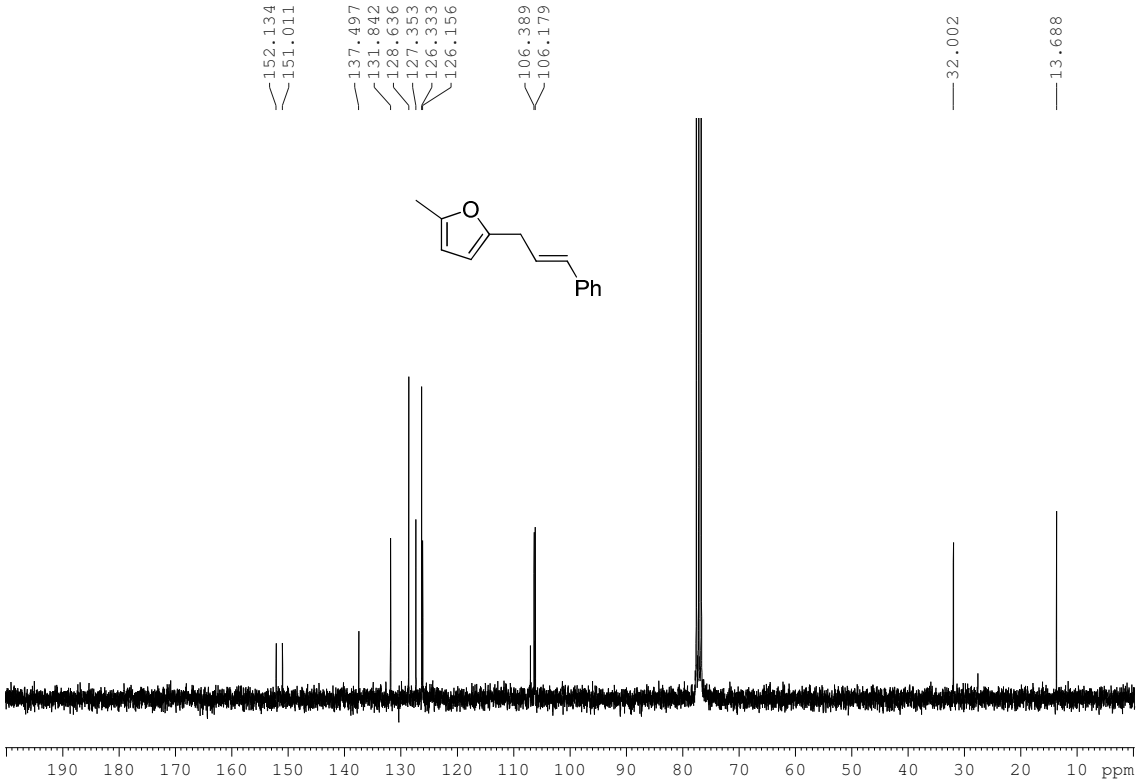
5o: ^{19}F-NMR ($CDCl_3$, 282 MHz)



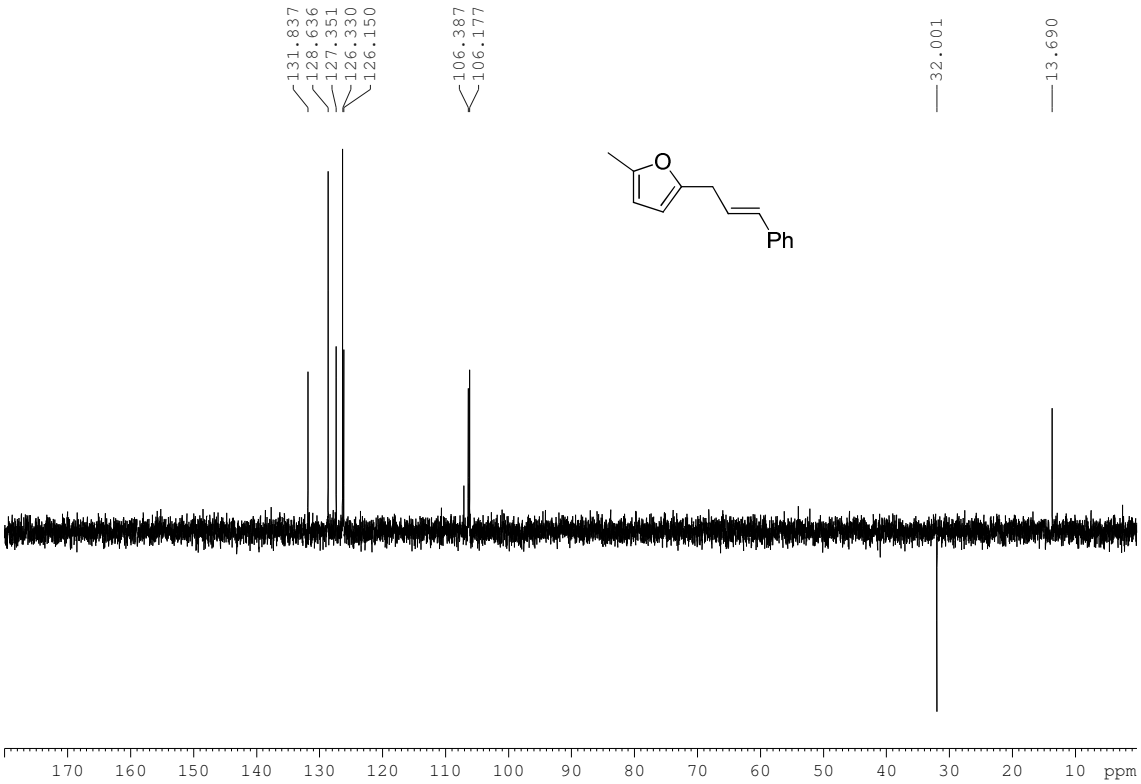
6: ^{1}H-NMR ($CDCl_3$, 300 MHz)



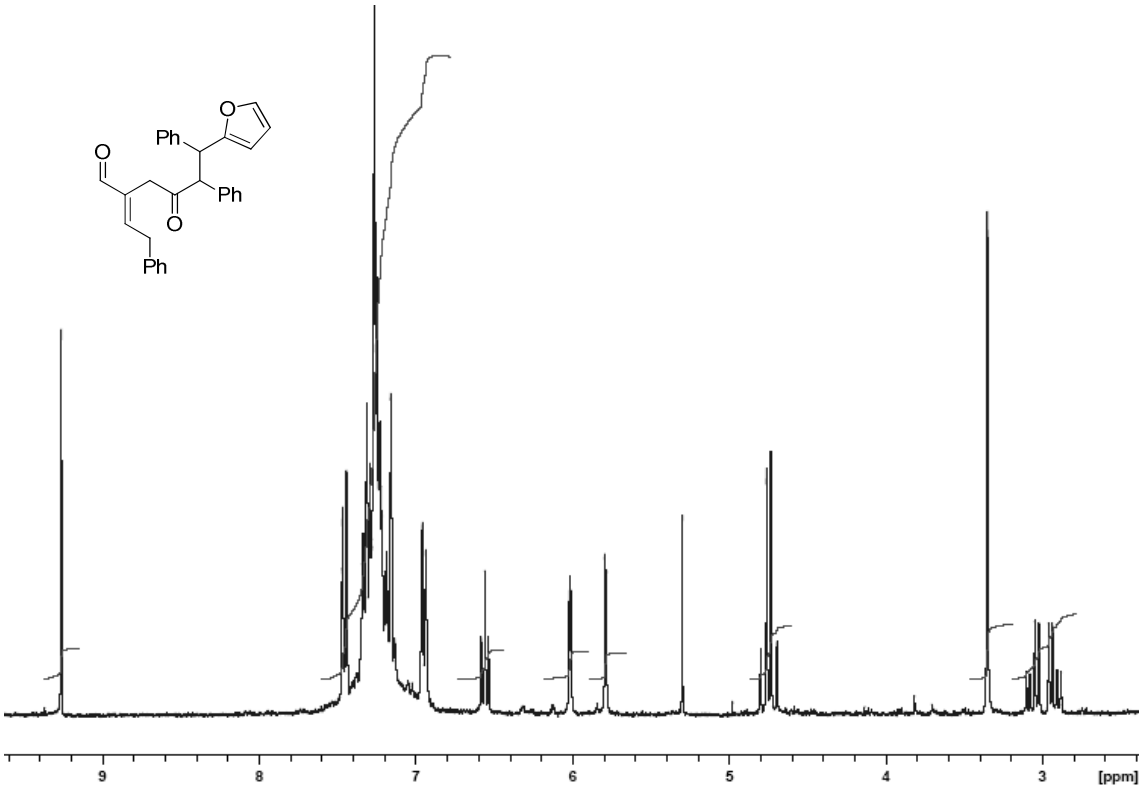
6: ^{13}C-NMR ($CDCl_3$, 75 MHz)



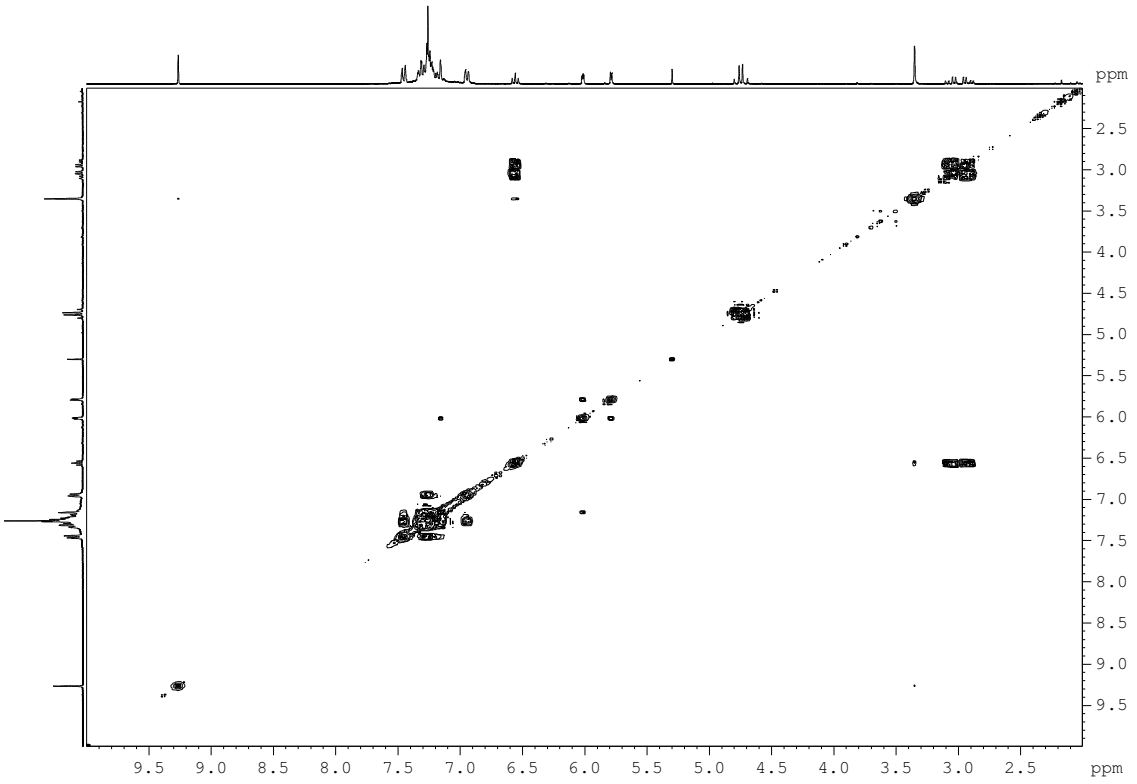
6: DEPT-135 ($CDCl_3$, 75 MHz)



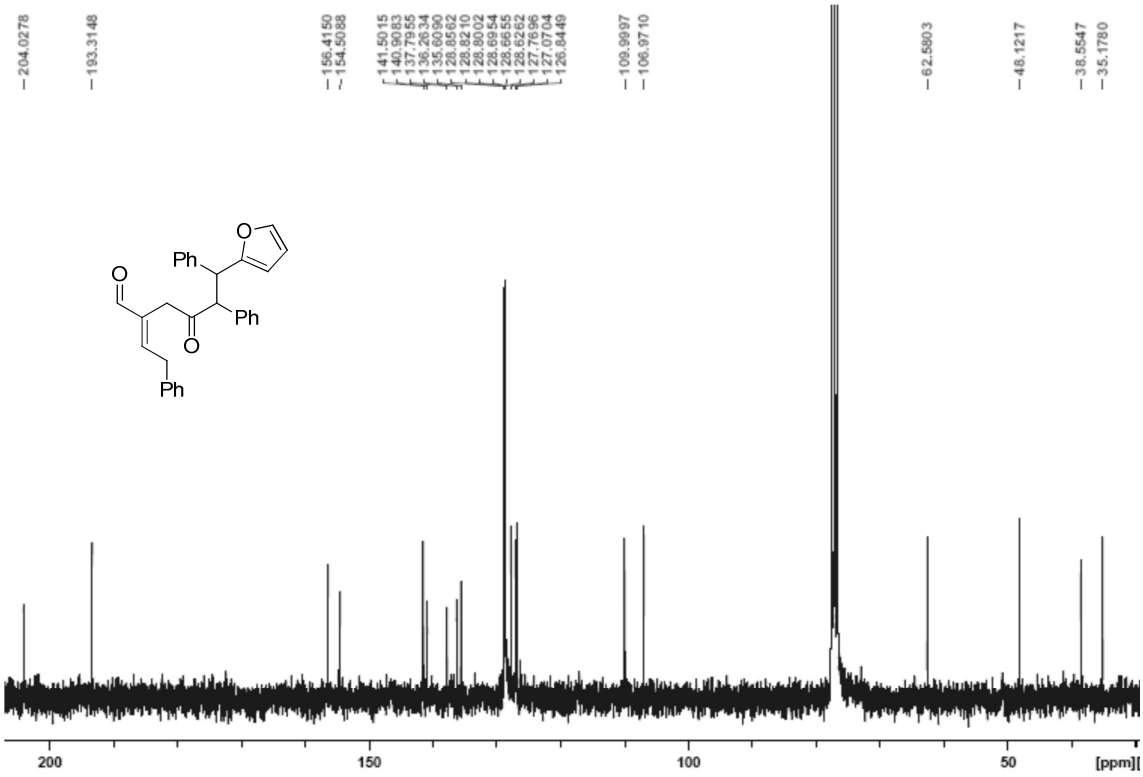
7a: ^{1}H-NMR ($CDCl_3$, 300 MHz)



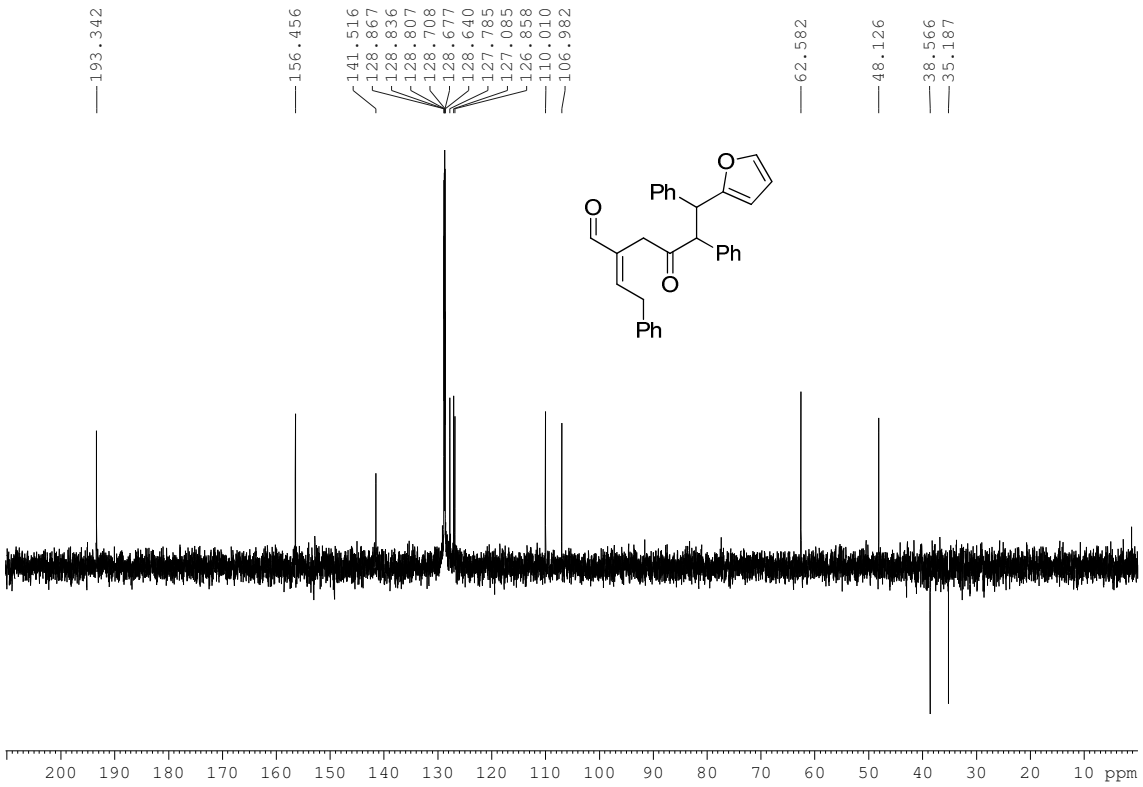
7a: COSY ($CDCl_3$, 300 MHz)



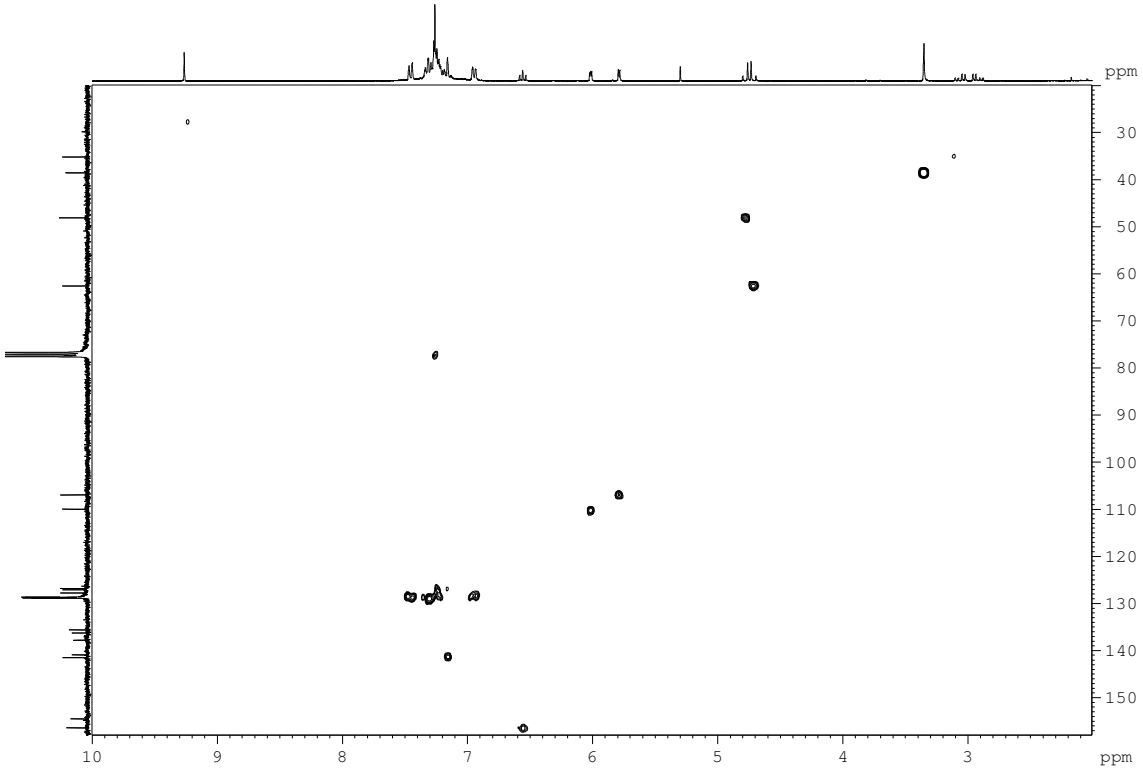
7a: ^{13}C-NMR ($CDCl_3$, 75 MHz)



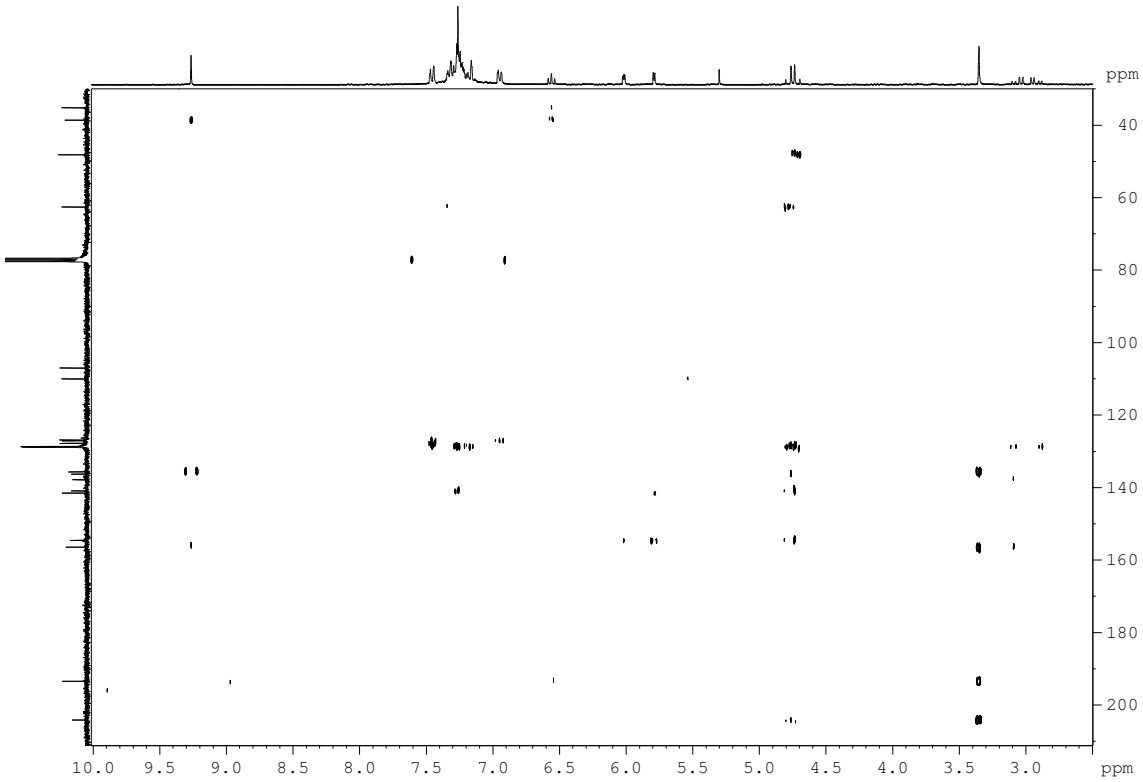
7a: DEPT-135 ($CDCl_3$, 75 MHz)



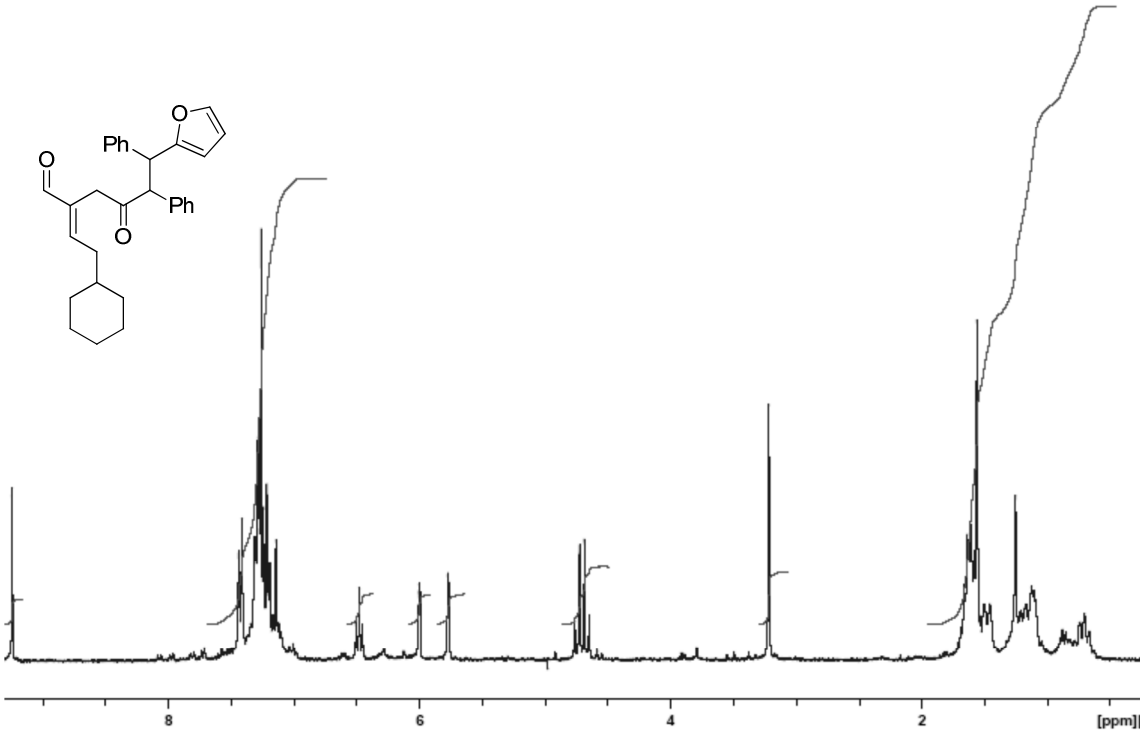
7a: HMQC ($CDCl_3$, 75 MHz)



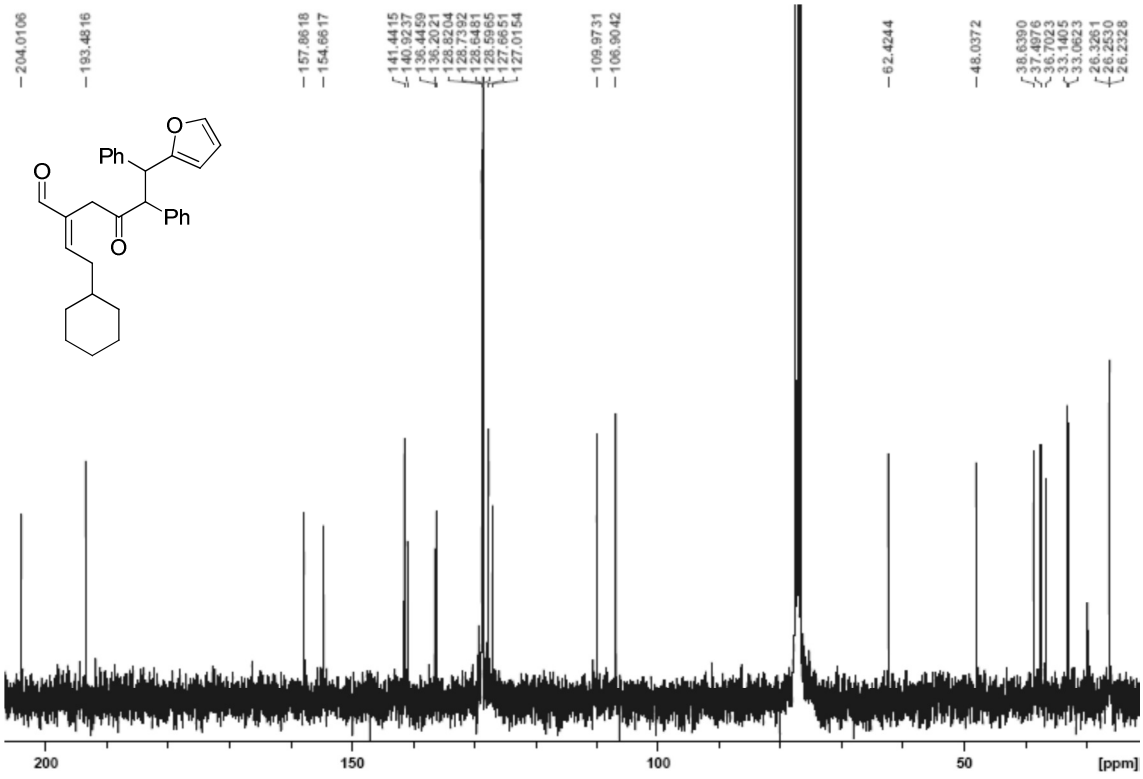
7a: HMBC ($CDCl_3$, 75 MHz)



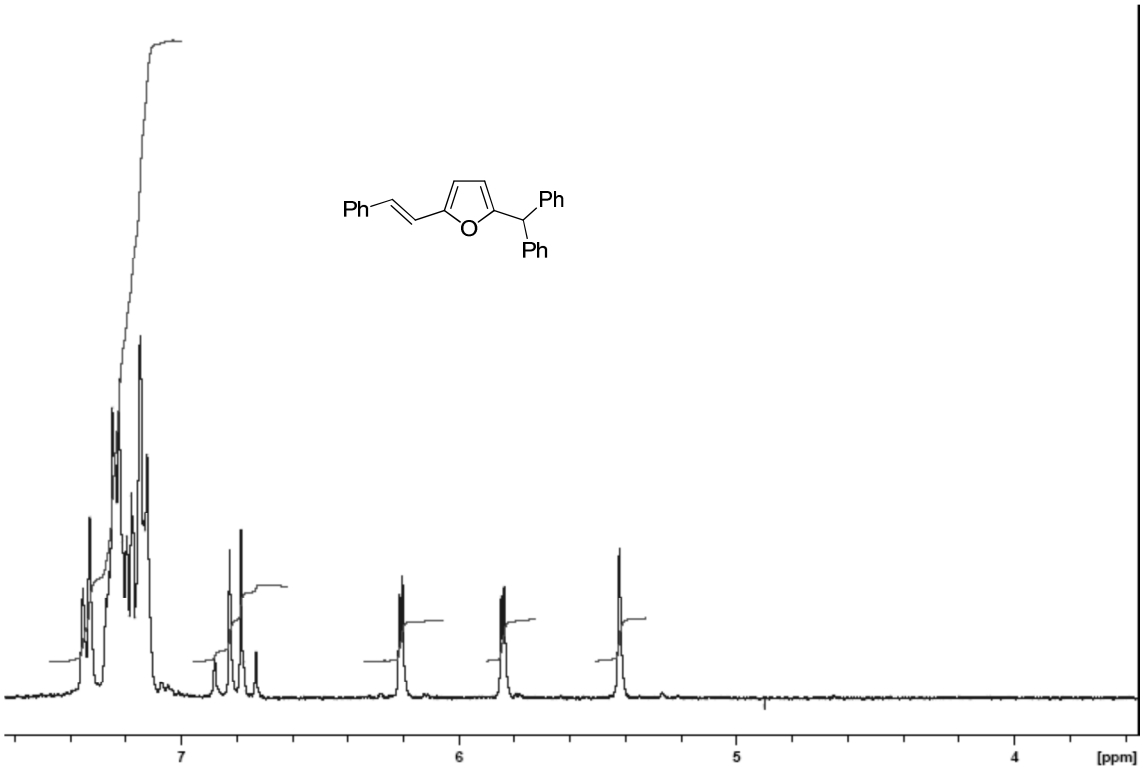
7b: ^{1}H-NMR ($CDCl_3$, 300 MHz)



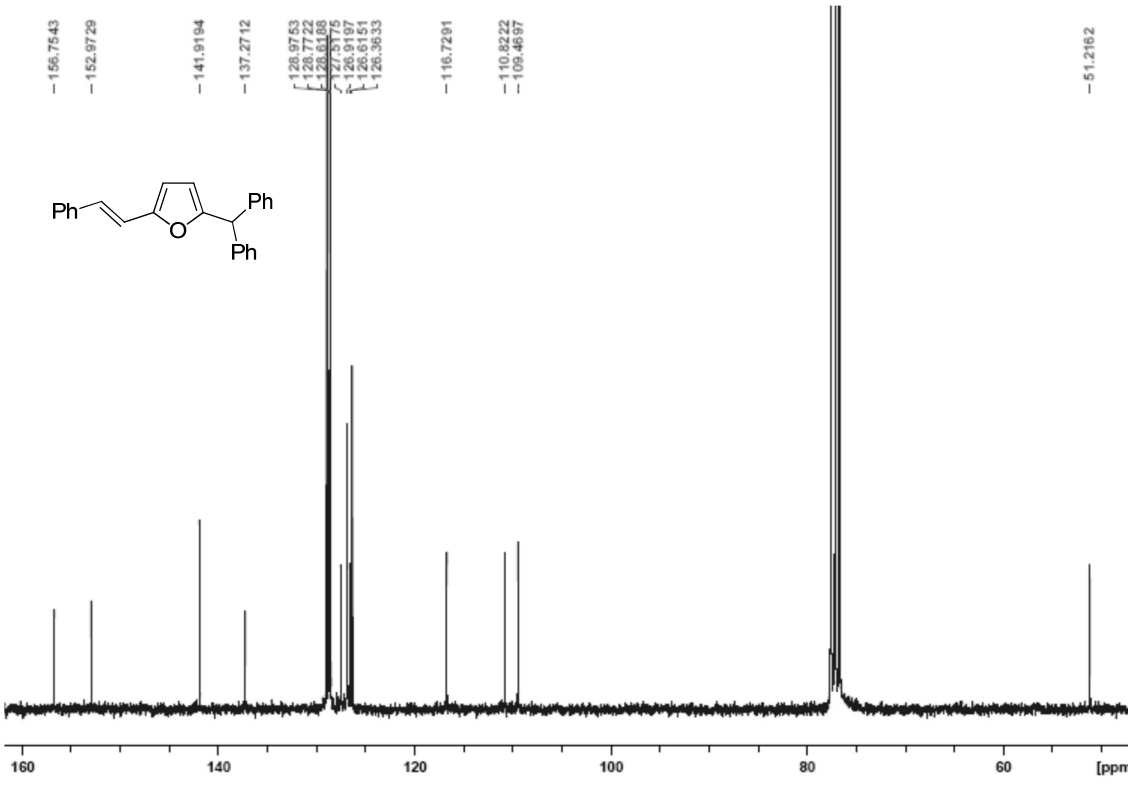
7b: ^{13}C-NMR ($CDCl_3$, 75 MHz)



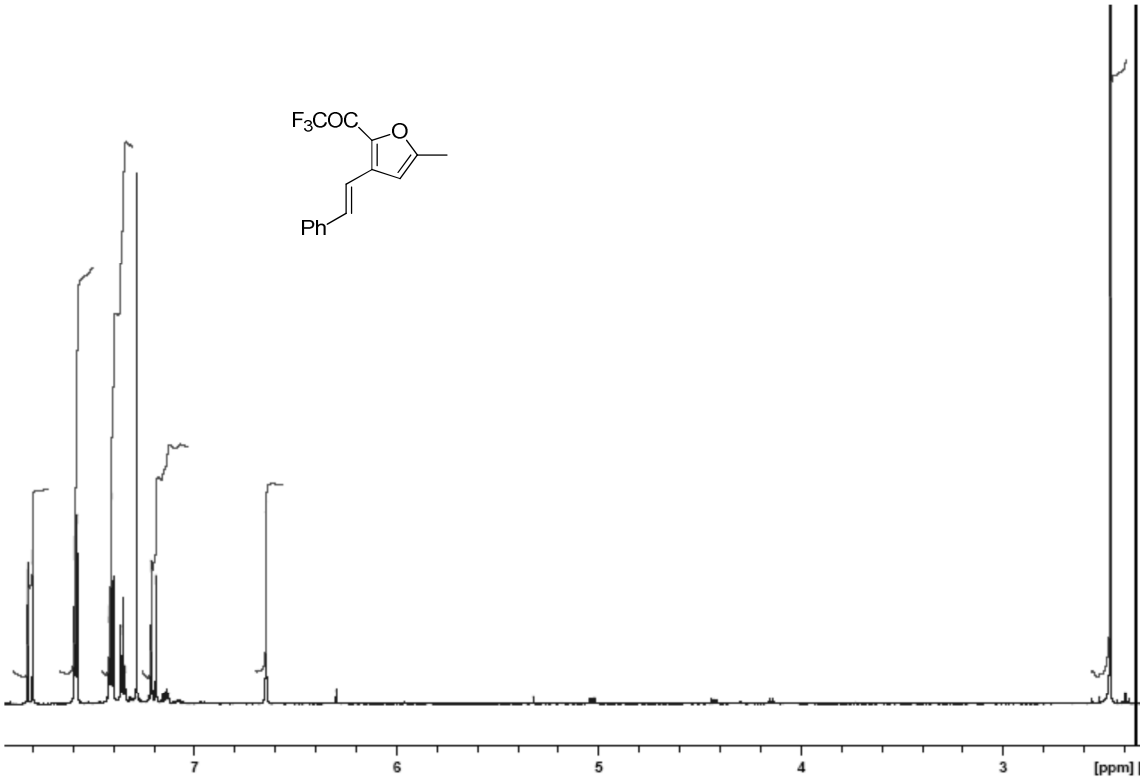
8: ^{1}H-NMR ($CDCl_3$, 300 MHz)



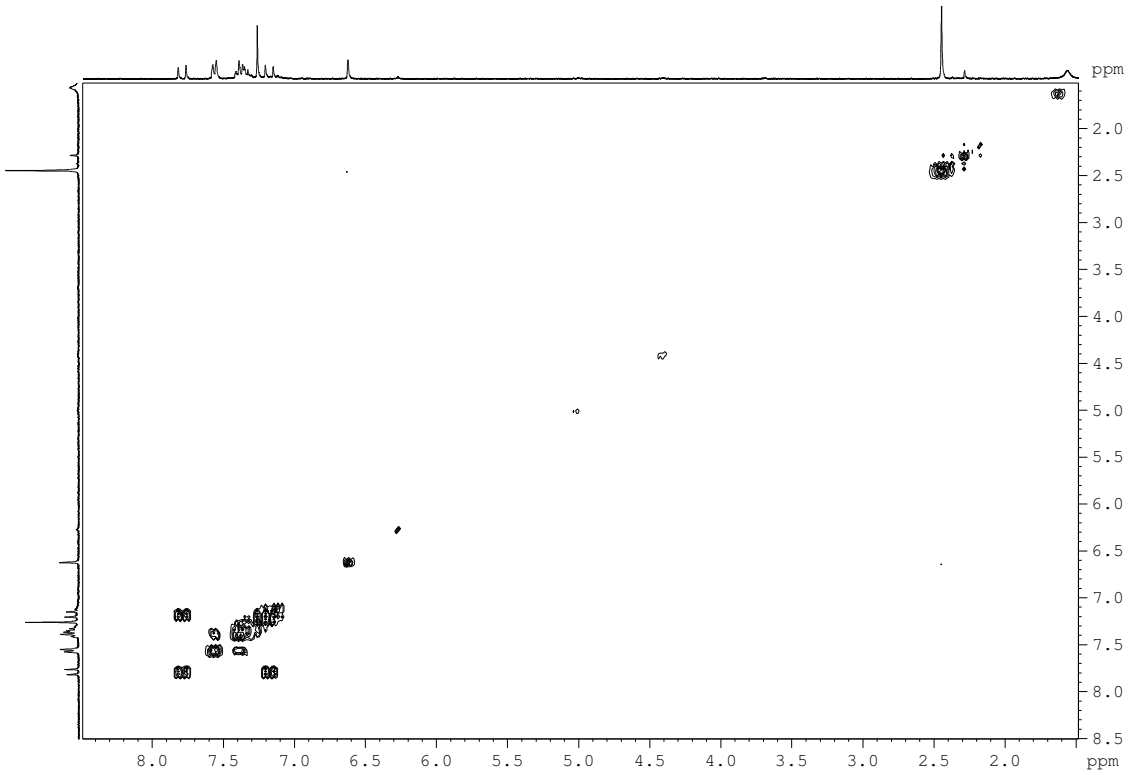
8: ^{13}C-NMR ($CDCl_3$, 75 MHz)



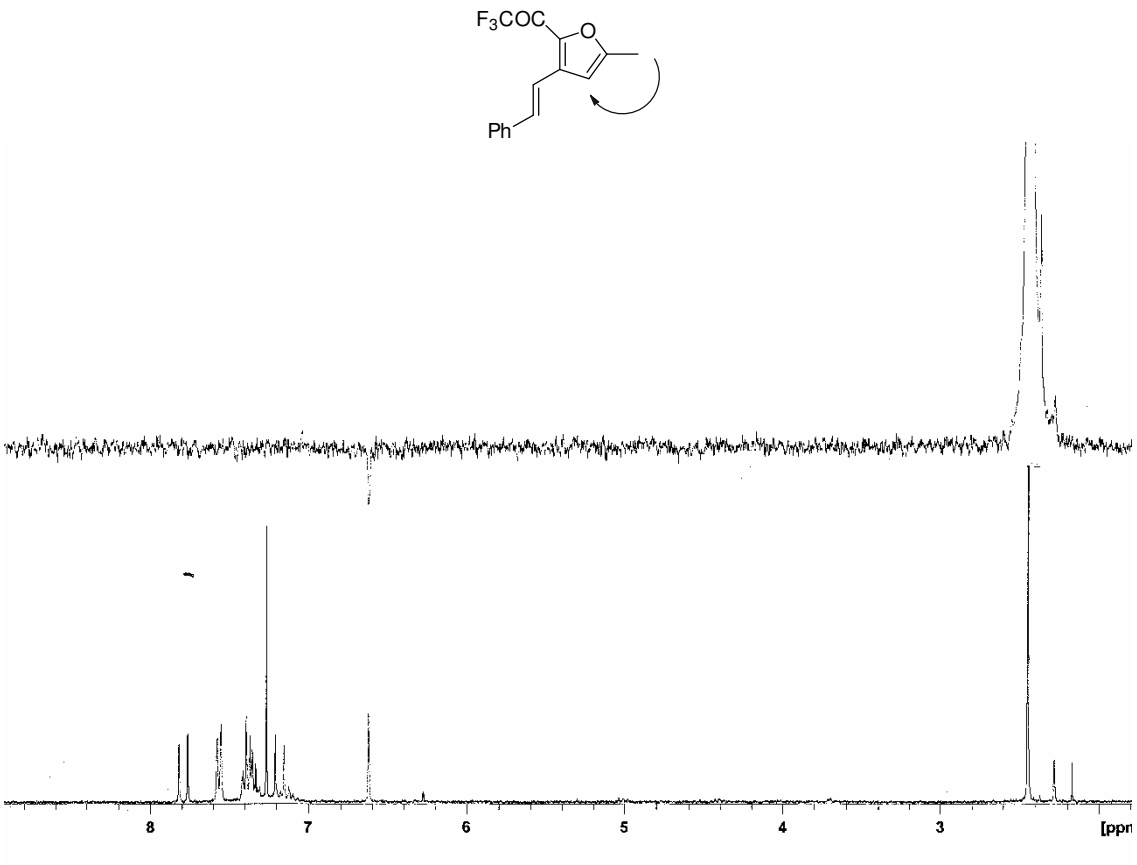
9a: ^{1}H-NMR ($CDCl_3$, 700 MHz)



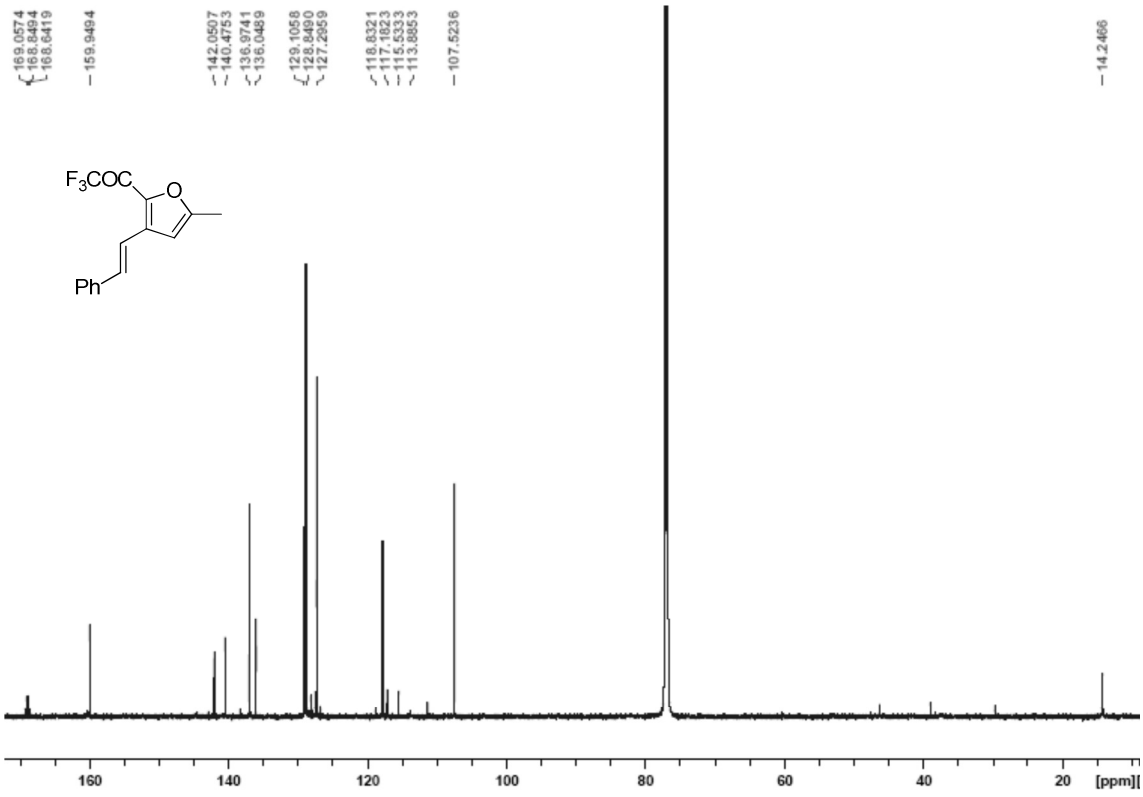
9a: COSY ($CDCl_3$, 300 MHz)



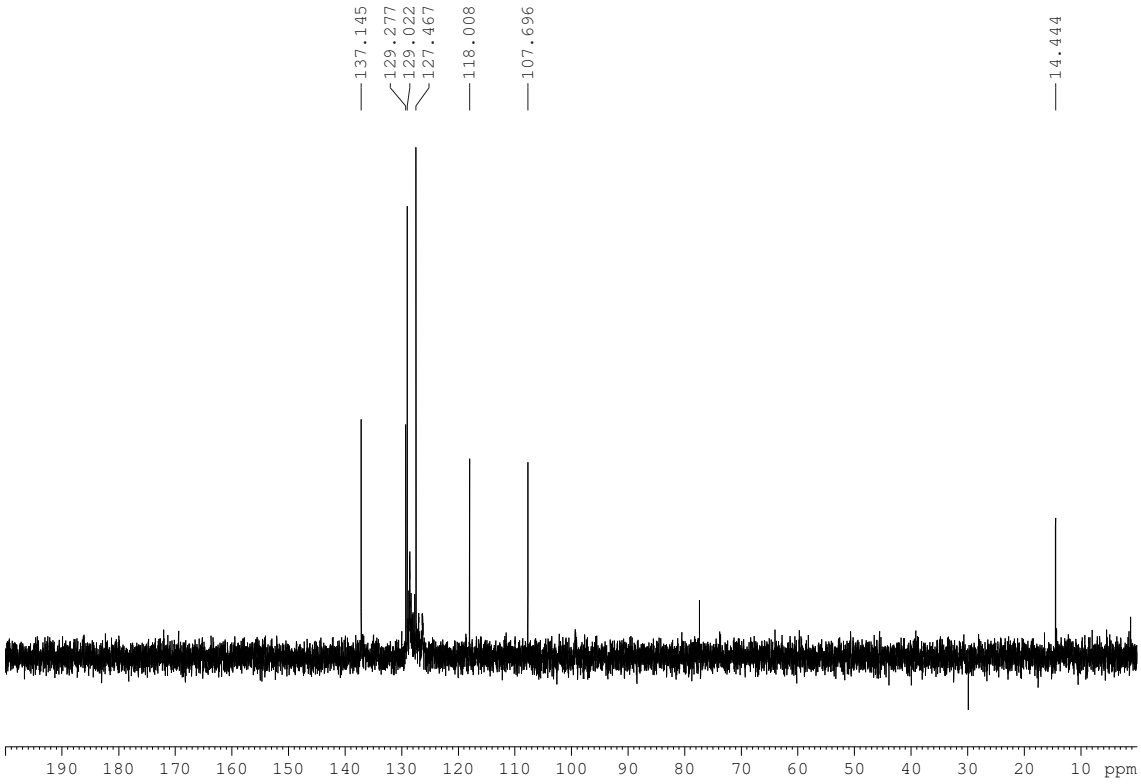
9a: NOE measurements ($CDCl_3$, 300 MHz)



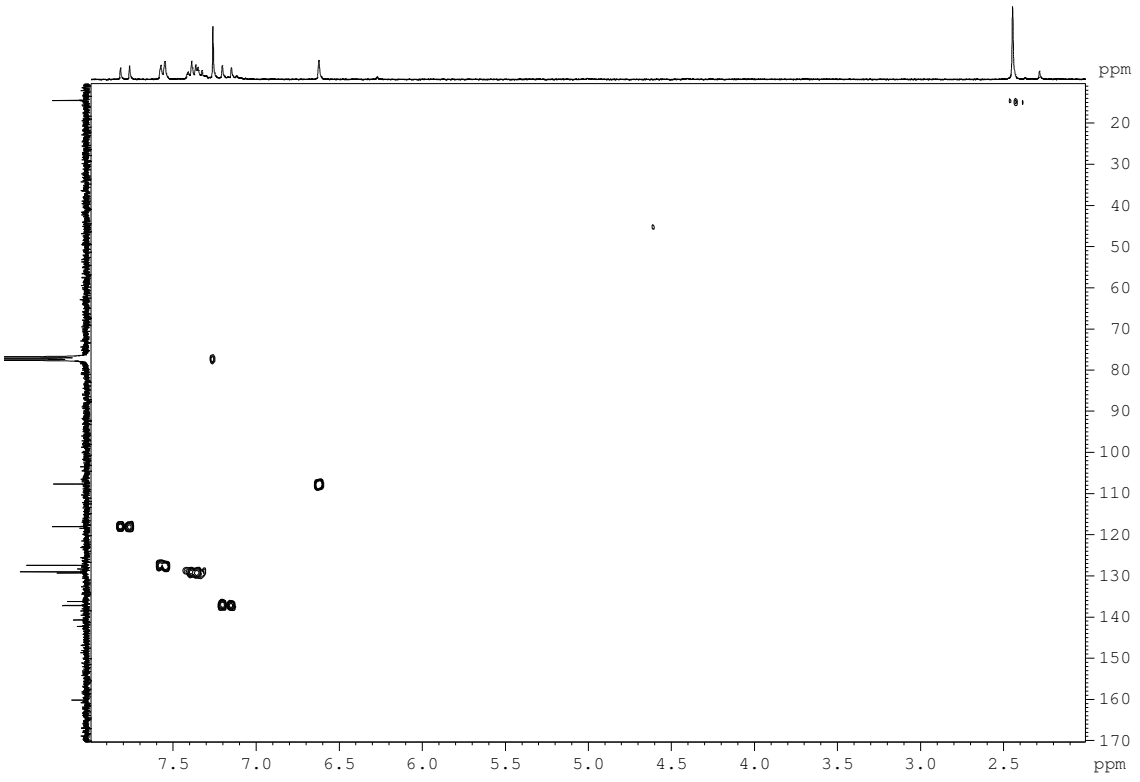
9a: ^{13}C-NMR ($CDCl_3$, 176 MHz)



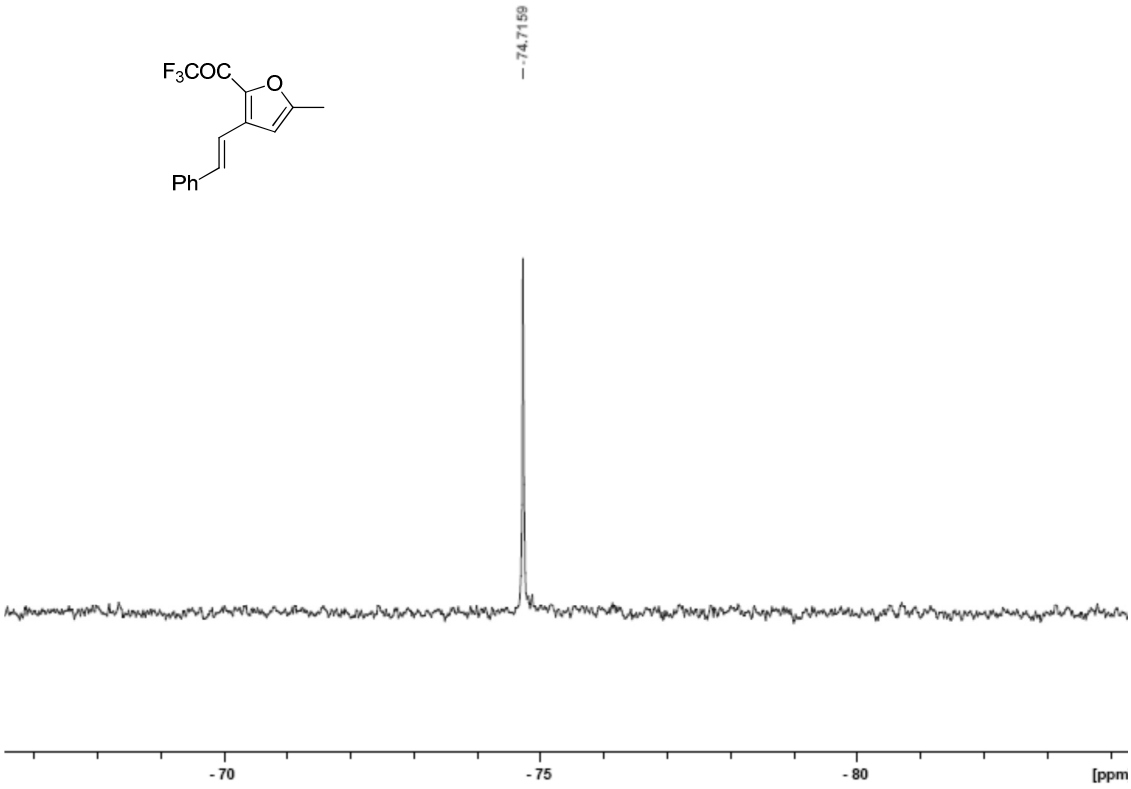
9a: DEPT-135 ($CDCl_3$, 75 MHz)



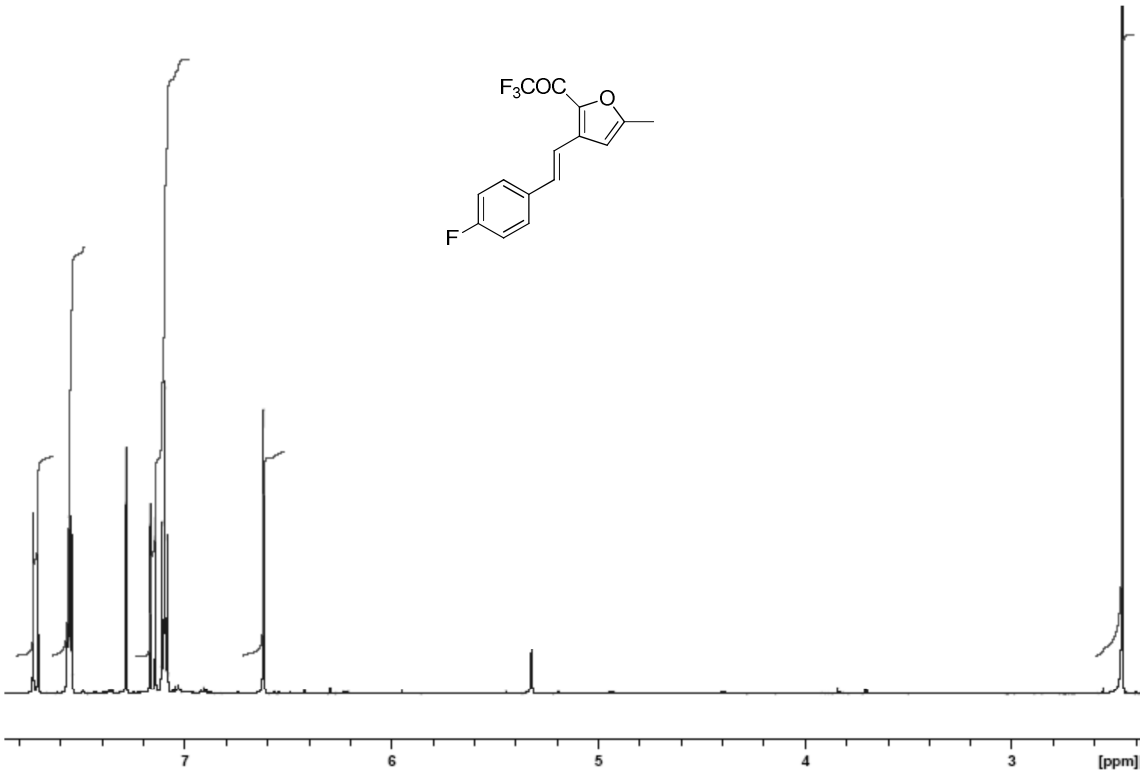
9a: HMQC ($CDCl_3$, 75 MHz)



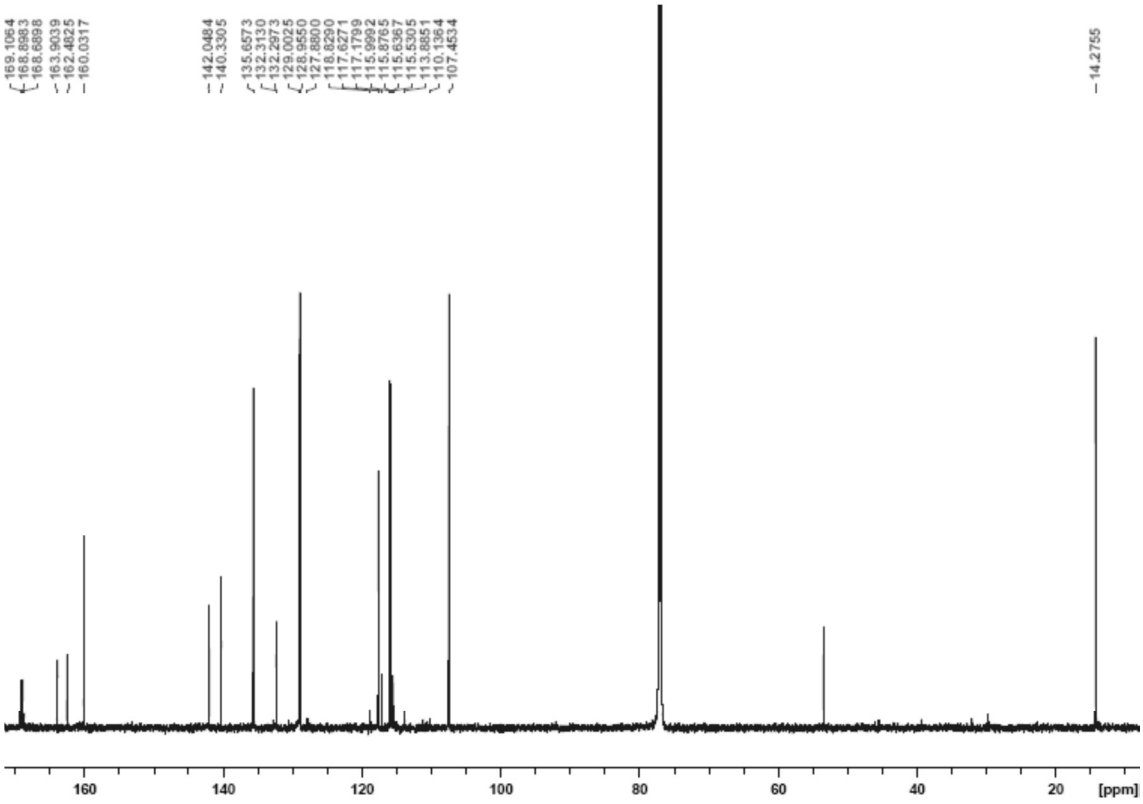
9a: ^{19}F-NMR ($CDCl_3$, 176 MHz)



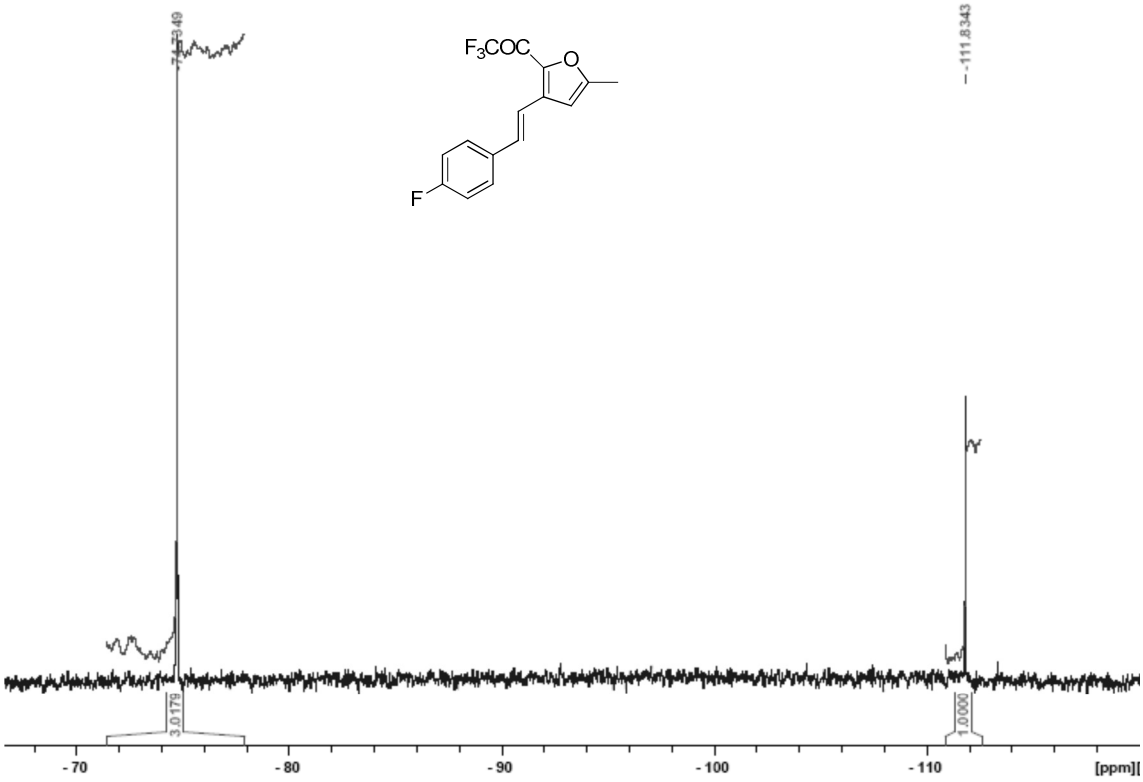
9b: ^{1}H-NMR ($CDCl_3$, 700 MHz)



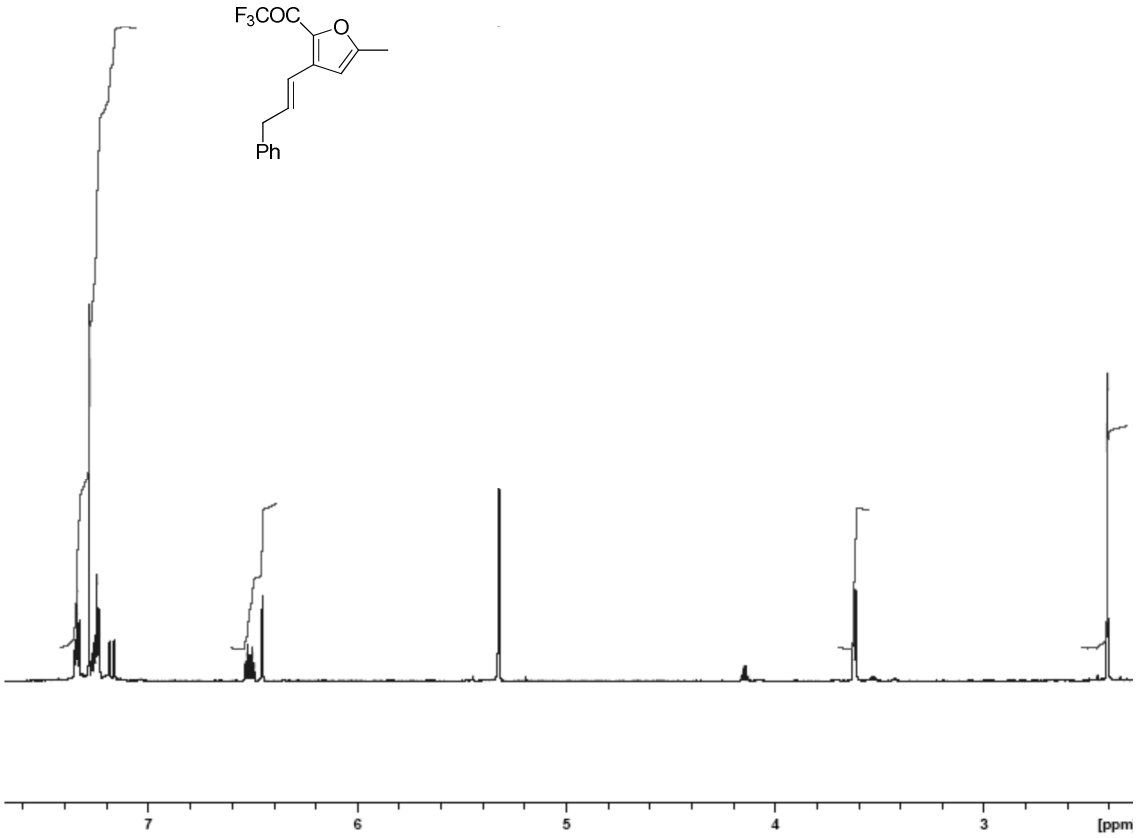
9b: ^{13}C-NMR ($CDCl_3$, 176 MHz)



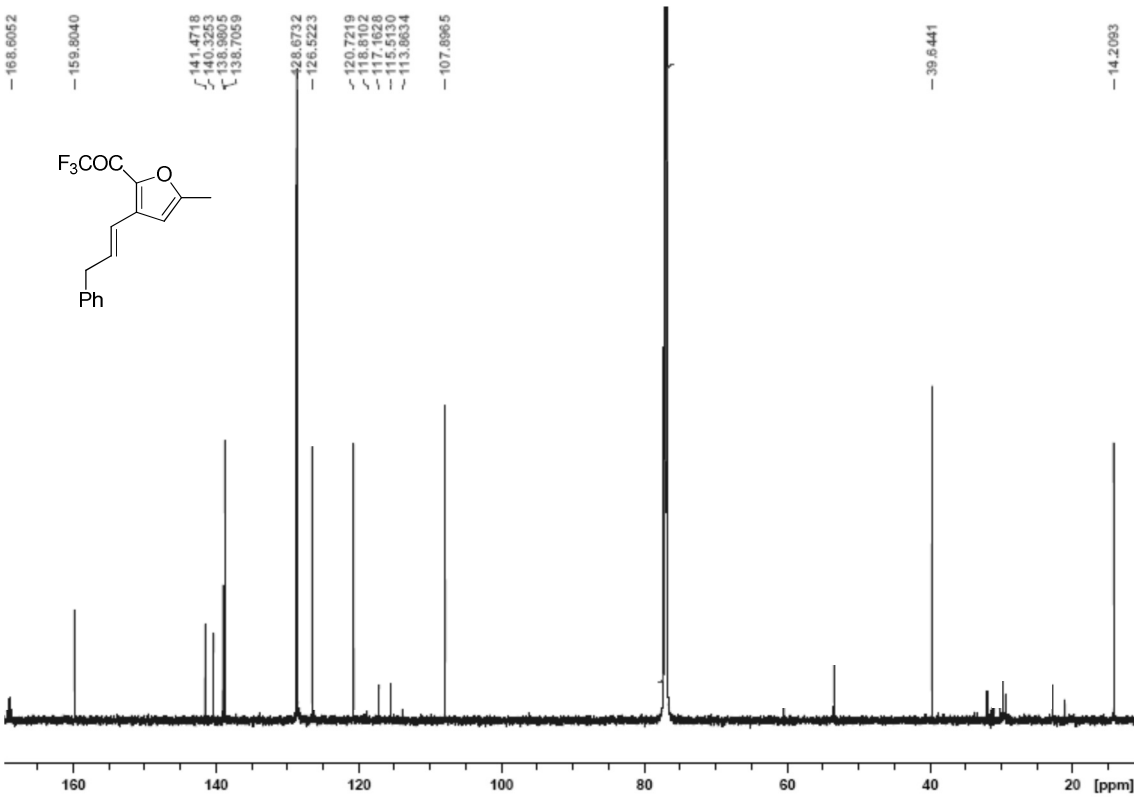
9b: ^{19}F-NMR ($CDCl_3$, 282 MHz)



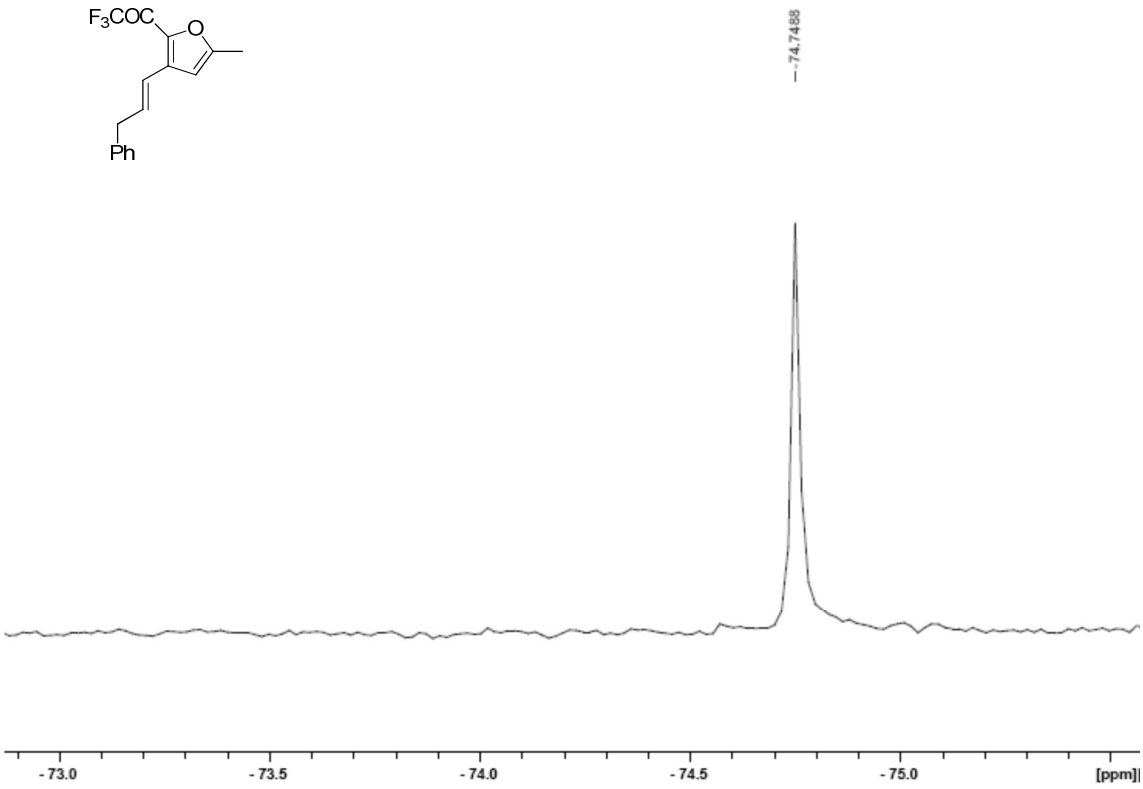
9c: ^{1}H-NMR ($CDCl_3$, 700 MHz)



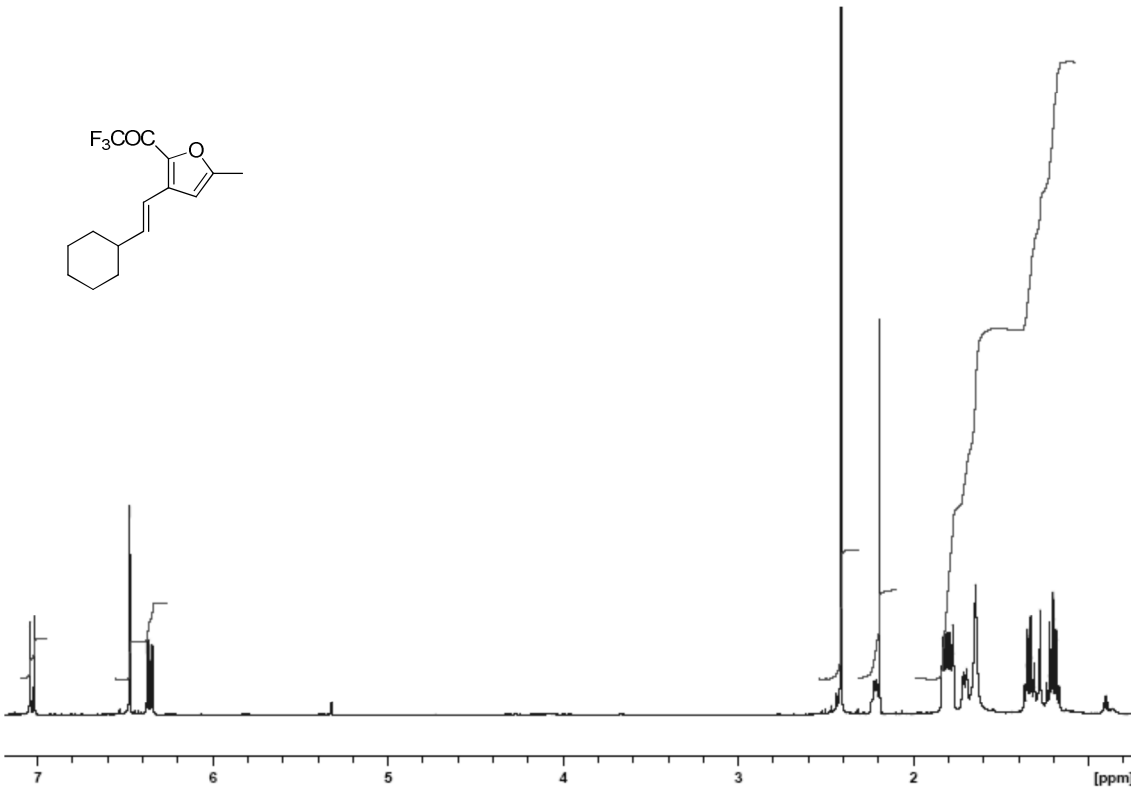
9c: ^{13}C-NMR ($CDCl_3$, 176 MHz)



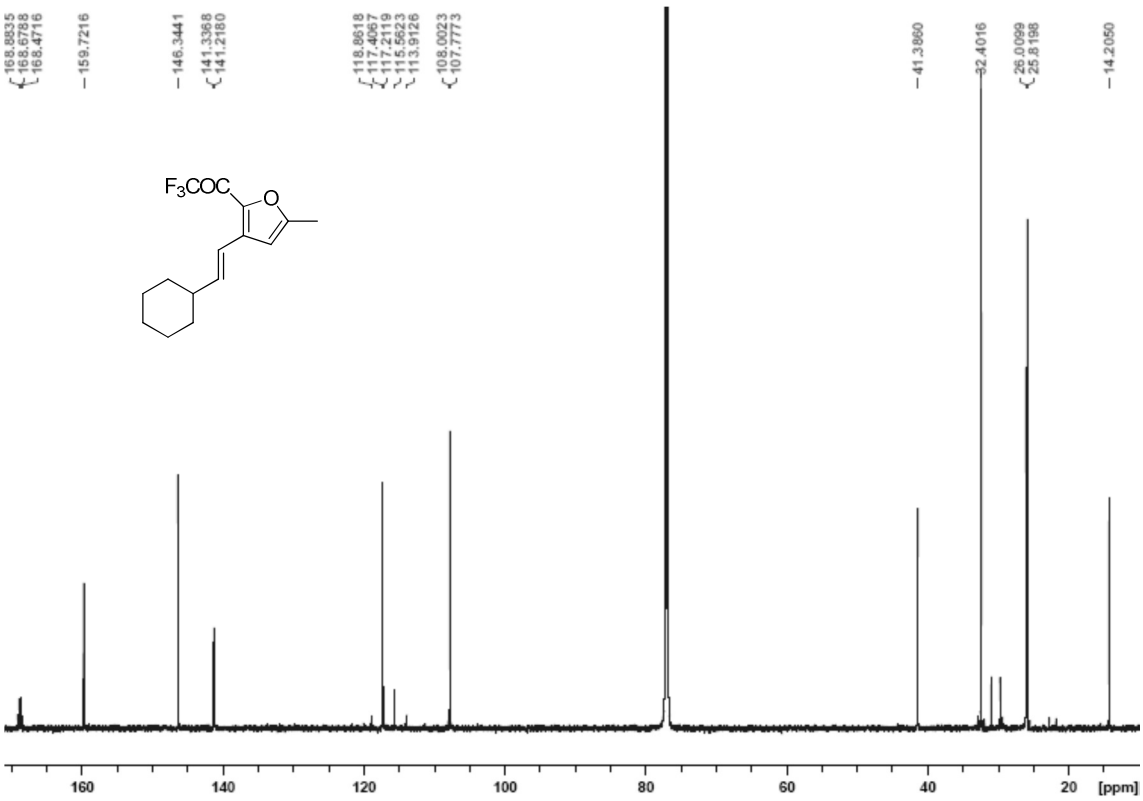
9c: ^{19}F-NMR ($CDCl_3$, 282 MHz)



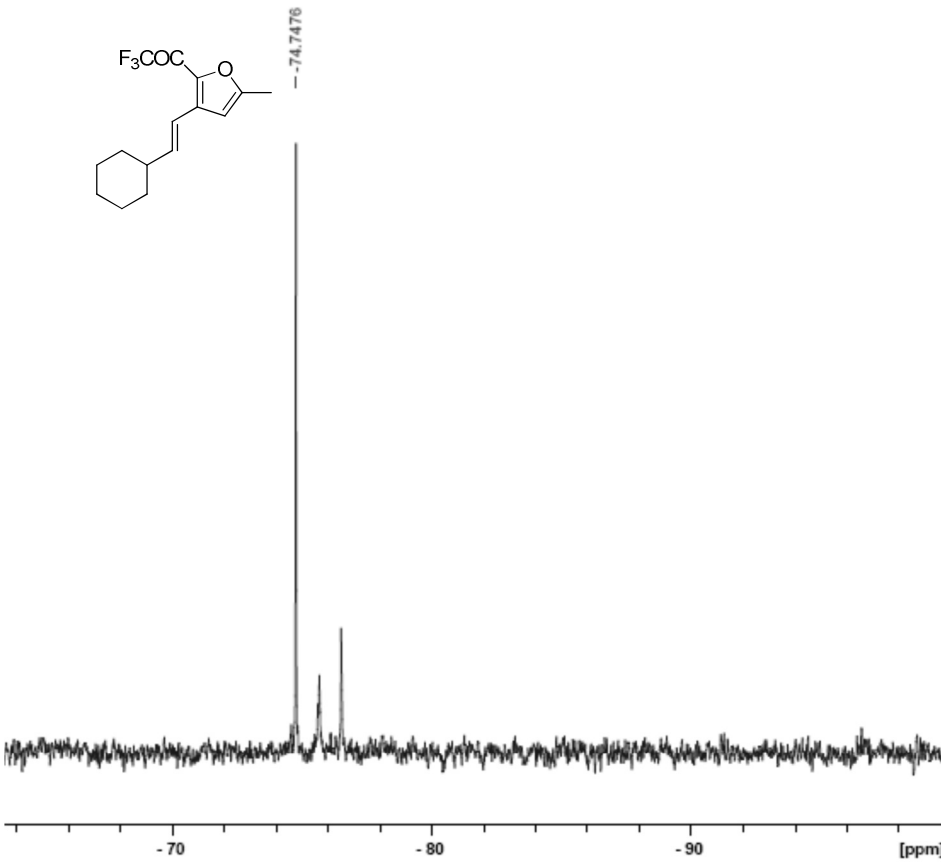
9d: ^{1}H-NMR ($CDCl_3$, 700 MHz)



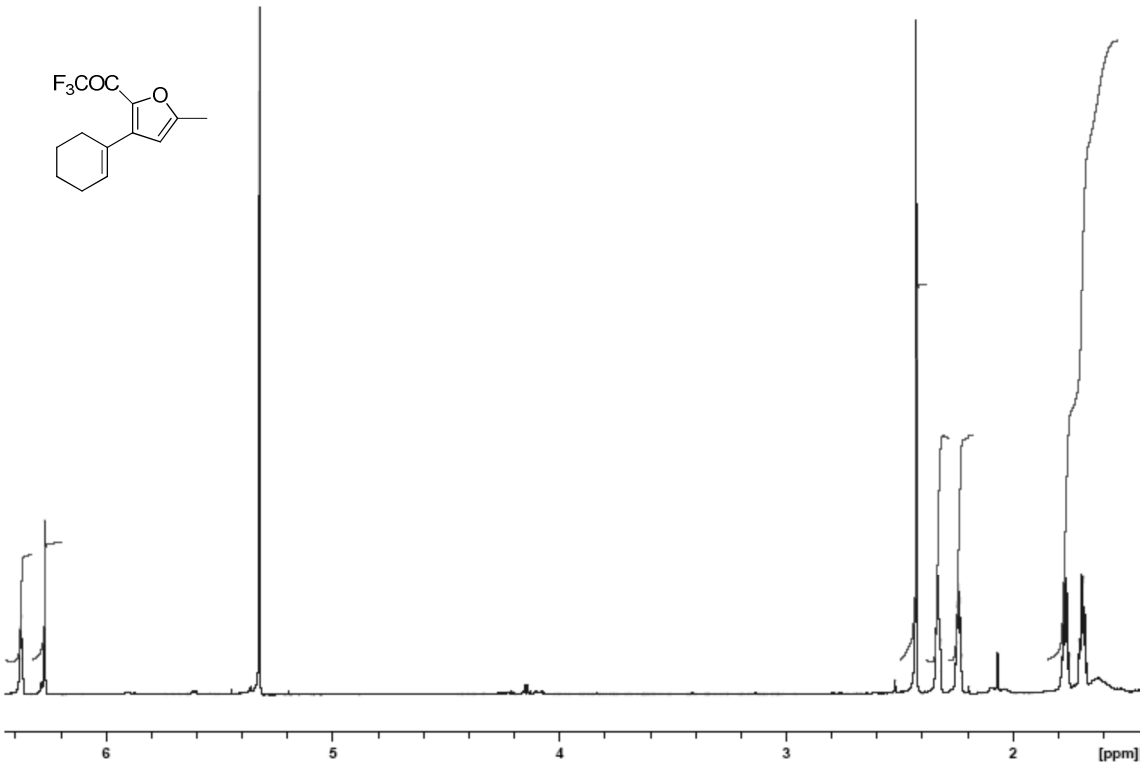
9d: ^{13}C-NMR ($CDCl_3$, 176 MHz)



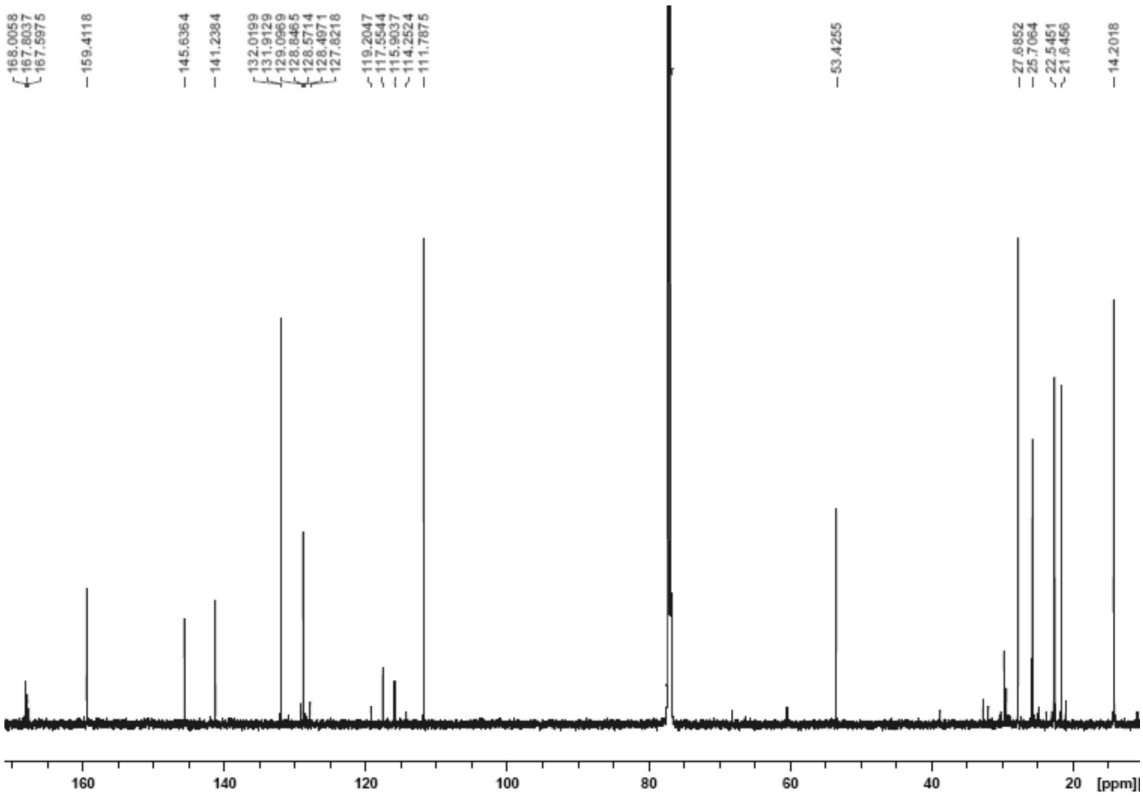
9d: ^{19}F-NMR ($CDCl_3$, 282 MHz)



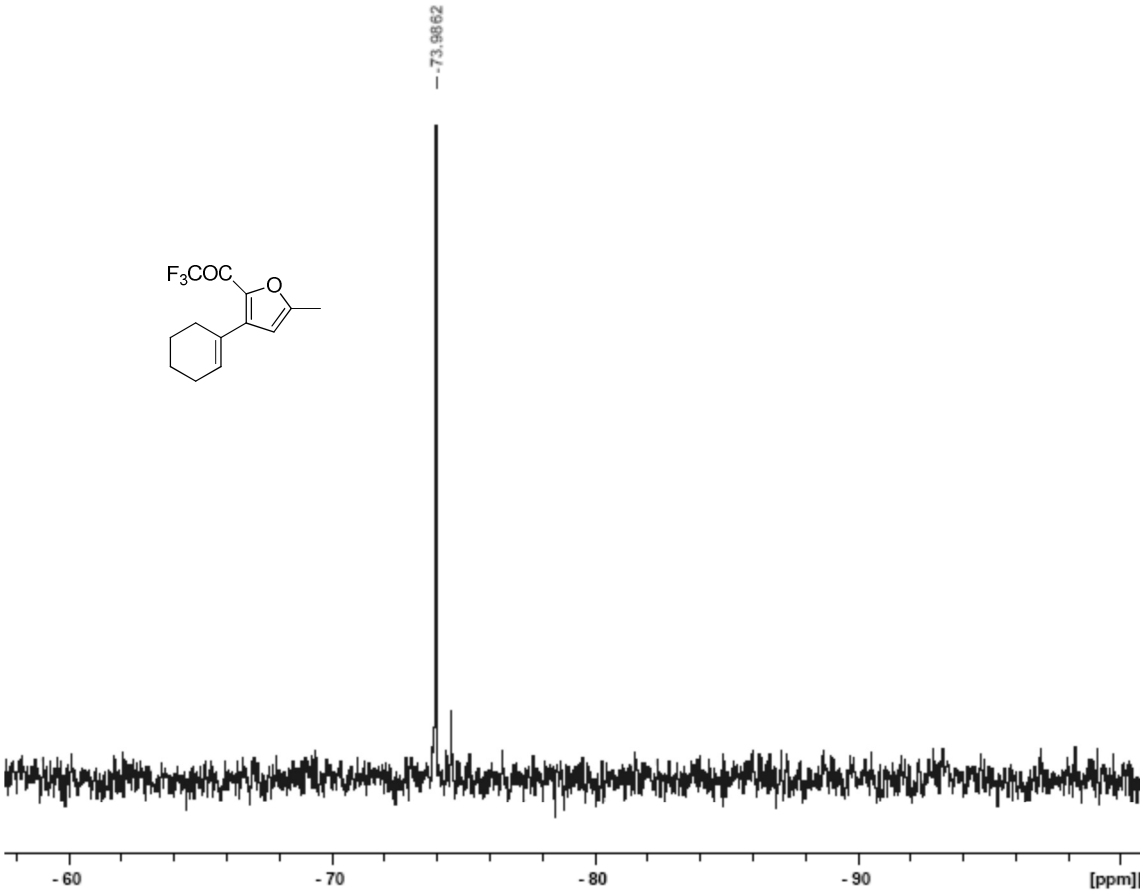
9e: ^{1}H-NMR ($CDCl_3$, 700 MHz)



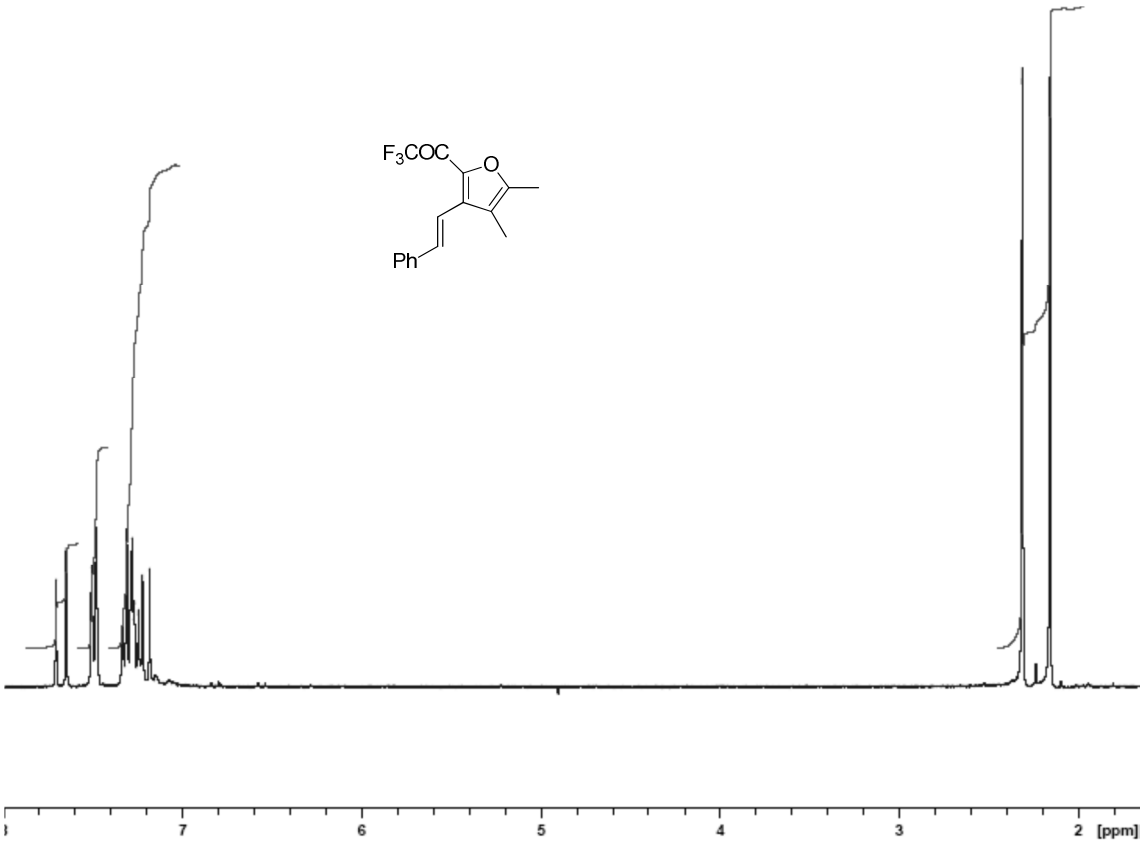
9e: ^{13}C-NMR ($CDCl_3$, 176 MHz)



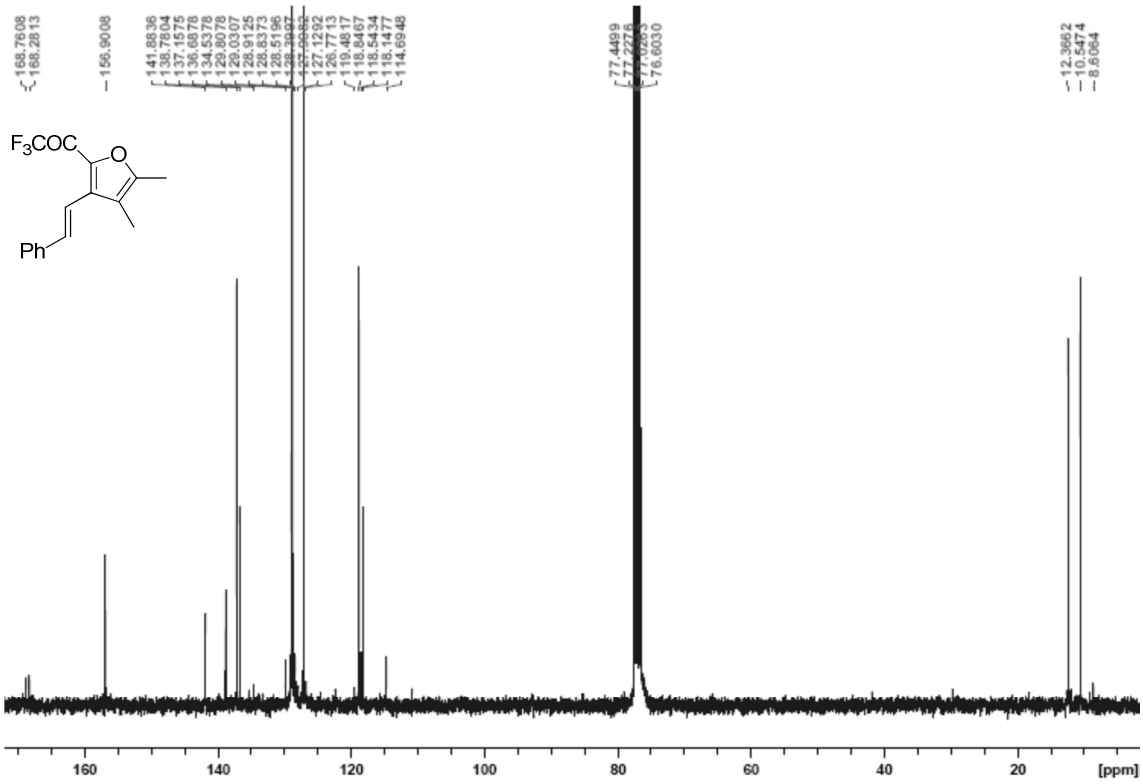
9e: ^{19}F-NMR ($CDCl_3$, 282 MHz)



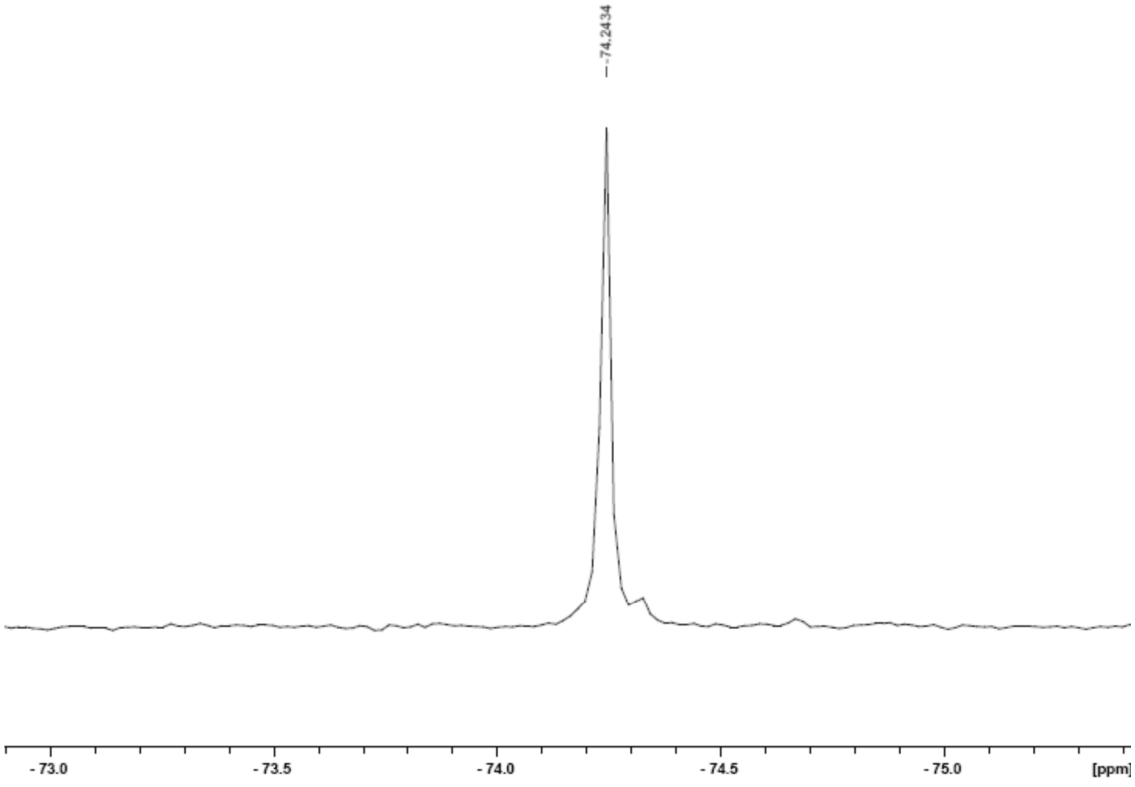
9f: ^{1}H-NMR ($CDCl_3$, 300 MHz)



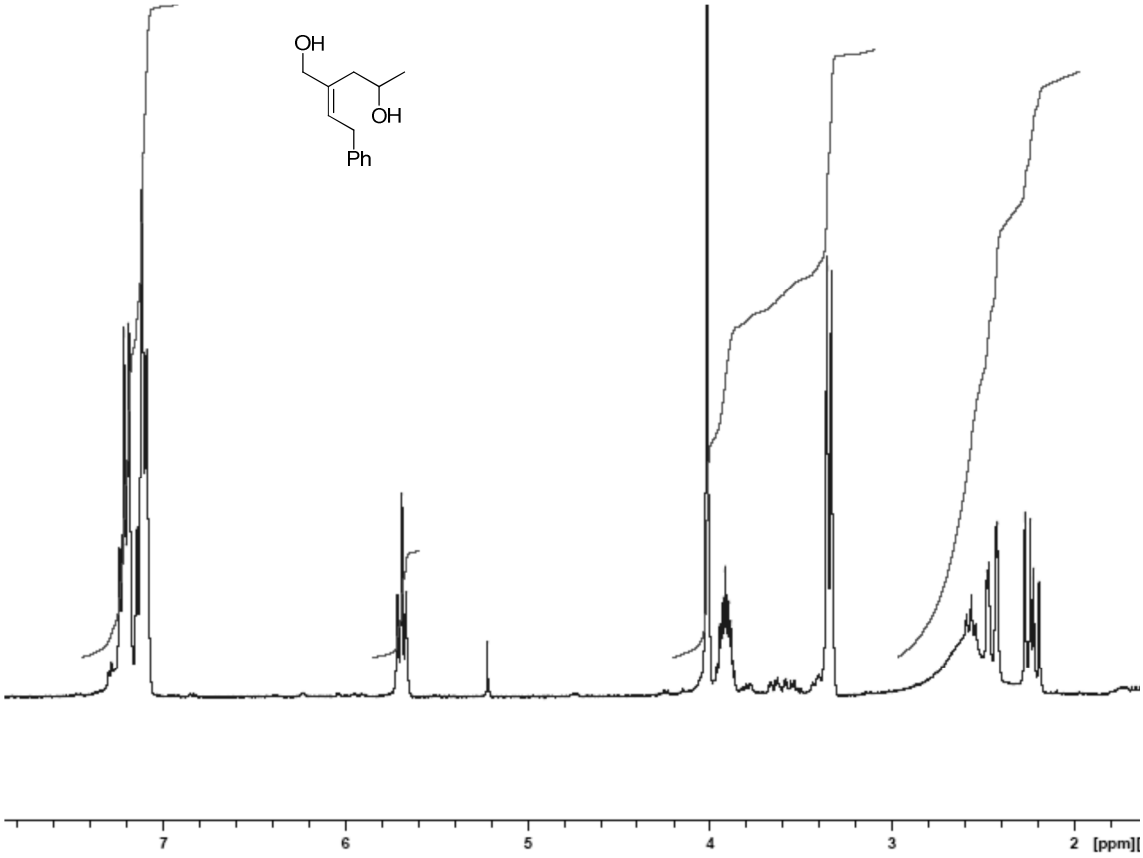
9f: ^{13}C-NMR ($CDCl_3$, 75 MHz)



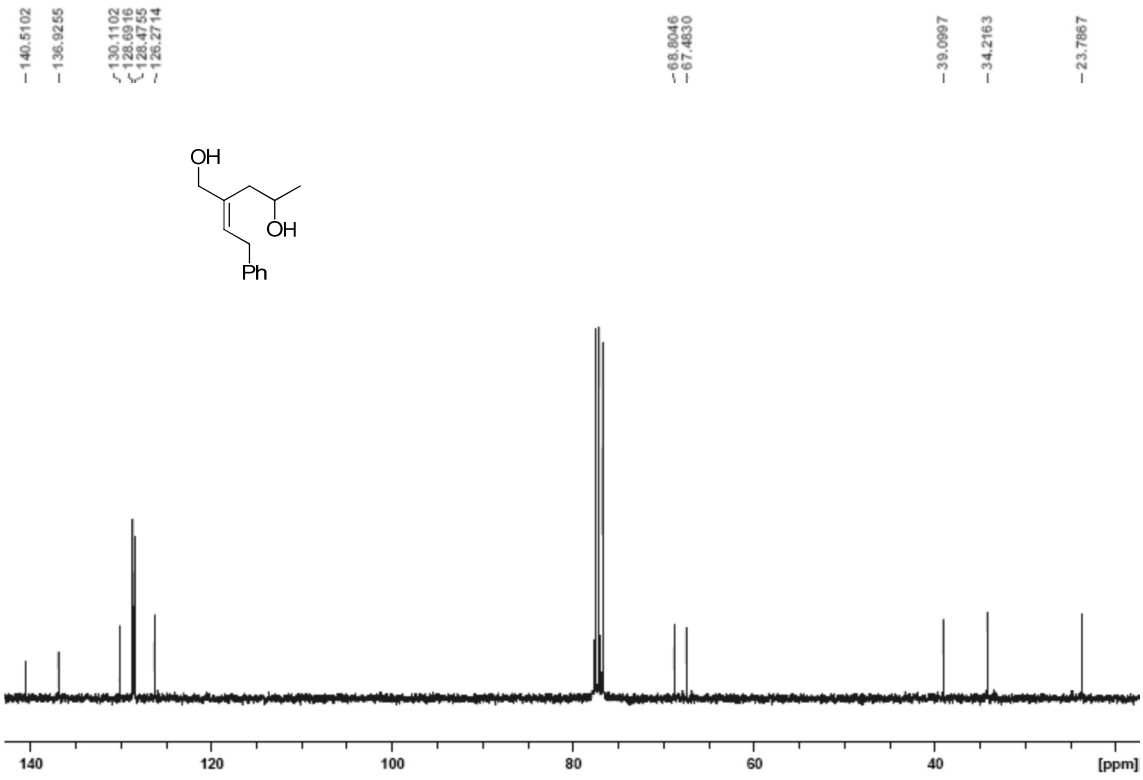
9f: ^{19}F-NMR ($CDCl_3$, 75 MHz)



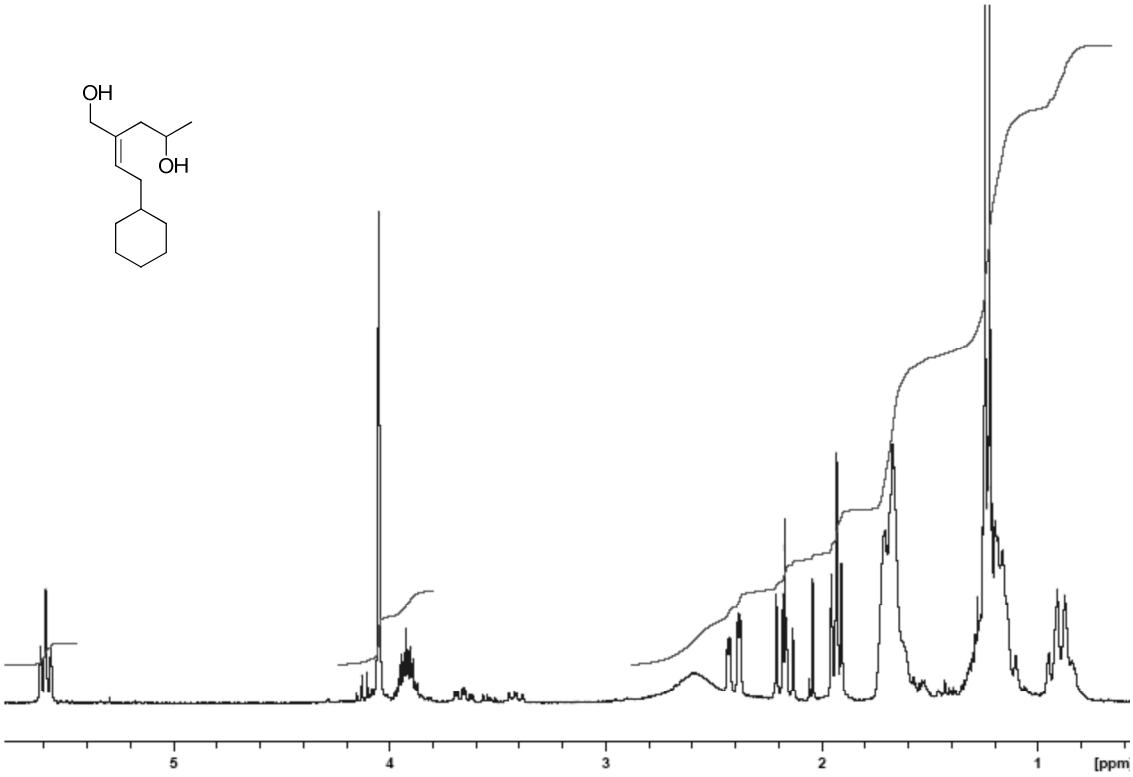
10a: ^{1}H-NMR ($CDCl_3$, 300 MHz)



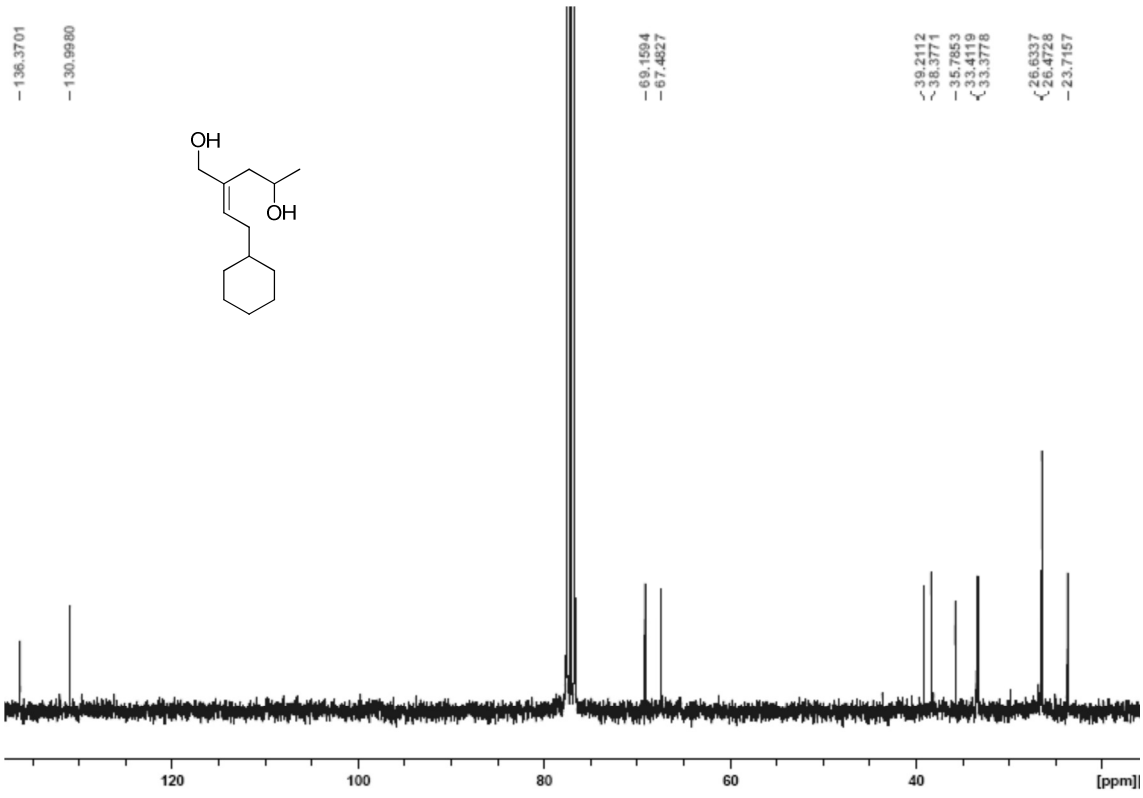
10a: ^{13}C-NMR ($CDCl_3$, 75 MHz)



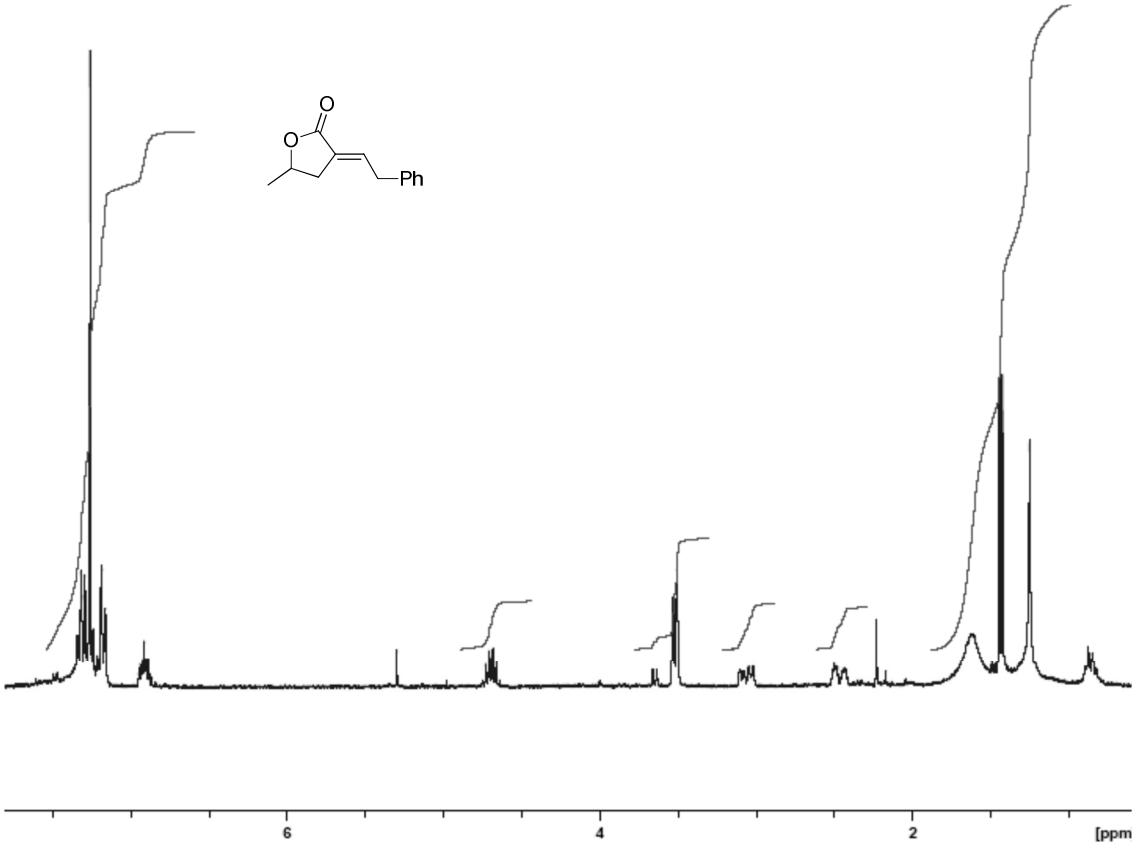
10b: ^{1}H-NMR ($CDCl_3$, 300 MHz)



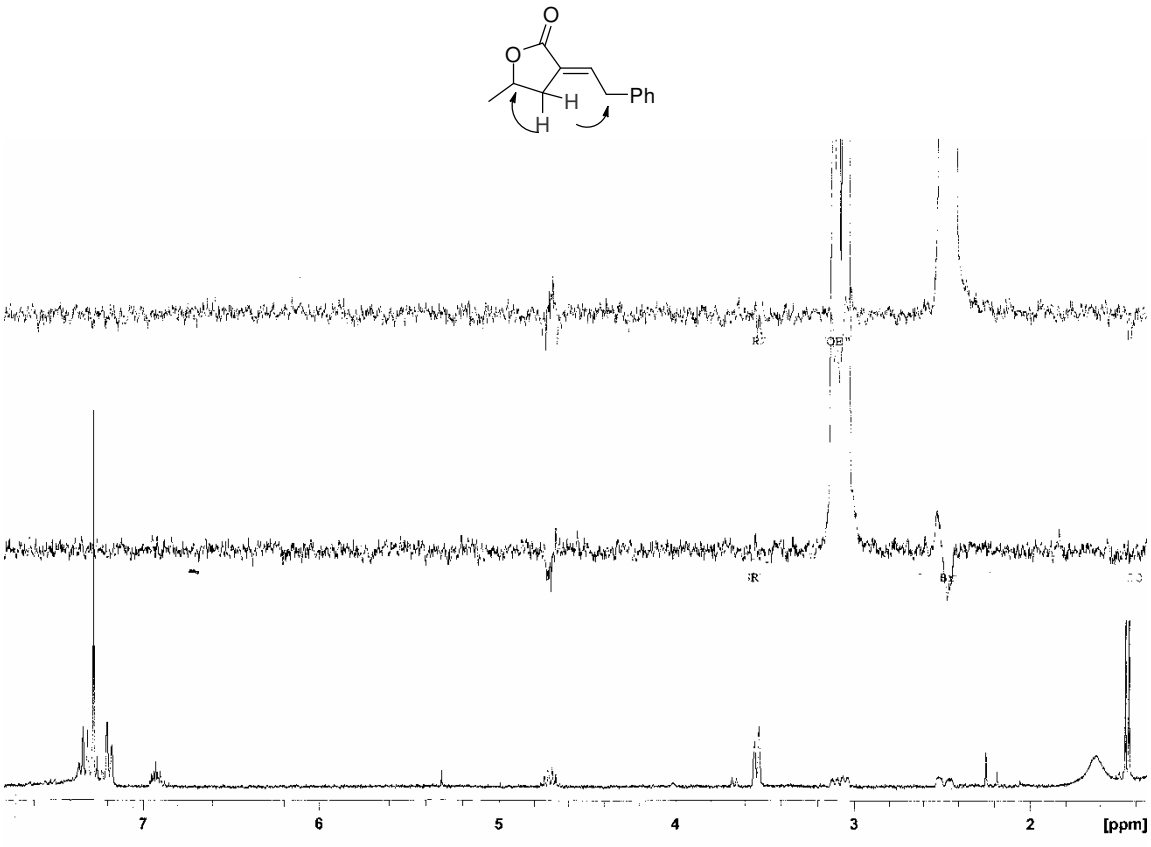
10b: ^{13}C-NMR ($CDCl_3$, 75 MHz)



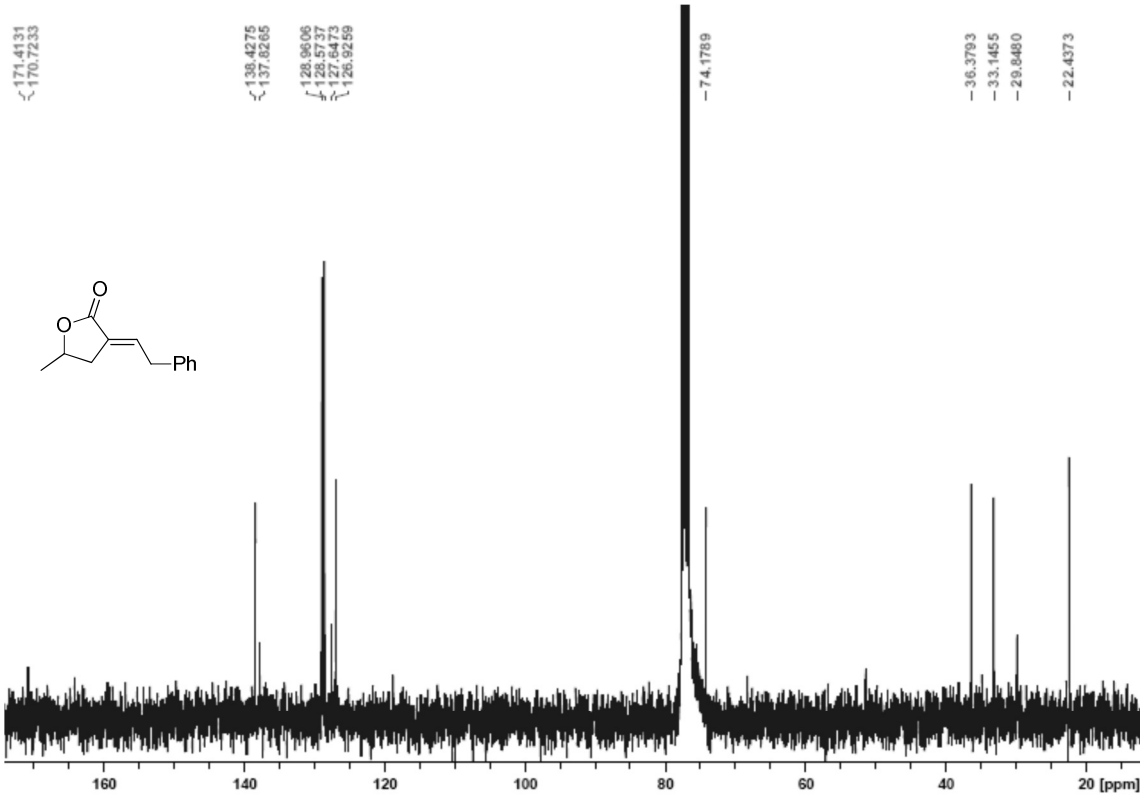
11a: ^{1}H-NMR ($CDCl_3$, 300 MHz)



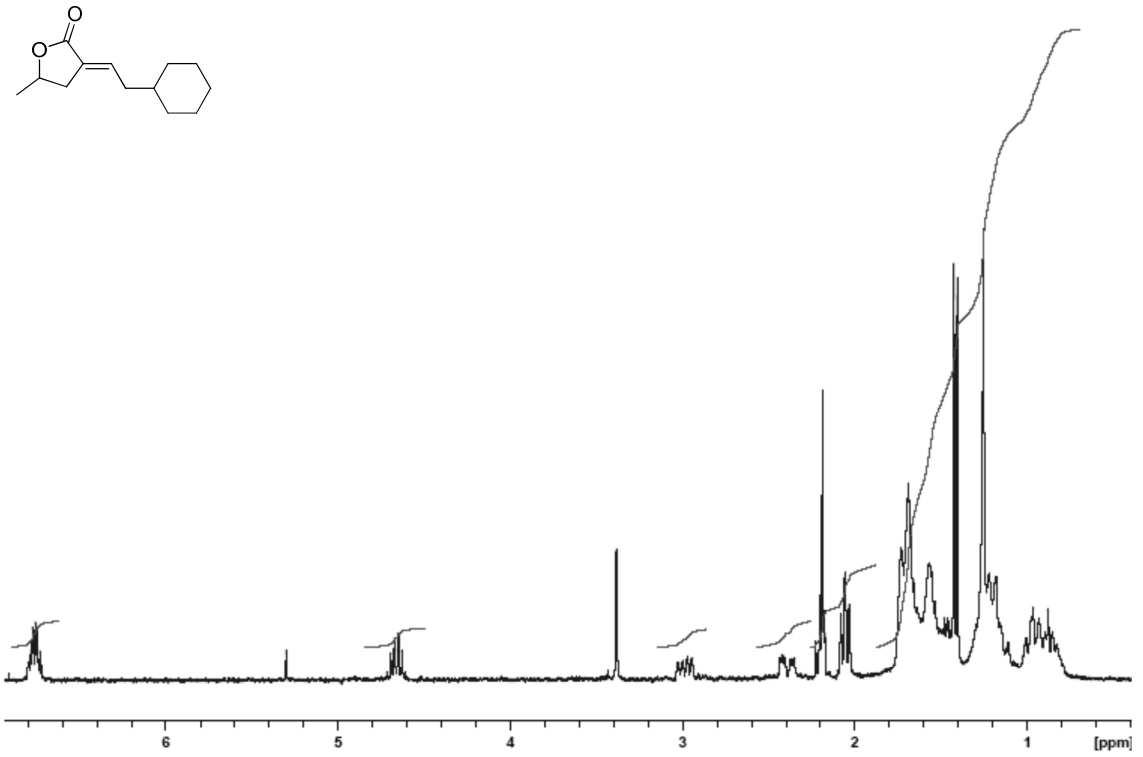
11a: NOE measurements ($CDCl_3$, 300 MHz)



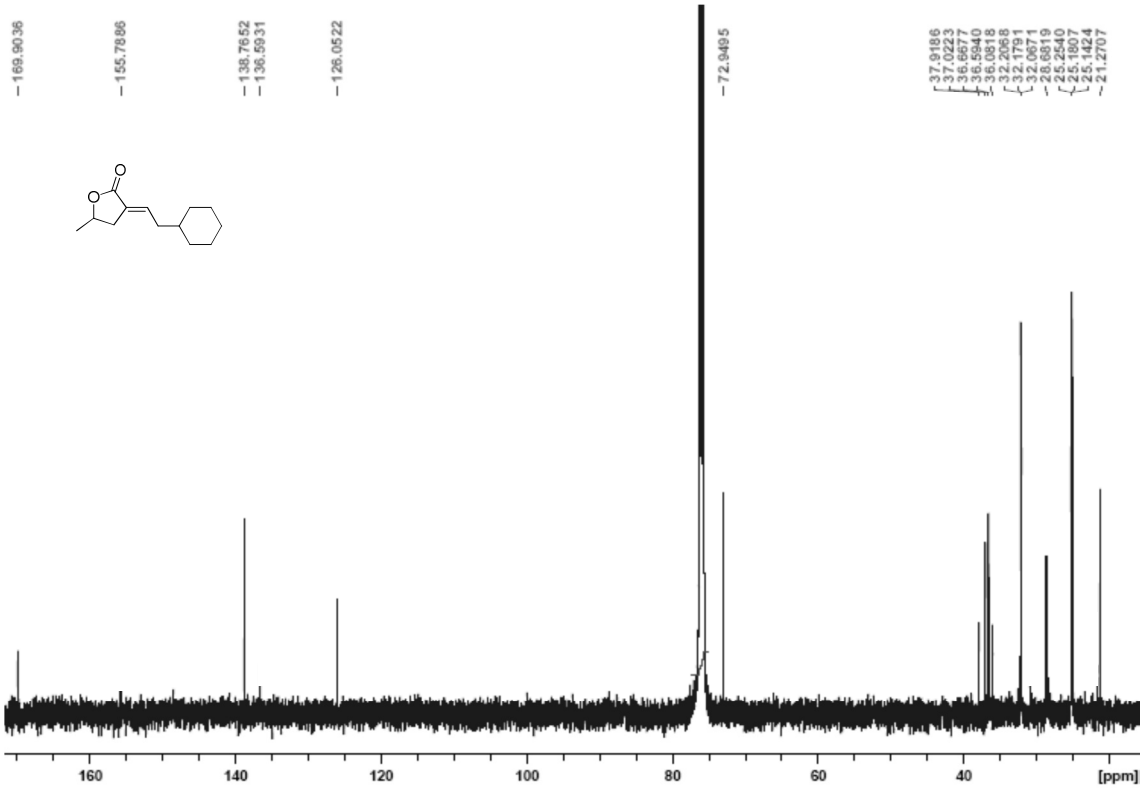
11a: ^{13}C-NMR ($CDCl_3$, 75 MHz)



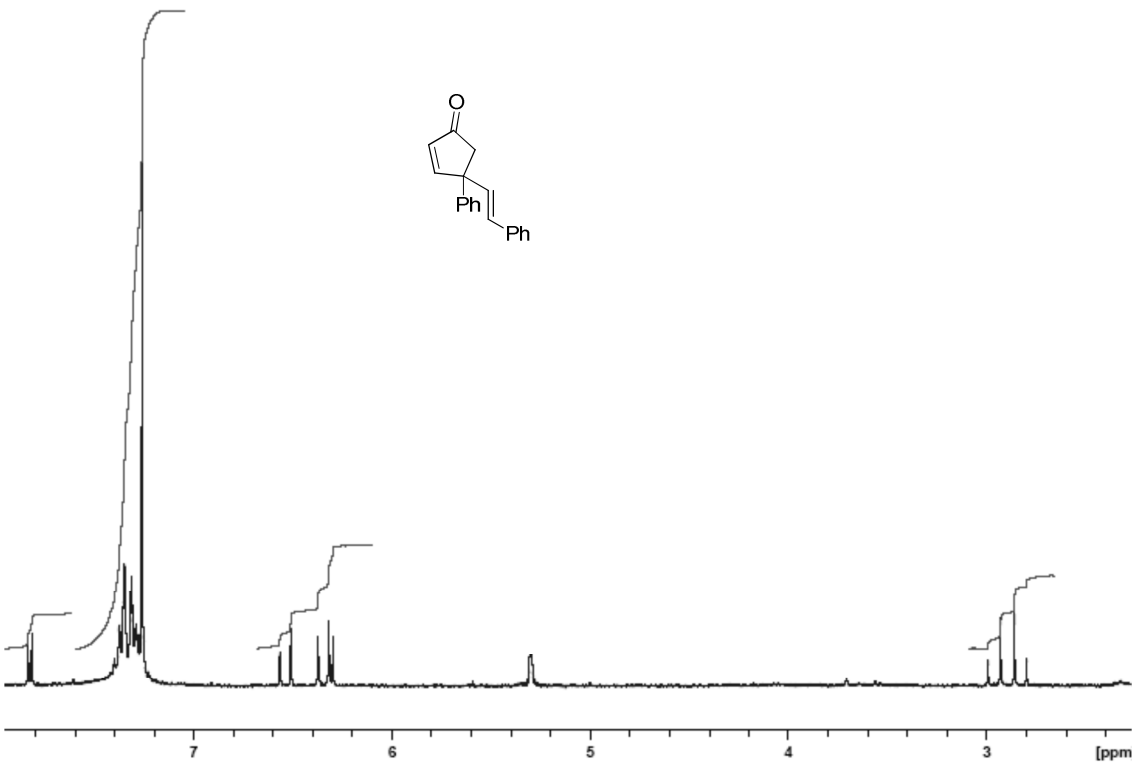
11b: ^{1}H-NMR ($CDCl_3$, 500 MHz)



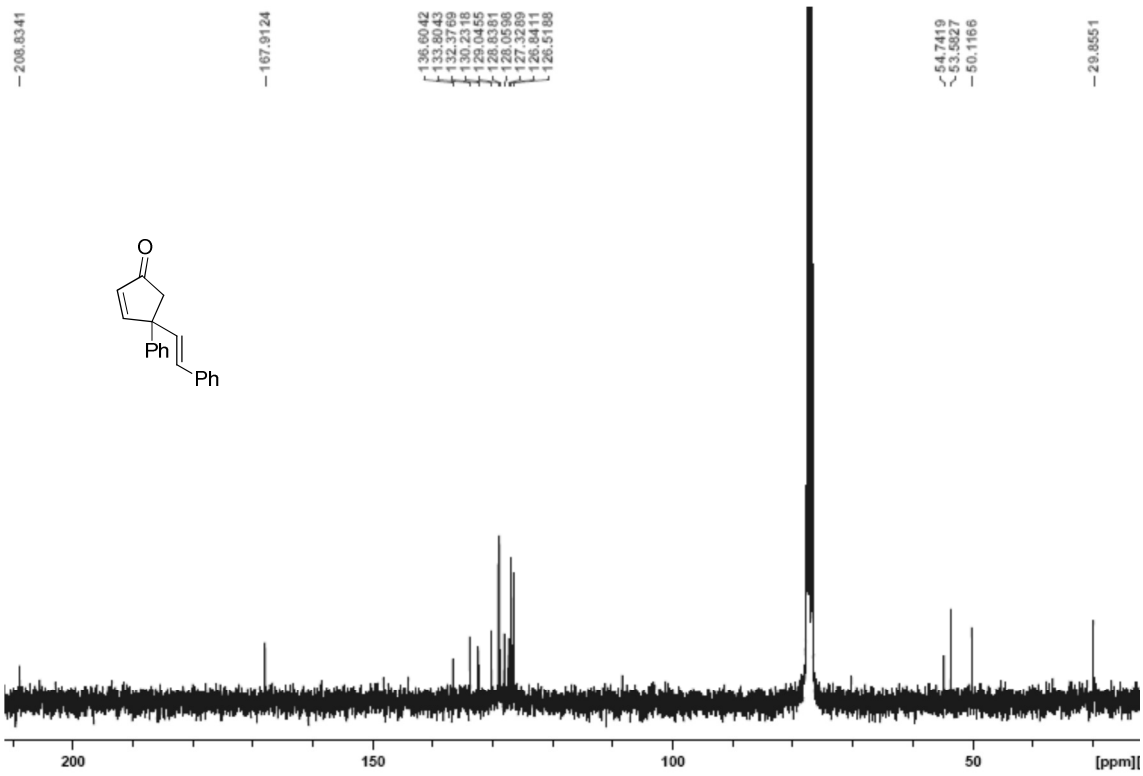
11b: ^{13}C-NMR ($CDCl_3$, 125 MHz)



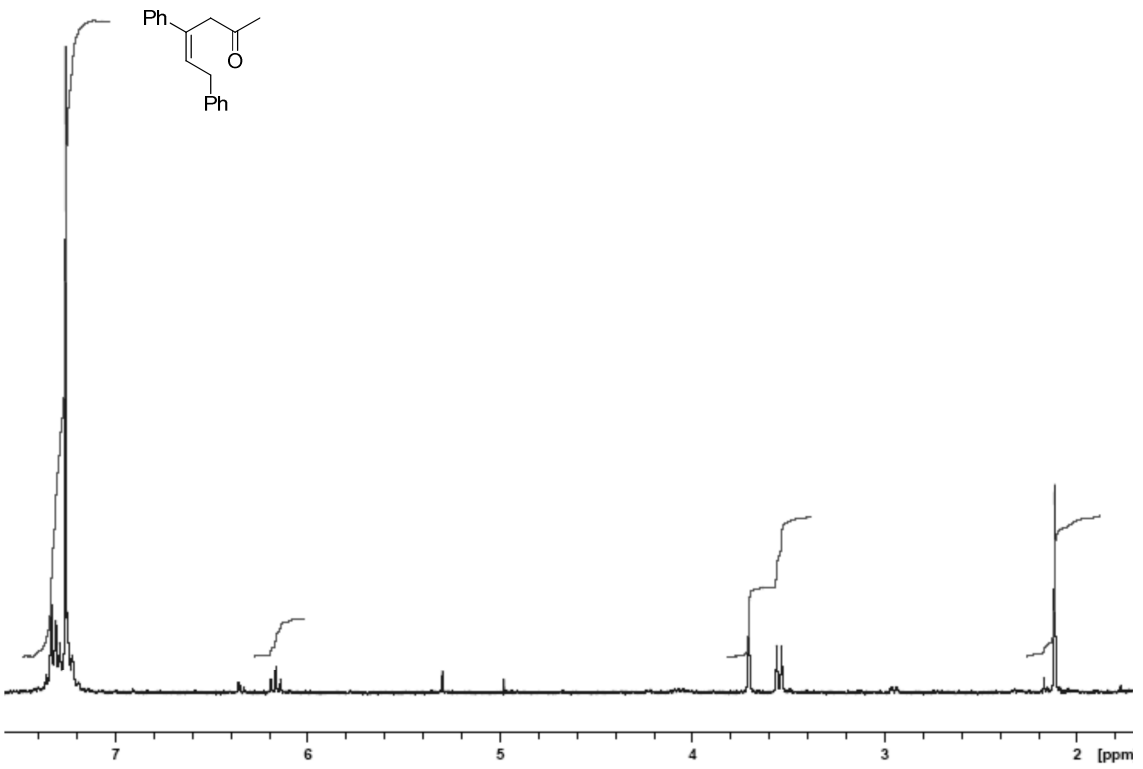
12: ^{1}H-NMR ($CDCl_3$, 300 MHz)



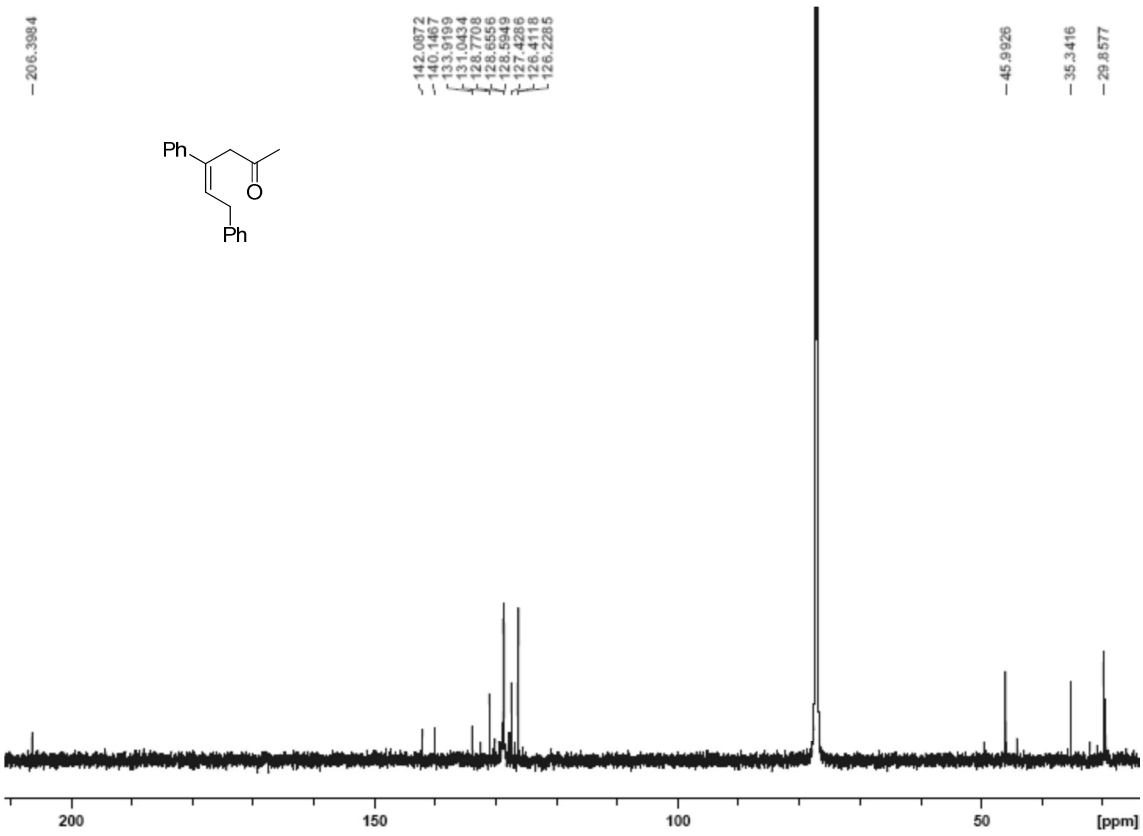
12: ^{13}C-NMR ($CDCl_3$, 75 MHz)



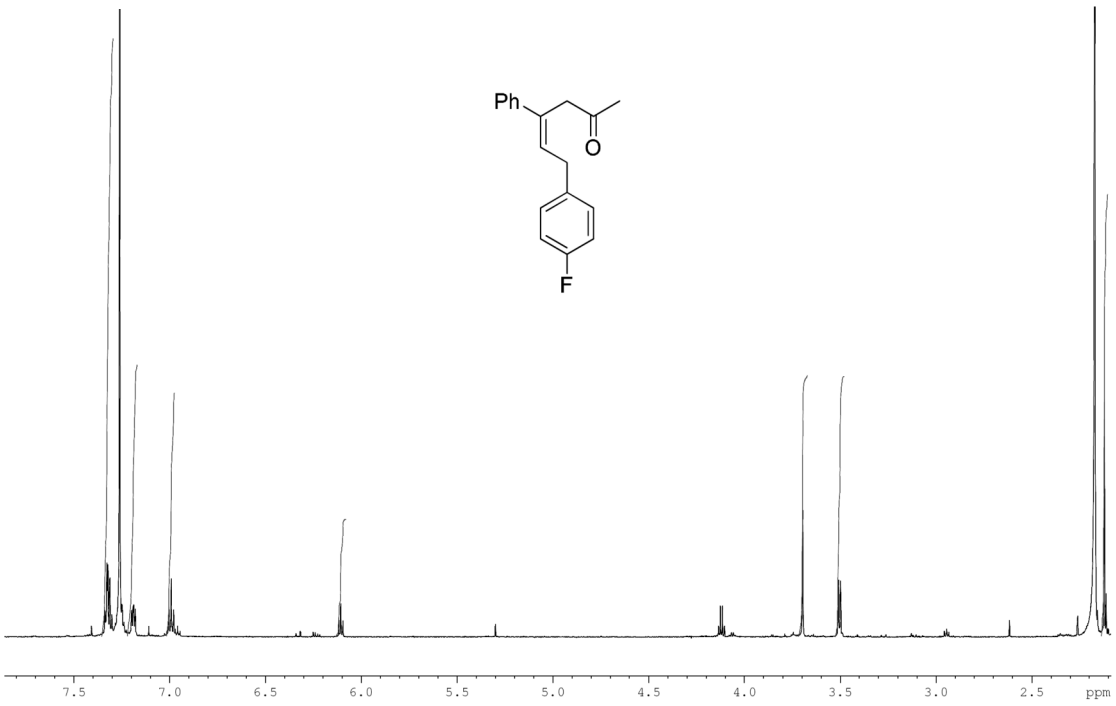
13a: ^{1}H-NMR ($CDCl_3$, 300 MHz)



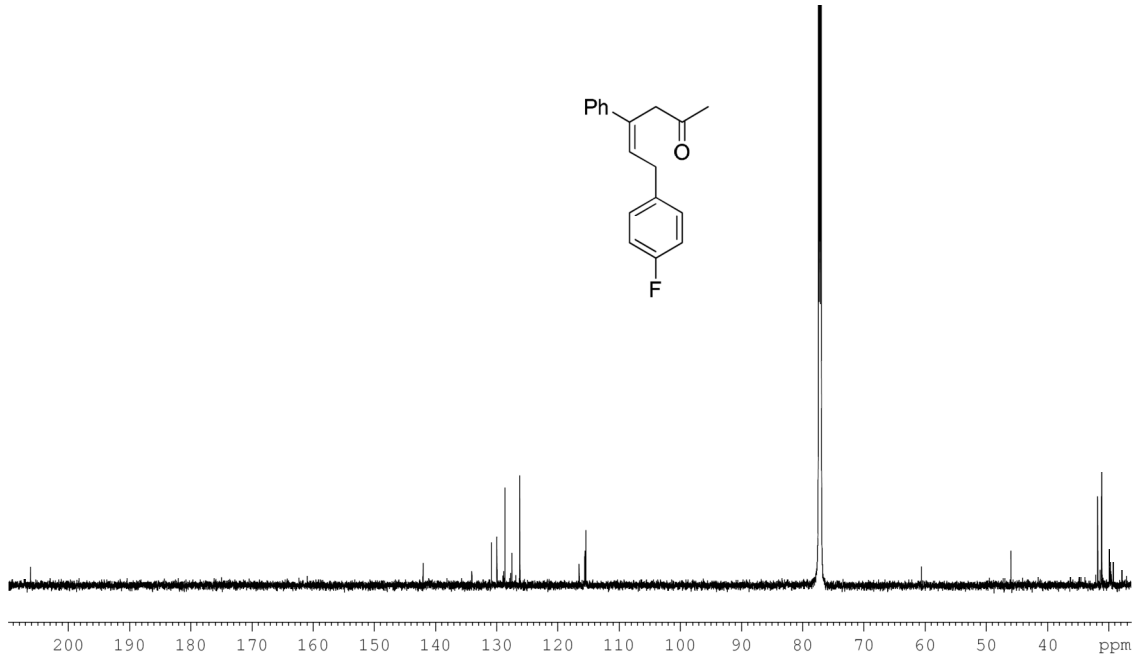
13a: ^{13}C-NMR ($CDCl_3$, 75 MHz)



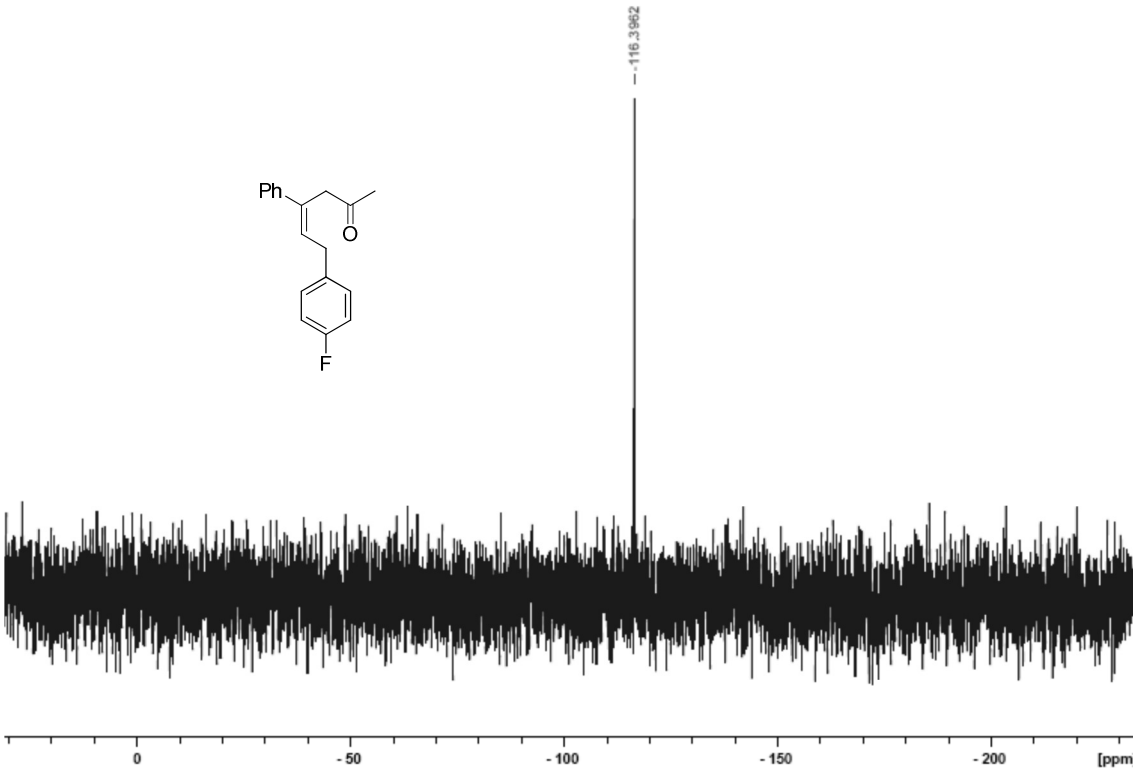
13b: ^{1}H-NMR ($CDCl_3$, 300 MHz)



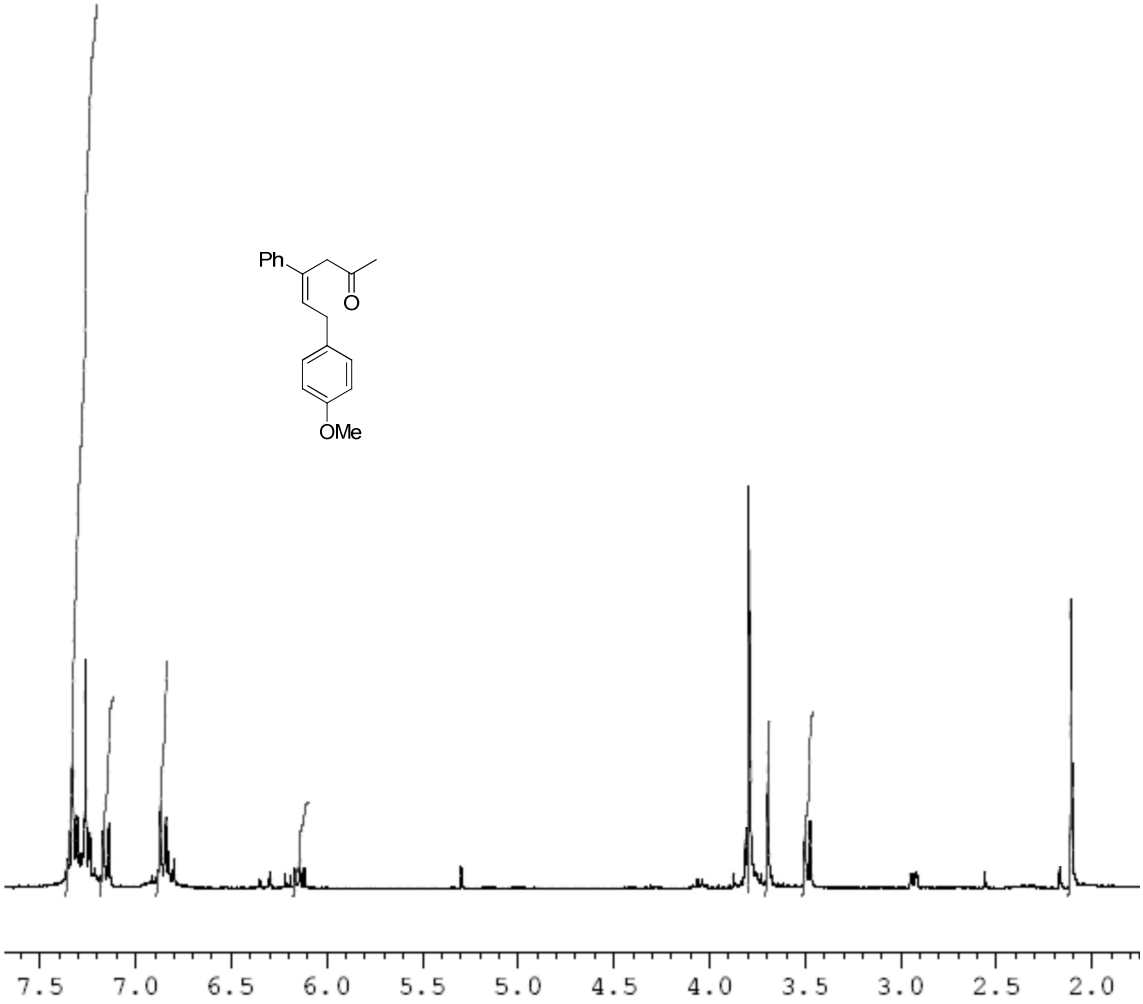
13b: ^{13}C-NMR ($CDCl_3$, 75 MHz)



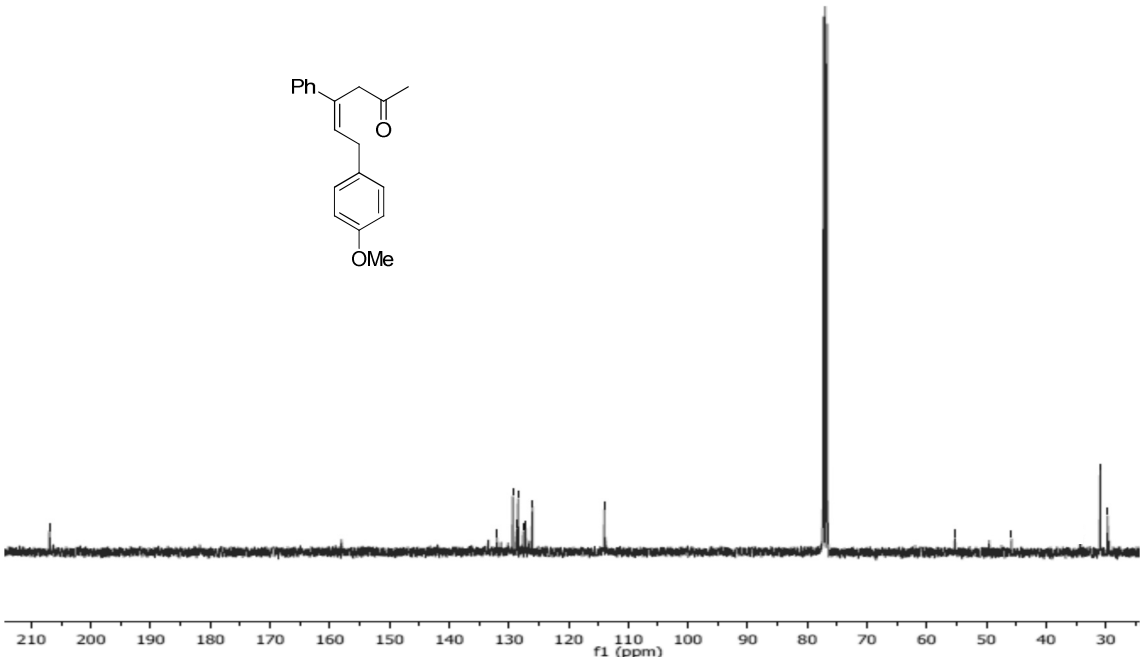
13b: ^{19}F-NMR ($CDCl_3$, 282 MHz)



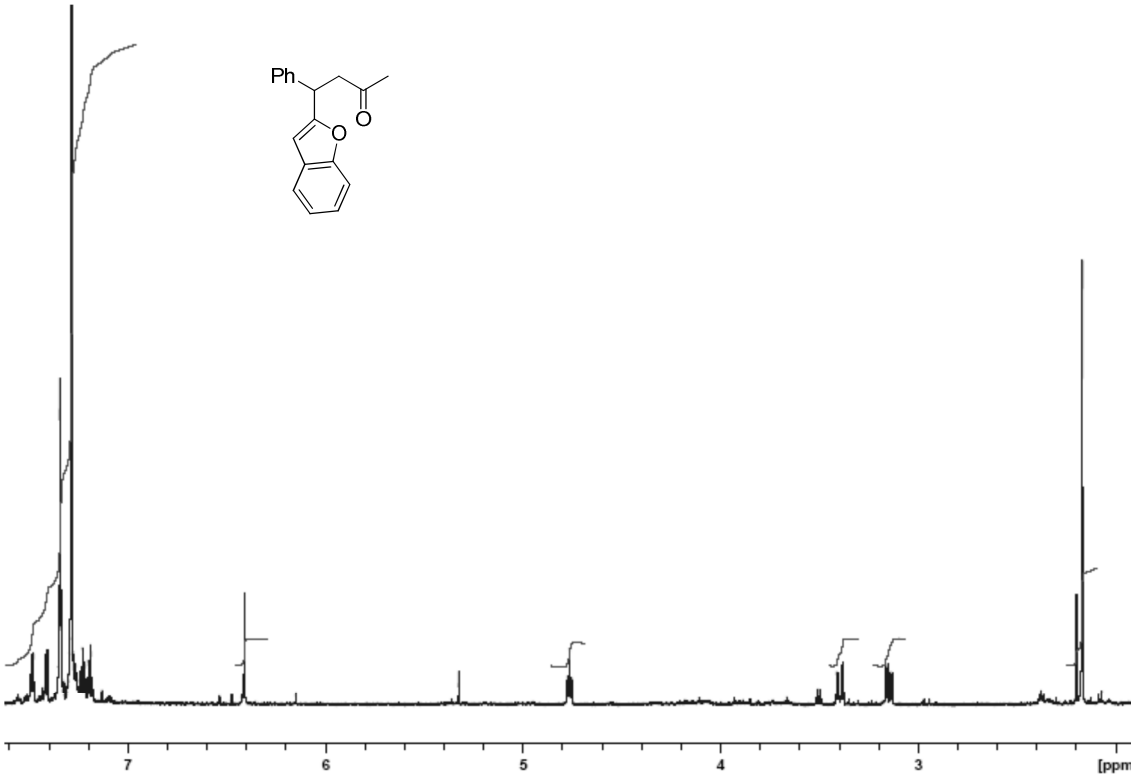
13c: ^{1}H-NMR ($CDCl_3$, 300 MHz)



13c: ^{13}C-NMR ($CDCl_3$, 75 MHz)



14: ^{1}H-NMR ($CDCl_3$, 700 MHz)



14: ^{13}C-NMR ($CDCl_3$, 176 MHz)