Radical C(sp3)-H Alkenylation, Alkynylation and Allylation of Ethers and Amides Enabled by Photocatalysis

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General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reagent-grade solvents were purchased from commercial sources and used without further purification for reaction, work-up and purification. All reactions were performed in oven-dried screw cap tube (10 mL) with a Teflon coated magnetic stirring bar at room temperature (30 °C), in front of a 36 W household CFL bulb unless otherwise noted. Reactions monitoring and determination of R_f values for all compounds were performed by thin layer chromatography (TLC) on silica gel 60 F_{254} and visualization was accomplished by irradiation with UV light at 254 nm or $KMnO_4$ stain. Column chromatography was performed on Merck silica gel (100-200 mesh) with eluent as mentioned, unless otherwise reported. Proton and carbon NMR spectra were recorded on Bruker AV-500, JEOL 400 and Bruker Avance III HD 300 MHz spectrometers in deuterated solvents at ambient probe temperature (300 K). Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sex= sextet, sept= septet, m = multiplet, br = broad, dd = double doublet), coupling constants (Hz) and integration. ^{13}C chemical shifts are reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.0 ppm). ^{19}F chemical shifts are reported in ppm (δ) with the solvent resonance as the internal standard (C_6F_6 δ - 165.0 ppm). High resolution mass spectra were taken using Q-TofMS/MS system by electron spray ionization (ESI) technique. IR spectra were taken using a Perkin-Elmer 1615 FT Infrared Spectrophotometer Model 60B, the wave numbers (n) of recorded IR-signals are reported in cm^{-1}. UV-Visible spectra were taken using a Cary60 UV-Vis Spectrophotometer.

Literature Preparations:

General Procedures for the Synthesis of Sulfones:

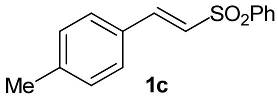
General Procedure A.[1]

To a suspension of benzenesulfinic acid sodium salt (3.0 equiv) and NaOAc (1.5 equiv) in MeCN (0.25 M) styrene derivative (1.0 equiv) was added followed by iodine (1.5 equiv). The mixture was heated under reflux for 3 h. The reaction mixture was allowed to cool to room temperature and excess iodine was quenched with saturated sodium thiosulfate solution (5 mL). The reaction mixture was basified with saturated aqueous $NaHCO_3$ (5 mL) and the organic compounds were extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with H_2O (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography and/or via recrystallization from ^{i}PrOH/hexane.

General Procedure B:

To a stirred solution of methylphenylsulfone (1.0 equiv) in THF (0.16 M), *n*-BuLi (1.6 M in hexanes, 2.2 equiv) was added drop wise at 0 °C. While maintaining the reaction temperature, the yellow suspension was stirred for another 10 min before diethyl chlorophosphate (1.2 equiv) was added to the solution. The resultant yellow solution was stirred at 0 °C for another 10 min before the reaction flask was placed in a –78 °C cooling bath. To the cold solution, aldehyde (1.0 equiv) was added and the solution was allowed to warm to room temperature for overnight. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution. Organic layer was extracted with Et_2O (3 x 10 mL), washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography and /or via recrystallization from ^{i}PrOH/hexane.

The following compounds were prepared according to general procedure **A**. Spectroscopic data of the sulfones are in good agreement with those previously reported.[1-2]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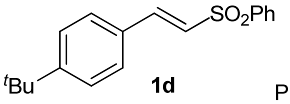
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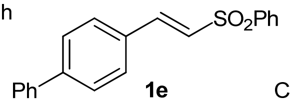
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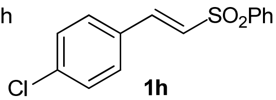
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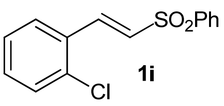
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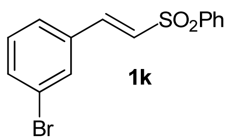
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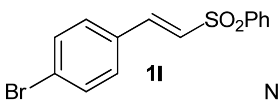
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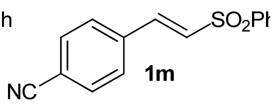
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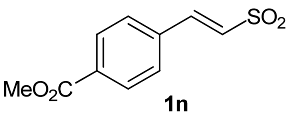
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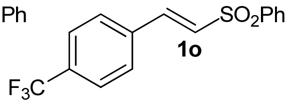
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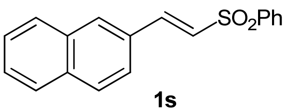
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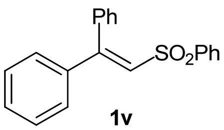
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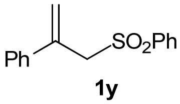
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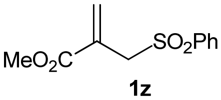
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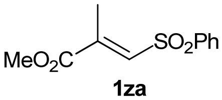
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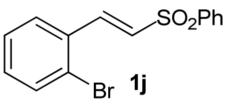
The following compounds were prepared according to general procedure **B**. Spectroscopic data of the sulfones are in good agreement with those previously reported. [1, 2c, 3]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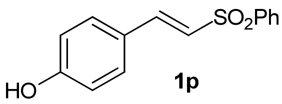
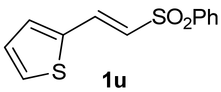

1p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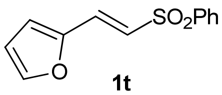
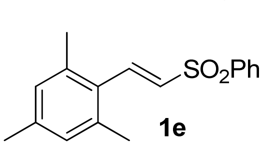

1t

(*E*)-1,3,5-Trimethyl-2-(2-(phenylsulfonyl)vinyl)benzene (1e)


1e

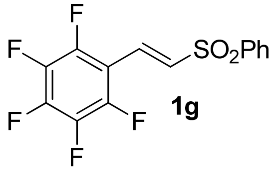
The reaction of 1,3,5-trimethyl-2-vinylbenzene (438.0 mg, 3.0 mmol) as outlined in general procedure **A** provided the title compound **1e** (670.0 mg, 78%) as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99-7.93 (m, 2H, 2×CH-aromatic), 7.87 (d, *J* = 15.7 Hz, 1H, CH-olefin), 7.67-7.50 (m, 3H, 3×CH-aromatic), 6.88 (s, 2H, 2×CH-aromatic), 6.54 (d, *J* = 15.7 Hz, 1H, CH-olefin), 2.29 (s, 6H, 2×CH_3), 2.27 (s, 3H, 1×CH_3) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.0, 140.9, 139.4, 137.1, 133.3, 131.7, 129.4, 129.3, 128.5, 127.5, 21.1, 21.0 ppm.

HRMS (ESI+) *m/z* calculated for $C_{17}H_{18}O_2SNa$ $[M+Na]^+$ 309.0925, found 309.0928

(*E*)-1,2,3,4,5-Pentafluoro-6-(2-(phenylsulfonyl)vinyl)benzene (1g)


1g

The reaction of 1,2,3,4,5-pentafluoro-6-vinylbenzene (271.0 µL, 2.0 mmol) as outlined in general procedure **A** provided the title compound **1g** (563.6 mg, 84%) as white solid.

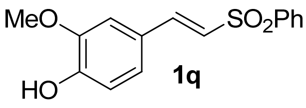
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00-7.91 (m, 2H, 2×CH-aromatic), 7.72-7.63 (m, 2H, 1×CH-aromatic, CH-olefin), 7.63-7.54 (m, 2H, 2×CH-aromatic), 7.22 (d, *J* = 15.9 Hz, 1H, CH-olefin) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.6-144.2 (m), 144.1-140.8 (m), 139.6, 139.6-136.2 (m), 135.4 (dt, *J* = 8.7, 2.8 Hz), 134.1, 129.7, 128.1, 126.0-125.9 (m), 108.2 (dt, *J* = 13.3, 4.2 Hz) ppm.

^{19}F NMR (470 MHz, $CDCl_3$) δ = -140.49 (d, *J* = 19.1 Hz), -151.10 (t, *J* = 20.0 Hz), -163.04 (t, *J* = 16.4 Hz) ppm.

HRMS (ESI+) *m/z* calculated for $C_{14}H_7F_5O_2SNa$ $[M+Na]^+$ 356.9985, found 356.9982

(*E*)-2-Methoxy-4-(2-(phenylsulfonyl)vinyl)phenol (1q)


1q

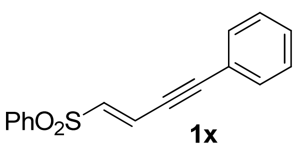
The reaction of vanillin (1.05 g, 7.0 mmol) as outlined in general procedure **B** provided the title compound **1q** (2.0 g, 98%) as a dense liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97-7.85 (m, 2H, 2×CH-aromatic), 7.61-7.44 (m, 4H, 3×CH-aromatic, CH-olefin), 7.01-6.92 (m, 2H, 2×CH-aromatic), 6.85 (d, *J* = 8.1 Hz, 1H, 1×CH-aromatic), 6.74 (d, *J* = 15.3 Hz, 1H, CH-olefin), 6.44 (br. s, 1H, OH), 3.81 (s, 3H, OCH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.9, 147.0, 142.9, 141.2, 133.3, 129.4, 127.6, 124.9, 124.4, 123.9, 115.0, 110.0, 56.1 ppm.

HRMS (ESI+) *m/z* calculated for $C_{15}H_{14}O_4SNa$ $[M+Na]^+$ 313.0511, found 313.0510

(*E*)-((4-Phenylbut-1-en-3-yn-1-yl)sulfonyl)benzene (1x)


1x

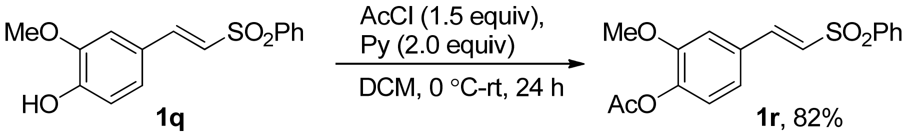
The reaction of (E)-5-phenylpent-2-en-4-ynal (260.0 mg, 2.0 mmol) as outlined in general procedure **B** provided the title compound **1x** (370.2 mg, 69%) as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97-7.87 (m, 2H, 2×CH-aromatic), 7.68-7.61 (m, 1H, 1×CH-aromatic), 7.60-7.52 (m, 2H, 2×CH-aromatic), 7.48-7.42 (m, 2H, 2×CH-aromatic), 7.40-7.30 (m, 3H, 3×CH-aromatic), 7.01 (d, *J* = 15.2 Hz, 1H, CH-olefin), 6.77 (d, *J* = 15.2 Hz, 1H, CH-olefin) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 139.8, 138.3, 133.7, 132.0, 129.8, 129.4, 128.5, 127.8, 123.4, 121.4, 100.9, 83.6 ppm.

HRMS (ESI+) *m/z* calculated for $C_{16}H_{13}O_2S$ $[M+H]^+$ 269.0631, found 269.0630

Synthesis of (*E*)-2-methoxy-4-(2-(phenylsulfonyl)vinyl)phenyl acetate (1r):



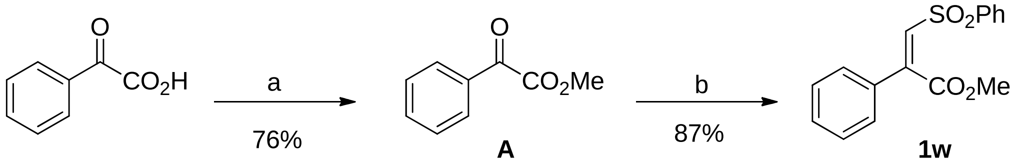
To a solution of (*E*)-2-methoxy-4-(2-(phenylsulfonyl)vinyl)phenol (609.0 mg, 2.1 mmol, 1.0 equiv) in DCM (21.0 mL, 0.1 M), pyridine (338.0 μL, 4.2 mmol, 2.0 equiv) was added at 0 °C. While maintaining the reaction temperature acetyl chloride (224.0 μL, 3.1 mmol, 1.5 equiv) was added to the solution. After complete addition of acetyl chloride, the reaction was brought to room temperature and stirring was continued for 24 h. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ solution (5.0 mL). The organic layer was extracted with DCM (3 x 15.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 2.3:1, R_f = 0.6) to afford the title compound **1r** (571.0 mg, 82%) as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 7.9 Hz, 2H, 2×CH-aromatic), 7.67-7.49 (m, 4H, 3×CH-aromatic, CH-olefin), 7.12-6.99 (m, 3H, 3×CH-aromatic), 6.83 (d, *J* = 15.4 Hz, 1H, CH-olefin), 3.81 (s, 3H, OCH_3), 2.29 (s, 3H, $CO\mathit{CH_3}$) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.7, 151.8, 142.4, 142.0, 140.9, 133.6, 131.4, 129.5, 127.8, 127.7, 123.7, 121.9, 111.9, 56.1, 20.7 ppm.

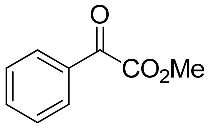
HRMS (ESI+) *m/z* calculated for $C_{17}H_{16}O_5SNa$ $[M+Na]^+$ 355.0616, found 355.0618

Synthesis of methyl 2-phenyl-3-(phenylsulfonyl)acrylate (1w):



Reaction conditions: a) $SOCl_2$ (1.2 equiv), MeOH (5.0 M), 0 °C - rt, 24 h. b) $PhSO_2Me$ (1.0 equiv), *n*-BuLi (1.6 M in hexanes,2.2 equiv), diethyl chlorophosphate (1.2 equiv), THF (0.16 M), -78 °C - rt, 24 h.

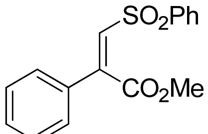
Methyl 2-oxo-2-phenylacetate (A)



A

Prepared according to the literature procedure.[4] To a stirred solution of 2-oxo-2-phenylacetic acid (1 g, 6.7 mmol, 1.0 equiv) in dry MeOH (1.4 mL) at -10 °C was added freshly distilled thionyl chloride (580.0 µL, 8.0 mmol, 1.2 equiv) dropwise over a period of 15 min. The solution was then brought to room temperature and stirring was continued for an additional 24 h. Excess thionyl chloride was removed by rotary evaporation, and the ester was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.5) to afford the title compound **A** (760.0 mg, 76%) as pale yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values. [4]

Methyl 2-phenyl-3-(phenylsulfonyl)acrylate (1w):



1w

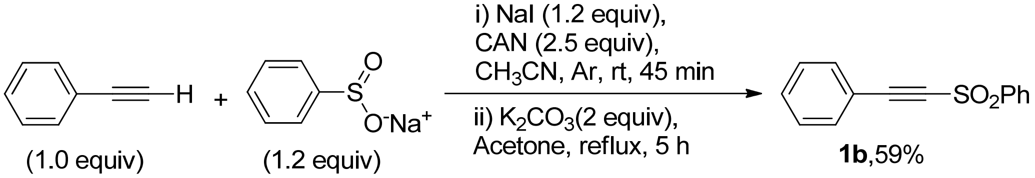
To a stirred solution of methylphenylsulfone (156.0 mg, 1.0 mmol, 1.0 equiv) in THF (0.16 M), *n*-BuLi (1.6 M in hexanes, 2.2 equiv) was added drop wise at 0 °C. While maintaining the reaction temperature, the yellow suspension was stirred for another 10 min before diethyl chlorophosphate (174.0 µL, 1.2 mmol, 1.2 equiv) was added to the solution. The resultant yellow solution was stirred at 0 °C for another 10 min before the reaction flask was placed in a –78 °C cooling bath. To the cold solution, methyl 2-oxo-2-phenylacetate (**A**) (164 mg, 1.0 mmol, 1.0 equiv) was added and the solution was allowed to warm to room temperature for overnight. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution. Organic layer was extracted with Et_2O (3 x 10 mL), washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, Hexane:EtOAc = 9:1, R_f = 0.3) to afford the title compound **1w** (264.0 mg, 87%) as white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 7.2 Hz, 2H, 2×CH-aromatic), 7.59-7.54 (m, 3H, 3×CH-aromatic), 7.44-7.38 (m, 5H, 5×CH-aromatic), 6.62 (s, 1H, CH-olefin), 4.02 (s, 3H, OCH_3) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.4, 146.1, 140.2, 133.8, 132.1, 131.2, 129.4, 129.2, 128.0, 126.9, 126.5, 53.1 ppm.

HRMS (ESI+) *m/z* calculated for $C_{16}H_{14}O_4SNa$ $[M+Na]^+$ 325.0511, found 325.0512.

***Synthesis of* (phenylethynyl)sulfonyl)benzene[5] (1b):**

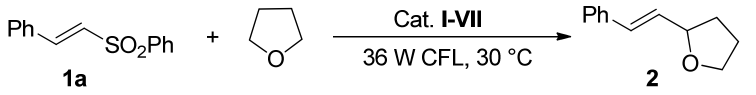


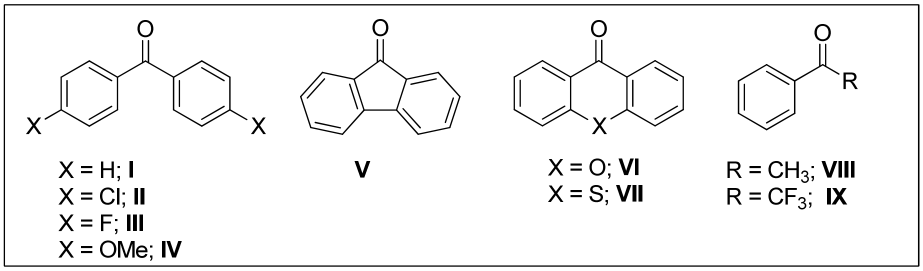
1b,59%

To a mixture of phenylacetylene (330.0 μL, 3.0 mmol, 1.0 equiv), benzenesulfinic acid sodium salt (591.0 mg, 3.6 mmol, 1.2 equiv) and NaI (540.0 mg, 3.6 mmol, 1.2 equiv) in anhydrous CH_3CN (0.07 M, 25 mL), was added a solution of CAN (4.1 g, 7.5 mmol, 2.5 equiv; in anhydrous CH_3CN, 20 mL) under argon atmosphere. After the complete consumption of phenylacetylene, the reaction mixture was diluted with CH_2Cl_2. The organic layer was separated, washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. To the residue anhydrous acetone (0.2 M, 30 mL) and K_2CO_3 (830.0 mg, 6.0 mmol, 2.0 equiv) were added. The mixture was then heated under reflux for 5 h. The reaction mixture was brought to room temperature and washed with H_2O (20 mL). The organic compound was extracted with CH_2Cl_2 (3x15 mL). The combined organic extracts were washed with brine (5 mL) and dried over anhydrous $Na_2S_2O_3$. The solvent was concentrated under reduced pressure. The crude product was purified by column to afford the title compound **1b** (429.0 mg, 59%) as pale yellow solid

Reaction Optimization:

Table 1: Catalyst Screening:



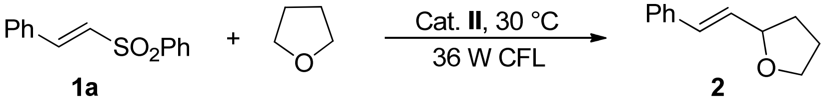


Entry[a]	Catalyst	Time (h)	Yield (%)
1	**I**	60	51
2	**II**	48	53
3	**III**	48	48
4	**IV**	48	36
5	**V**	48	22
6	**VI**	48	48
7	**VII**	51	45
8	**VIII**	48	19
9	**IX**	48	17

[a] Reaction conditions: a solution of **1a** (0.2 mmol, 1.0 equiv) and cat. **I-IX** (20.0 mol%) in THF (1.34 mL, 0.15 M) was allowed to stir in front of a 36 W CFL bulb; yields refer to the isolated product **2**.

To identify an appropriate photocatalyst for the reaction, various aromatic ketones were examined in this reaction. Among these ketones, benzophenone and 4,4'-dichlorobenzophenone were found to be most effective for our reaction, furnishing the desired product **2** in 51% and 53% yield, respectively. Furthermore, a slight improvement on the rate of the reaction was realized with 4,4'-dichlorobenzophenone. Hence, further optimization studies was then continued using 4,4'-dichlorobenzophenone as catalyst.

Table 2: Concentration Screening:

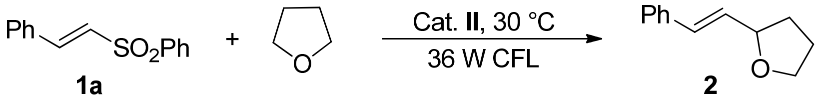


Entry[a]	Conc.(M)[b]	Time (h)	Catalyst	Yield (%)
1	0.30	48	**II**	25
2	0.15	48	**II**	53
3	0.10	48	**II**	66
4	0.05	24	**II**	80
5	0.02	18	**II**	97
6	0.02	18	**I**	59
7	0.02	51	**VII**	61

[a]Reaction conditions: a solution of **1a** (0.2 mmol, 1.0 equiv) and cat. **II** (20.0 mol%) in THF was allowed to stir in front of a 36 W CFL bulb; yields refer to the isolated product **2**. [b]Conc. with respect to **1a**.

To improve isolated yield of the final product of the reaction, we next performed the reaction varying with concentration of the reaction mixture with respect to the vinyl sulfone. By using a dilute reaction concentration 0.02 (M), a remarkable improvement on the rate as well as isolated yield of the reaction were realized.

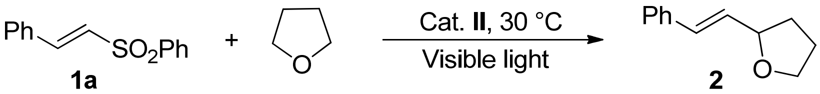
Table 3: Catalyst loading variation:



Entry[a]	Catalyst mol%	Time (h)	Yield (%)
1	25	18	98
2	20	18	97
3	15	20	76
4	10	24	55
5	-	24	NR

[a]Reaction conditions: a solution of **1a** (0.2 mmol, 1.0 equiv) and cat. **II** in THF (10.0 mL, 0.02 M) was allowed to stir in front of a 36 W CFL bulb; yields refer to the isolated product **2**. NR = No reaction.

Table 4: Variation of light source:



Entry[a]	Light source	Time (h)	Yield (%)
1	27 W CFL bulb	24	92
2	30 W Blue LED (λ=450-490 nm)	47	55
3	40 W White LED (λ=550-650 nm)	48	42
4	36 W CFL bulb	18	97
5[b]	UV Lamp (λ=350 nm)	1	60
6	Sunlight	6	82

[a]Reaction conditions: a solution of **1a** (0.2 mmol, 1.0 equiv) and cat. **II** (20.0 mol%) in THF (10.0 mL, 0.02 M) was allowed to stir in front of a visible light source; yields refer to the isolated product **2**. [b]Catalyst destroyed completely.

To study the effect of light source on our photocatalytic C-H vinylation reaction, we carried out the model reaction with different light sources. The results are summarized in Table 4. It was observed that the reaction can be performed using blue as well as white LED. However, the reaction exhibited a very sluggish reactivity with LED light, delivering the desired product **2** in moderate yield with an extended reaction time (entry 2 and entry 3). On the contrary, when the reaction was carried out using 36 W CFL bulb, an excellent yield of the final product was obtained along with good catalyst recovery in 18 h (entry 4). The complete consumption of the starting sulfone was obtained within an hour while performing the reaction with high energy UV Lamp (λ=350 nm). However, only moderate yield of the desired product was obtained along with complete decomposition of the photocatalyst (entry 5). Sunlight also found to be suitable for our method (entry 6).

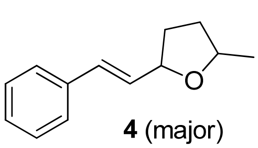
General Procedure I: C-H vinylation of ethers:

To an oven dried screw cap tube (10 mL) equipped with a magnetic stir bar, charged with sulphone (1.0 equiv) and photocatalyst (20.0-30.0 mol%, amount is specified in the individual experiment) followed by ether (10.0 mL, 0.02 M). The resultant reaction mixture was placed in front of a 36 W household CFL bulb and allowed to stir at room temperature (30 °C) for 12-83 h (appropriate reaction time is specified in the individual experiment). After complete consumption of starting sulfone (confirmed by TLC analysis), reaction mixture was neutralized with saturated aqueous solution of $NaHCO_3$ (2.0 mL). The mixture was diluted with distilled water (4.0 mL) and the organic layer was extracted with ethyl acetate (3 x 4.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography to afford the desired product.

General Procedure II: C-H vinylation of amides:

To an oven dried screw cap tube (10 mL) equipped with a magnetic stir bar, charged with sulphone (1.0 equiv) and photocatalyst (20.0-30.0 mol%, amount is specified in the individual experiment) followed by amide (10.0 mL, 0.02 M). The resultant reaction mixture was placed in front of a 36 W household CFL bulb and allowed to stir at room temperature (30 °C) for 20-108 h (reaction time is specified in the individual experiments). After complete consumption of starting sulfone (confirmed by TLC analysis), the reaction mixture was diluted with distilled water (50.0 mL) and the organic layer was extracted with ethyl acetate (3 x 20.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography to afford the desired product.

***(E)*-2-Methyl-5-styryltetrahydrofuran (4)**



4 (major)

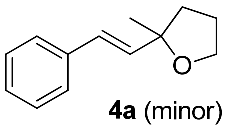
Prepared according to GP-I, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in 2-methyltetrahydrofuran (10.0 mL, 0.02 M) for 22 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 99:1, R_f = 0.25) to afford the title compound **4** as an inseparable mixture of diastereoisomers with dr = 1.5:1 (25.2 mg, 67%, 98:2 *E:Z*) as colourless liquid along with minor regioisomer **4a** (7.4 mg, 20%, 97:3 *E:Z*) as colourless liquid with rr = 3.4:1 ratio. The Spectroscopic data are in good agreement with the previously reported values.[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42-7.34 (m, 3H, 3×CH-aromatic$_{major}$), 7.34-7.28 (m, 2H, 2×CH-aromatic$_{major}$), 7.28-7.18 (m, 5H, 5×CH-aromatic$_{minor}$), 6.59 (d, *J* = 15.8 Hz, 1H, ArC*H*=CH$_{minor}$), 6.57 (d, *J* = 15.8 Hz, 1H, ArC*H*=CH$_{major}$), 6.22 (dd, *J* = 15.8, 6.9 Hz, 1H, ArCH=C*H*$_{minor}$), 6.20 (dd, *J* = 15.8, 6.7 Hz, 1H, ArCH=C*H*$_{major}$), 4.68-4.56 (m, 1H, *CH*OCHMe$_{major}$), 4.50-4.41 (m, 1H, *CH*OCHMe$_{minor}$), 4.29-4.16 (m, 1H, CHO*CH*Me$_{major}$), 4.13-4.01 (m, 1H, CHO*CH*Me$_{minor}$), 2.27-1.98 (m, 4H, C*H*H*CH*$_{2major}$, C*H*HCH$_{2minor}$), 1.84-

1.71 (m, 2H, $CHHCH_{2major}$, $CHHCH_{2minor}$), 1.56-1.48 (m, 2H, CH_{2minor}), 1.31 (d, J = 6.1 Hz, 3H, CH_{3minor}), 1.27 (d, J = 6.1 Hz, 3H, CH_{3major}) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ = 137.0, 136.9, 131.1, 130.6, 130.6, 128.5, 127.4, 127.4, 126.5, 126.4, 80.0, 79.2, 75.8, 75.2, 34.0, 33.2, 33.0, 32.4, 21.4, 21.3 ppm.

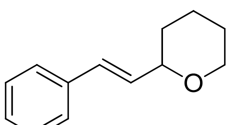
***(E)*-2-Methyl-2-styryltetrahydrofuran** (**4a**)



4a (minor)

(SiO_2, Hexane:EtOAc = 99:1, R_f = 0.28)
(7.4 mg, 20%, 97:3 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[7]

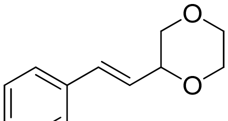
***(E)*-2-Styryltetrahydro-2H-pyran** (**5**)



5

Prepared according to GP-I, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THP (10.0 mL, 0.02 M) for 41 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 49:1, R_f = 0.4) to afford the title compound **5** (33.5 mg, 89%, 94:6 *E:Z*) as colourless liquid. Spectroscopic data are in agreement with those previously reported.[7-8]

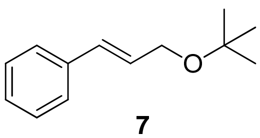
***(E)*-2-Styryl-1,4-dioxane** (**6**)



6

Prepared according to GP-I, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in 1,4-dioxane (10.0 mL, 0.02 M) for 45 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.3) to afford the title compound **6** (23.5 mg, 62%, 85:15 *E:Z*) as white solid. Spectroscopic data are in agreement with those previously reported.[7-8]

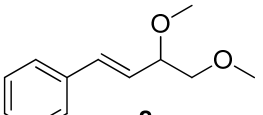
***(E)*-(3-(tert-Butoxy)prop-1-en-1-yl)benzene** (**7**)



7

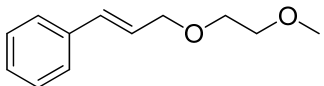
Prepared according to GP-I, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **I** (11.0 mg, 0.06 mmol, 30.0 mol%) in TBME (10.0 mL, 0.02 M) for 82 h in front of a 36 W & 23 W household CFL bulb. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 49:1, R_f = 0.6) to afford the title compound **7** (23.7 mg, 62%, 97:3 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[9]

(E)-(3,4-Dimethoxybut-1-en-1-yl)benzene (8a) & *(E)*-(3-(2-Methoxyethoxy)prop-1-en-1-yl)benzenene (8b)



8a

+



8b

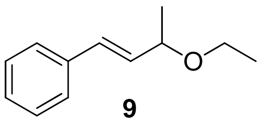
Prepared according to GP-I, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **I** (7.2 mg, 0.04 mmol, 20.0 mol%) in 1,2-dimethoxyethane (10.0 mL, 0.02 M) for 83 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 9:1, R_f = 0.4) to afford the regioisomeric products **8a** and **8b** as an inseparable mixture (20.4 mg, 53% combined yield, 96:4 *E:Z*) with rr = 1.5:1 ratio (determined by GC analysis) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[10]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45-7.36 (m, 4H, 2×CH-aromatic$_{major}$, 2×CH-aromatic$_{minor}$), 7.36-7.30 (m, 3H, 3×CH-aromatic$_{major}$), 7.29-7.20 (m, 3H, 3×CH-aromatic$_{minor}$), 6.57 (d, *J* = 16.0 Hz, 1H, ArC*H*=CH$_{major}$), 6.54 (d, *J* = 15.9 Hz, 1H, ArC*H*=CH$_{minor}$), 6.31 (td, *J* = 15.9, 6.1 Hz, 1H, ArCH=C*H*$_{minor}$), 6.10 (dd, *J* = 16.0, 7.8 Hz, 1H, ArCH=C*H*$_{major}$), 4.20 (dd, *J* = 6.1, 1.3 Hz, 2H, $CH_2OCH_2CH_{2minor}$), 4.01-3.93 (m, 1H, $CHOCH_{3major}$), 3.68-3.62 (m, 2H, $CH_2OCH_2CH_2O_{minor}$), 3.61-3.55 (m, 2H, $CH_2OCH_2CH_2O_{minor}$), 3.54-3.46 (m, 2H, $CHCH_2OCH_{3major}$), 3.41 (s, 3H, OCH_{3major}), 3.41 (s, 3H, OCH_{3major}), 3.39 (s, 3H, OCH_{3minor}) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.7, 136.3, 133.6, 132.6, 128.6, 128.5, 127.9, 127.6, 126.5, 126.8, 126.0, 81.4, 75.6, 72.0, 71.9, 69.3, 59.3, 59.1, 56.7 ppm.

HRMS (ESI$^+$) *m/z* calculated for $C_{12}H_{16}O_2Na$ $[M+Na]^+$ 215.1048, found 215.1049.

(E)-(3-Ethoxybut-1-en-1-yl)benzene (9)



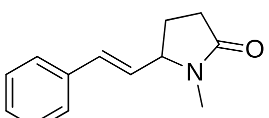
9

Prepared according to GP-I, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **I** (7.2 mg, 0.04 mmol, 20.0 mol%) in diethyl ether (10.0 mL, 0.02 M) for 94 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 49:1, R_f = 0.4) to afford the title compound **9** (9.6 mg, 27%, 43% NMR yield using mesitylene as internal standard, 78:22 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[7]

^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.35-7.29 (m, 2H, 2×CH-aromatic$_{\text{major}}$), 7.28-7.21 (m, 2H, 2×CH-aromatic$_{\text{major}}$), 7.19-7.12 (m, 6H, 1×CH-aromatic$_{\text{major}}$, 5×CH-aromatic$_{\text{minor}}$), 6.51 (d, *J* = 11.8 Hz, 1H, ArC*H*=CH$_{\text{minor}}$), 6.44 (d, *J* = 15.9 Hz, 1H, ArC*H*=CH$_{\text{major}}$), 6.05 (dd, *J* = 15.9, 7.5 Hz, 1H, ArCH=*CH*$_{\text{major}}$), 5.54 (dd, *J* = 11.8, 9.1 Hz, 1H, ArCH=*CH*$_{\text{minor}}$), 4.32 (dqd, *J* = 9.1, 6.3, 0.6 Hz, 1H, HCO$_{\text{minor}}$), 4.00-3.87 (m, 1H, HCO$_{\text{major}}$), 3.50 (qd, *J* = 9.3, 7.0 Hz, 1H, OC*H*HCH$_{3\text{major}}$), 3.43-3.28 (m, 2H, OCH*H*CH$_{3\text{major}}$, OC*H*HCH$_{3\text{minor}}$), 3.20 (qd, *J* = 9.2, 7.0 Hz, 1H, OCH*H*CH$_{3\text{minor}}$), 1.27 (d, *J* = 6.3 Hz, 3H, CH*CH*$_{3\text{minor}}$), 1.26 (d, *J* = 6.3 Hz, 3H, CH*CH*$_{3\text{major}}$), 1.14 (t, *J* = 7.0 Hz, 3H, CH$_2$*CH*$_{3\text{major}}$), 1.06 (t, *J* = 7.0 Hz, 3H, CH$_2$*CH*$_{3\text{ minor}}$) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) δ = 137.0, 136.7, 135.3, 132.2, 130.7, 130.6, 128.7, 128.5, 128.2, 127.5, 127.0, 126.4, 76.3, 70.8, 63.6, 63.3, 29.7, 21.7, 21.2, 15.4 ppm.

***(E)*-1-Methyl-5-styrylpyrrolidin-2-one (10)**



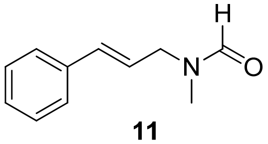
10

Prepared according to GP-II, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in NMP (10.0 mL, 0.02 M) for 35 h. The crude material was purified by column chromatography (SiO$_2$, Hexane:EtOAc = 1:2.4, R$_f$ = 0.3) to afford the title compound **10** (31.3 mg, 78% combined yield, 97:3 *E:Z*) as an inseparable mixture the regioisomer in rr = 7.3:1 ratio (determined by GC analysis) as yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[11]

^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.42-7.32 (m, 4H, 4×CH-aromatic$_{\text{major}}$), 7.32-7.25 (m, 6H, 1×CH-aromatic$_{\text{major}}$, 5×CH-aromatic$_{\text{minor}}$), 6.56 (d, *J* = 15.7 Hz, 2H, ArC*H*=CH$_{\text{major}}$, ArC*H*=CH$_{\text{minor}}$), 6.17-6.06 (m, 1H, ArCH=*CH*$_{\text{minor}}$), 6.02 (dd, *J* = 15.7, 8.5 Hz, 1H, ArCH=*CH*$_{\text{major}}$), 4.15-4.01 (m, 3H, *CH*NMe$_{\text{major}}$, *CH$_2$*NCO$_{\text{minor}}$), 3.43-3.36 (m, 2H, *CH$_2$*NCH$_{2\text{minor}}$), 2.78 (s, 3H, NCH$_{3\text{major}}$), 2.56-2.52 (m, 1H, *CH*HCON$_{\text{minor}}$), 2.51-2.37 (m, 2H, CO*CH*$_{2\text{major}}$), 2.36-2.24 (m, 1H, COCH$_2$C*H*H$_{\text{major}}$), 2.06-1.98 (m, 3H, *CH$_2$*CH*H*CON$_{\text{minor}}$), 1.89-1.81 (m, 1H, COCH$_2$CH*H*$_{\text{major}}$) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) δ = 175.0, 174.8, 136.4, 135.9, 133.3, 133.0, 128.8, 128.7, 128.6, 128.1, 127.8, 126.5, 126.4, 123.9, 62.9, 46.7, 44.7, 30.1, 30.0, 27.9, 25.7, 17.7 ppm.

N-Cinnamyl-N-methylformamide (11)

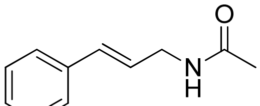

11

Prepared according to GP-II, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in DMF (10.0 mL, 0.02 M) for 68 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1, R_f = 0.3) to afford the title compound **11** as an inseparable mixture of rotamer in 1.4:1 ratio (23.8 mg, 68%, 97:3 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[11b]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.15 (s, 1H, HCO $_{rotamer1}$), 8.10 (s, 1H, HCO $_{rotamer2}$), 7.40-7.23 (m, 10H, 5×CH-aromatic$_{rotamer1,}$ 5×CH-aromatic$_{rotamer2}$), 6.59-6.48 (m, 2H, ArC*H*=CH $_{rotamer1}$, ArC*H*=CH $_{rotamer2}$), 6.08 (dtd, *J* = 15.9, 6.4, 6.2, 1.7 Hz, 2H, ArCH=C*H* $_{rotamer1}$, ArCH=C*H* $_{rotamer2}$), 4.10 (dd, *J* = 6.4, 1.1 Hz, 2H, CH_2NMe $_{rotamer2}$), 3.98 (dd, *J* = 6.2, 1.4 Hz, 2H, CH_2NMe $_{rotamer1}$), 2.93 (s, 3H, NCH_3 $_{rotamer2}$), 2.88 (s, 3H, NCH_3 $_{rotamer1}$) ppm.

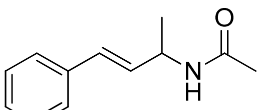
^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.6, 162.3, 136.3, 135.9, 133.6, 128.7, 128.6, 128.5, 128.1, 127.8, 126.4, 126.3, 123.9, 123.2, 51.6, 46.1, 34.0, 29.5 ppm.

N-Cinnamylacetamide (12):


12

Prepared according to GP-II, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in *N*-methylacetamide (10.0 mL, 0.02 M) for 36 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1.5:1, R_f = 0.4) to afford the title compound **12** (23.2 mg, 66%, 95:5 *E:Z*) as white coloured solid. The Spectroscopic data are in good agreement with the previously reported values.[11b]

***(E)*-N-(4-Phenylbut-3-en-2-yl)acetamide (13)**

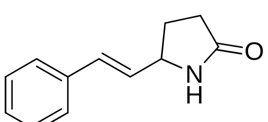

13

Prepared according to GP-II, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in *N*-ethylacetamide (10.0 mL, 0.02 M) for 36 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1.5:1, R_f = 0.3) to afford the title compound **13** (29.3 mg, 78%, 90:10 *E:Z*) as white colour solid. The Spectroscopic data are in good agreement with the previously reported values.[12]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.18 (m, 10H, 5×CH-aromatic$_{major}$, 5×CH-aromatic$_{minor}$), 6.50 (dd, *J* = 16.0, 1.1 Hz, 2H, Ar*CH*=CH$_{major}$, Ar*CH*=CH$_{minor}$), 6.16 (dd, *J* = 16.0, 5.7 Hz, 1H, ArCH=*CH*$_{major}$), 5.76 (br. d, *J* = 6.2 Hz, 1H, NH), 5.51 (dd, *J* = 11.6, 9.1 Hz, 1H, ArCH=*CH*$_{minor}$), 5.05-4.93 (m, 1H, *CH*NH$_{minor}$), 4.82-4.65 (m, 1H, *CH*NH$_{major}$), 2.00 (s, 3H, COCH$_{3major}$), 1.91 (s, 3H, COCH$_{3minor}$), 1.32 (d, *J* = 6.8 Hz, 3H, CH*CH*$_{3major}$), 1.26 (d, *J* = 6.5 Hz, 3H, CH*CH*$_{3minor}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.2, 169.0, 136.6, 136.3, 132.7, 130.9, 130.2, 129.6, 128.6, 128.5, 128.3, 127.5, 127.2, 126.3, 46.4, 43.8, 23.4, 23.3, 21.9, 20.5 ppm.

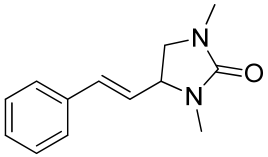
***(E)*-5-Styrylpyrrolidin-2-one (14)**



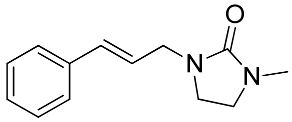
14

Prepared according to GP-II, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in 2-pyrrolidone (10.0 mL, 0.02 M) for 58 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:9, R_f = 0.4) to afford the title compound **14** (26.6 mg, 71%, 97:3 *E:Z*) as white colour solid. The Spectroscopic data are in good agreement with the previously reported values.[11]

***(E)*-1,3-Dimethyl-4-styrylimidazolidin-2-one (15); 1-Cinnamyl-3-methylimidazolidin-2-one (15a)**



15



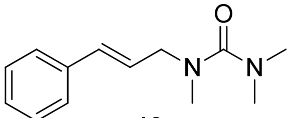
15a

Prepared according to GP-II, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in 1,3-dimethyl-2-imidazolidinone (DMEU) (10.0 mL, 0.02 M) for 35 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1.5:1, R_f = 0.3) to afford the regioisomeric products **15** and **15a** as an inseparable mixture (40.4 mg, 94% combined yield, 98:2 *E:Z*) with rr = 4:1 (determined by GC analysis) as colourless liquid. Spectroscopic data are in agreement with those previously reported.[11a, 13]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42-7.36 (m, 2H, 2×CH-aromatic$_{major}$), 7.36-7.24 (m, 8H, 3×CH-aromatic$_{major}$, 5×CH-aromatic$_{minor}$), 6.62 (d, *J* = 15.8 Hz, 1H, Ar*CH*=CH$_{major}$), 6.52 (d, *J* = 15.9 Hz, 1H, Ar*CH*=CH$_{minor}$), 6.20-6.10 (m, 1H, ArCH=*CH*$_{minor}$), 6.05 (dd, *J* = 15.8, 8.6 Hz, 1H, ArCH=*CH*$_{major}$), 4.02-3.90 (m, 3H, *CH*NCH$_{3major}$, *CH$_2$*NCO$_{minor}$), 3.51 (t, *J* = 8.4 Hz, 1H, *CH*HNCH$_{3major}$), 3.29 (s, 4H, 2×CH$_2$N$_{minor}$), 3.03 (t, *J* = 8.4 Hz, 1H, CH*H*NCH$_{3major}$), 2.81 (s, 6H, NCH$_{3major}$, NCH$_{3minor}$), 2.72 (s, 3H, NCH$_{3major}$) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) δ = 161.5, 161.3, 136.5, 135.8, 134.2, 132.8, 128.6, 128.5, 128.2, 127.6, 127.3, 126.5, 126.3, 125.0, 58.9, 51.6, 46.7, 45.1, 42.3, 31.4, 31.3, 29.4 ppm.

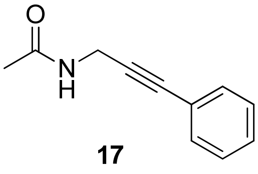
1-Cinnamyl-1,3,3-trimethylurea (**16**)



16

Prepared according to GP-II, combining *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**)(48.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in tetramethylurea (10.0 mL, 0.02 M) for 35 h. The crude material was purified by column chromatography (SiO$_2$, Hexane:EtOAc = 1.5:1, R$_f$ = 0.4) to afford the title compound **16** (38.8 mg, 89%, 97:3 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[13]

N-(3-Phenylprop-2-yn-1-yl)acetamide (**17**)



17

Prepared according to GP-II, combining ((phenylethynyl)sulfonyl)benzene (**1b**) (24.2 mg, 0.1 mmol, 1.0 equiv), and Cat. **II** (5.0 mg, 0.02 mmol, 20.0 mol%) in *N*-methylacetamide (5.0 mL, 0.02 M) for 13 h. The crude material was purified by column chromatography (SiO$_2$, Hexane:EtOAc = 1:1, R$_f$ = 0.5) to afford the title compound **17** (11.5 mg, 66%) as colourless liquid.

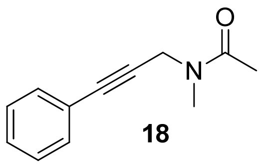
^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.45-7.37 (m, 2H, 2×CH-aromatic), 7.34-7.27 (m, 3H, 3×CH-aromatic), 5.72 (br. s, 1H, NH), 4.28 (d, *J* = 5.1 Hz, 2H, *CH$_2$*NH), 2.03 (s, 3H, CO*CH$_3$*) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) δ = 169.6, 131.7, 128.5, 128.3, 122.5, 84.7, 83.5, 30.1, 23.1 ppm.

IR (Neat) ῡ = 2205, 1680, 1604 cm^{-1}.

HRMS (ESI+) *m/z* calculated for$C_{11}H_{11}NONa$ [M+Na]$^+$ 196.0738, found 196.0737

N-Methyl-N-(3-phenylprop-2-yn-1-yl)acetamide (**18**)

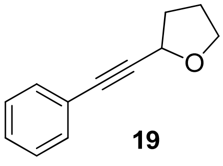


18

Prepared according to GP-II, combining ((phenylethynyl)sulfonyl)benzene (**1b**) (48.4 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in DMA (10.0

mL, 0.02 M) for 14 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1.5:1, $R_f = 0.3$) to afford the title compound **18** (21.2 mg, 54%) as pale yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[14]

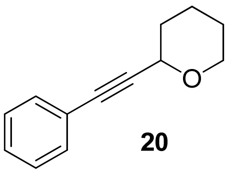
2-(Phenylethynyl)tetrahydrofuran (**19**)



19

Prepared according to GP-I, combining ((phenylethynyl)sulfonyl)benzene (**1b**) (48.4 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 36 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.4$) to afford the title compound **19** (29.8 mg, 87%) as pale yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[14]

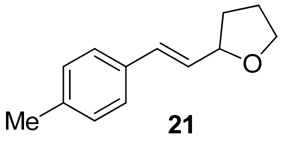
2-(Phenylethynyl)tetrahydro-2H-pyran (**20**)



20

Prepared according to GP-I, combining ((phenylethynyl)sulfonyl)benzene (**1b**) (24.2 mg, 0.1 mmol, 1.0 equiv), and Cat. **II** (5.0 mg, 0.02 mmol, 20.0 mol%) in THP (5.0 mL, 0.02 M) for 17 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.5$) to afford the title compound **20** (9.8 mg, 53%) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[14]

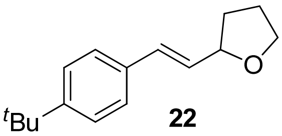
***(E)*-2-(4-Methylstyryl)tetrahydrofuran** (**21**)



21

Prepared according to GP-I, combining *(E)*-1-methyl-4-(2-(phenylsulfonyl)vinyl)benzene (51.6 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 24 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.5$) to afford the title compound **21** (23.6 mg, 63%, 96:4 *E:Z*) as colourless liquid. Spectroscopic data are in agreement with those previously reported.[7, 15]

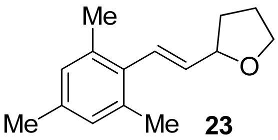
***(E)*-2-(4-(*tert*-Butyl)styryl)tetrahydrofuran** (**22**)



22

Prepared according to GP-I, combining *(E)*-1-(*tert*-butyl)-4-(2-(phenylsulfonyl)vinyl)benzene (60.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 24 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.5$) to afford the title compound **22** (34.4 mg, 75%, 83:17 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[16]

***(E)*-2-(2,4,6-Trimethylstyryl)tetrahydrofuran** (**23**)



23

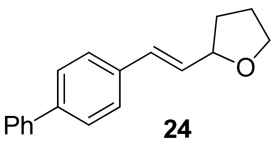
Prepared according to GP-I, combining *(E)*-1,3,5-trimethyl-2-(2-(phenylsulfonyl)vinyl)benzene (57.2 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 60 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.5$) to afford the title compound **23** (20.5 mg, 47%, 95:5 *E:Z*) as colourless liquid.

^{1}H NMR (300 MHz, Acetone-*d₆*) δ = 6.83 (s, 2H, 2×CH-aromatic), 6.52 (d, *J* = 16.2 Hz, 1H, ArC*H*=CH), 5.67 (dd, *J* = 16.2, 6.3 Hz, 1H, ArCH=C*H*), 4.49-4.38 (m, 1H, ArCH=CHC*H*O), 3.94-3.83 (m, 1H, OC*H*H), 3.74 (dt, *J* = 7.8, 6.6 Hz, 1H, OCH*H*), 2.22 (s, 6H, 2×CH_3), 2.21 (s, 3H, 1×CH_3), 2.18-2.06 (m, 1H, ArCH=CHCHC*H*H), 2.00-1.86 (m, 2H, OCH_2*CH_2*), 1.76-1.62 (m, 1H, ArCH=CHCHCH*H*) ppm.

^{13}C NMR (75 MHz, Acetone-*d₆*) δ = 138.0, 137.5, 137.3, 135.6, 130.2, 128.9, 81.4, 69.3, 34.2, 27.4, 21.9 ppm.

HRMS (ESI+) *m/z* calculated for $C_{15}H_{20}O$ $[M+H]^+$ 217.1587, found 217.1585.

***(E)*-2-(2-([1,1'-Biphenyl]-4-yl)vinyl)tetrahydrofuran** (**24**)



24

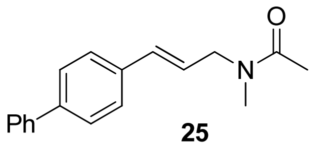
Prepared according to GP-I, combining *(E)*-4-(2-(phenylsulfonyl)vinyl)-1,1'-biphenyl (64.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 35 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.4$) to afford the title compound **24** (36.5 mg, 73%, 87:13 *E:Z*) as white colour solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.64-7.52 (m, 4H, 4×CH-aromatic), 7.50-7.40 (m, 4H, 4×CH-aromatic), 7.38-7.30 (m, 1H, CH-aromatic), 6.64 (d, *J* = 15.9 Hz, 1H, ArC*H*=CH), 6.27 (dd, *J* = 15.9, 6.6 Hz, 1H, ArCH=C*H*), 4.51 (dt, *J* = 7.5, 0.9 Hz, 1H, ArCH=CHC*H*O), 4.05-3.95 (m, 1H, OC*H*H), 3.86 (dt, *J* = 8.1, 7.8, 6.3 Hz, 1H, OCH*H*), 2.22-2.09 (m, 1H, ArCH=CHCHC*H*H), 2.06-1.92 (m, 2H, OCH_2*CH_2*), 1.81-1.68 (m, 1H, ArCH=CHCHCH*H*) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.7, 140.2, 135.9, 130.6, 129.9, 128.7, 127.2, 127.1, 126.9, 126.8, 79.6, 68.2, 32.4, 25.9 ppm.

HRMS (ESI+) *m/z* calculated for $C_{18}H_{18}OK$ $[M+K]^+$ 289.0995, found 289.0998.

(E)-N-(3-([1,1'-Biphenyl]-4-yl)allyl)-N-methylacetamide (25)



25

Prepared according to GP-II, combining *(E)*-4-(2-(phenylsulfonyl)vinyl)-1,1'-biphenyl (64.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in DMA (10.0 mL, 0.02 M) for 45 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1, R_f = 0.3) to afford the title compound **25** as an inseparable mixture of rotamer in 1:1 ratio (42.3 mg, 80% overall yield, 73:27 *E:Z*) as white colour solid.

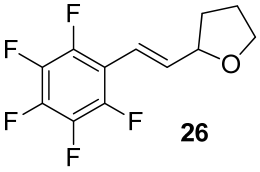
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.64-7.53 (m, 8H, 4×CH-aromatic$_{\text{rotamer1,}}$4×CH-aromatic$_{\text{rotamer2}}$), 7.49-7.39 (m, 8H, 4×CH-aromatic$_{\text{rotamer1,}}$4×CH-aromatic$_{\text{rotamer2}}$), 7.38-7.30 (m, 2H, 1×CH-aromatic$_{\text{rotamer1,}}$1×CH-aromatic$_{\text{rotamer2}}$), 6.53 (d, *J* = 15.9 Hz, 1H, ArC*H*=CH $_{\text{rotamer1}}$), 6.51 (d, *J* = 15.9 Hz, 1H, ArC*H*=CH $_{\text{rotamer2}}$), 6.25-6.10 (m, 2H, ArCH=C*H* $_{\text{rotamer1,}}$ ArCH=C*H* $_{\text{rotamer2}}$), 4.17 (dd, *J* = 6.6, 0.7 Hz, 2H, *CH_2*NMe $_{\text{rotamer1}}$), 4.08 (dd, *J* = 5.4, 1.5 Hz, 2H, *CH_2*NMe $_{\text{rotamer2}}$), 3.00 (s, 3H, N*CH_3* $_{\text{rotamer1}}$), 2.99 (s, 3H, N*CH_3* $_{\text{rotamer2}}$), 2.16 (s, 3H, CO*CH_3* $_{\text{rotamer1}}$), 2.14 (s, 3H, CO*CH_3* $_{\text{rotamer2}}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.8, 170.5, 140.7, 140.6, 140.5, 140.4, 135.6, 135.1, 132.3, 131.3, 128.8, 128.7, 127.4, 127.3, 127.3, 127.2, 126.9, 126.8, 126.8, 124.7, 123.7, 52.6, 49.3, 35.4, 33.5, 21.8, 21.3 ppm.

IR (Neat) $\bar{\upsilon}$ = 1625 cm^{-1}.

HRMS (ESI+) *m/z* calculated for $C_{18}H_{19}NONa$ $[M+Na]^+$ 288.1364, found 288.1365

(E)-2-(2-(Perfluorophenyl)vinyl)tetrahydrofuran (26)



26

Prepared according to GP-I, combining *(E)*-1,2,3,4,5-pentafluoro-6-(2-(phenylsulfonyl)vinyl)benzene (66.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 14 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.4) to afford the title compound **26** (44.2 mg, 84%, 89:11 *E:Z*) as colouriess liquid.

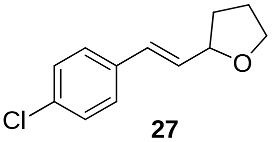
^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.63-6.47 (m, 2H, ArC*H*=C*H*), 4.50 (dt, *J* = 7.0, 4.3 Hz, 1H, ArCH=CHC*H*O), 4.04-3.93 (m, 1H, OC*H*H), 3.92-3.81 (m, 1H, OCH*H*), 2.24-2.10 (m, 1H, ArCH=CHCHC*H*H), 2.04-1.90 (m, 2H, OCH_2*CH_2*), 1.80-1.64 (m, 1H, ArCH=CHCHCH*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.8-143.7 (m), 140.9-138.6 (m), 140.1 (t, *J* = 7.0 Hz), 138.9-136.6 (m), 113.9, 111.9-111.7 (m), 79.4, 68.4, 32.2, 25.7 ppm.

^{19}F NMR (125 MHz, $CDCl_3$) δ = -146.2 (dd, *J* = 21.3, 7.4 Hz), -159.9-(-160.0) (m), -166.5 (dt, *J* = 21.3, 7.8 Hz) ppm.

HRMS (ESI+) *m/z* calculated for $C_{12}H_9F_5ONa$ $[M+Na]^+$ 287.0471, found 287.0470.

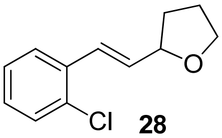
(E)-2-(4-Chlorostyryl)tetrahydrofuran (27)



27

Prepared according to GP-I, combining *(E)*-1-chloro-4-(2-(phenylsulfonyl)vinyl)benzene (55.7 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 19 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.4) to afford the title compound **27** (37.5 mg, 90%, 94:6 *E:Z*) as colourless liquid. Spectroscopic data are in agreement with those previously reported.[7-8]

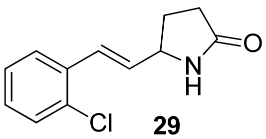
(E)-2-(2-Chlorostyryl)tetrahydrofuran (28)



28

Prepared according to GP-I, combining *(E)*-1-chloro-2-(2-(phenylsulfonyl)vinyl)benzene (55.7 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 12 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.5$) to afford the title compound **28** (35.7 mg, 86%, 91:9 *E:Z*) as pale yellow colour liquid. Spectroscopic data are in agreement with those previously reported.[7, 15]

(E)-5-(2-Chlorostyryl)pyrrolidin-2-one (29)


29

Prepared according to GP-II, combining *(E)*-1-chloro-2-(2-(phenylsulfonyl)vinyl)benzene (55.7 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in 2-pyrrolidone (10.0 mL, 0.02 M) for 23 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1, $R_f = 0.3$) to afford the title compound **29** (35.5 mg, 81%, 97:3 *E:Z*) as pale yellow colour liquid.

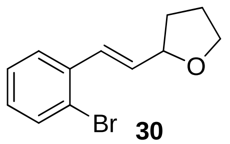
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.50 (dd, *J* = 7.2, 2.2 Hz, 1H, 1×CH-aromatic), 7.35 (dd, *J* = 7.2, 1.9 Hz, 1H, 1×CH-aromatic), 7.24-7.15 (m, 2H, 2×CH-aromatic), 6.94 (d, *J* = 15.8 Hz, 1H, ArC*H*=CH), 6.12 (dd, *J* = 15.8, 7.6 Hz, 1H, ArCH=C*H*), 6.01 (br. s, 1H, NH), 4.45-4.31 (m, 1H, C*H*NH), 2.51-2.32 (m, 3H, COCH_2C*H*H), 2.02-1.89 (m, 1H, C*H*HCHNH) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 178.1, 134.2, 133.2, 132.7, 129.8, 129.0, 127.5, 127.1, 126.9, 56.4, 29.9, 28.4 ppm.

IR (Neat) ῡ = 3222, 1693 cm^{-1}.

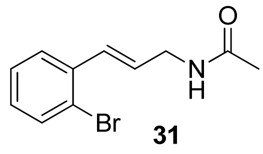
HRMS (ESI+) *m/z* calculated for $C_{12}H_{12}NOClNa$ $[M+Na]^+$ 244.0505, found 244.0506.

(E)-2-(2-Bromostyryl)tetrahydrofuran (30)


30

Prepared according to GP-I, combining *(E)*-1-bromo-2-(2-(phenylsulfonyl)vinyl)benzene (64.6 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 26 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.3$) to afford the title compound **30** (41.2 mg, 81%, 93:7 *E:Z*) as pale yellow colour liquid. Spectroscopic data are in agreement with those previously reported.[8, 15]

(E)-N-(3-(2-Bromophenyl)allyl)acetamide (31)


31

Prepared according to GP-II, combining *(E)*-1-bromo-2-(2-(phenylsulfonyl)vinyl)benzene (64.6 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in *N*-methylacetamide

(10.0 mL, 0.02 M) for 36 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1.5:1, $R_f = 0.4$) to afford the title compound **31** (36.7 mg, 72%, 94:6 *E:Z*) as pale yellow solid.

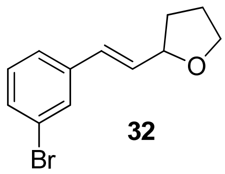
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.51 (ddd, *J* = 15.7, 7.9, 1.4 Hz, 2H, 2×CH-aromatic), 7.29-7.22 (m, 1H, CH-aromatic), 7.14-7.06 (m, 1H, CH-aromatic), 6.85 (d, *J* = 15.8 Hz, 1H, ArC*H*=CH), 6.15 (td, *J* = 15.8, 6.1 Hz, 1H, ArCH=C*H*), 5.72 (br. s, 1H, NH), 4.07 (dt, *J* = 6.1, 1.4 Hz, 2H, CH_2NH), 2.04 (s, 3H, COCH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.9, 136.3, 132.9, 130.7, 129.0, 128.6, 127.5, 127.1, 123.5, 41.6, 23.3 ppm.

IR (Neat) ῡ = 3303, 1639 cm^{-1}.

HRMS (ESI+) *m/z* calculated for $C_{11}H_{12}BrNO$ $[M+Na]^+$ 276.0000 & 277.9980, found 276.0001 & 277.9950.

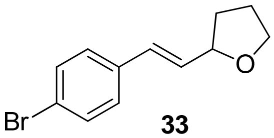
(E)-2-(3-Bromostyryl)tetrahydrofuran (32)



32

Prepared according to GP-I, combining *(E)*-1-bromo-3-(2-(phenylsulfonyl)vinyl)benzene (64.6 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 21 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.4$) to afford the title compound **32** (43.5 mg, 86%, 94:6 *E:Z*) colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[15]

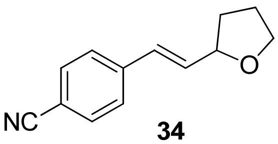
(E)-2-(4-Bromostyryl)tetrahydrofuran (33)



33

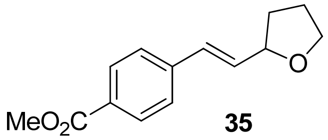
Prepared according to GP-I, combining *(E)*-1-bromo-4-(2-(phenylsulfonyl)vinyl)benzene (64.6 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 21 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.5$) to afford the title compound **33** (44.0 mg, 87%, 96:4 *E:Z*) as colourless liquid. Spectroscopic data are in agreement with those previously reported.[7, 15]

(*E*)-4-(2-(Tetrahydrofuran-2-yl)vinyl)benzonitrile (34)


34

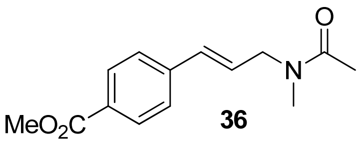
Prepared according to GP-I, combining *(E)*-4-(2-(phenylsulfonyl)vinyl)benzonitrile (53.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 19 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 9:1, R_f = 0.3) to afford the title compound **34** (32.2 mg, 81%, 82:18 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[8]

(*E*)-Methyl 4-(2-(tetrahydrofuran-2-yl)vinyl)benzoate (35)


35

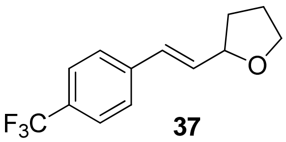
Prepared according to GP-I, combining *(E)*-methyl 4-(2-(phenylsulfonyl)vinyl)benzoate (60.4 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 22 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 9:1, R_f = 0.5) to afford the title compound **35** (35.8 mg, 77%, 93:7 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[15]

(*E*)-Methyl 4-(3-(N-methylacetamido)prop-1-en-1-yl)benzoate (36)


36

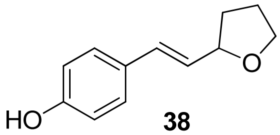
Prepared according to GP-II, combining *(E)*-methyl 4-(2-(phenylsulfonyl)vinyl)benzoate (60.4 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in DMA (10.0 mL, 0.02 M) for 20 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1, R_f = 0.3) to afford the title compound **36** (38.1 mg, 77%, 92:8 *E:Z*) as white colour solid. The Spectroscopic data are in good agreement with the previously reported values.[11b]

(*E*)-2-(4-(Trifluoromethyl)styryl)tetrahydrofuran (37)


37

Prepared according to GP-I, combining *(E)*-1-(2-(phenylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (62.4 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 21 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.4) to afford the title compound **37** (37.3 mg, 78%, 93:7 *E:Z*) as white colour solid. Spectroscopic data are in agreement with those previously reported.[8, 17]

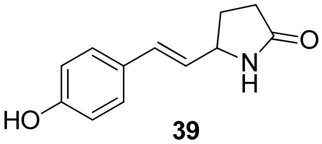
(*E)*-4-(2-(Tetrahydrofuran-2-yl)vinyl)phenol (38)



38

Prepared according to GP-I, combining *(E)*-4-(2-(phenylsulfonyl)vinyl)phenol (52.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 40 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 4:1, R_f = 0.3) to afford the title compound **38** (22.6 mg, 59%, >99:1 *E:Z*) as white colour solid. The Spectroscopic data are in good agreement with the previously reported values.[7]

(*E)*-5-(4-Hydroxystyryl)pyrrolidin-2-one (39)



39

Prepared according to GP-II, combining *(E)*-4-(2-(phenylsulfonyl)vinyl)phenol (52.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in 2-pyrrolidone (10.0 mL, 0.02 M) for 42 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:4, R_f = 0.4) to afford the title compound **39** (22.6 mg, 56%, 97:3 *E:Z*) as white colour solid.

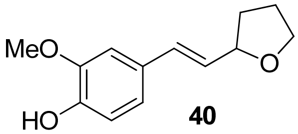
^{1}H NMR (300 MHz, DMSO-d_6) δ = 9.51 (s, 1H, OH), 7.80 (s, 1H, NH), 7.24 (d, *J* = 8.5 Hz, 2H, 2×CH-aromatic), 6.71 (d, *J* = 8.5 Hz, 2H, 2×CH-aromatic), 6.39 (d, *J* = 15.8 Hz, 1H, ArC*H*=CH), 5.99 (dd, *J* = 15.8, 7.3 Hz, 1H, ArCH=C*H*), 4.22-4.10 (m, 1H, C*H*NH), 2.30-2.10 (m, 3H, COCH_2*CH*H), 1.80-1.65 (m, 1H, C*H*HCHNH) ppm.

^{13}C NMR (75 MHz, DMSO-d_6) δ = 176.6, 157.0, 129.3, 128.1, 127.5, 127.2, 115.3, 55.7, 29.8, 28.0 ppm.

IR (Neat) $\bar{\upsilon}$ = 3203, 1672 cm^{-1}.

HRMS (ESI+) *m/z* calculated for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.1019, found 204.1017.

(*E)*-2-Methoxy-4-(2-(tetrahydrofuran-2-yl)vinyl)phenol (40)



40

Prepared according to GP-I, combining *(E)*-2-methoxy-4-(2-(phenylsulfonyl)vinyl)phenol (58.0 mg, 0.2 mmol, 1.0 equiv), and **Cat. II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02

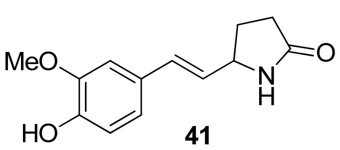
M) for 22 h in front of a 36 W & 23 W household CFL bulb. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 2.3:1, R_f = 0.3) to afford the title compound **40** (31.8 mg, 73%, >99:1 *E:Z*) as pale yellow colour liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.96-6.81 (m, 3H, 3×CH-aromatic), 6.50 (d, *J* = 15.8 Hz, 1H, ArC*H*=CH), 6.05 (dd, *J* = 15.8, 6.8 Hz, 1H, ArCH=C*H*), 5.69 (s, 1H, OH), 4.44 (q, *J* = 6.8 Hz, 1H, ArCH=CHC*H*O), 4.02-3.91 (m, 1H, OC*H*H), 3.89 (s, 3H, OCH_3), 3.86-3.78 (m, 1H, OCH*H*), 2.19-2.04 (m, 1H, ArCH=CHCHC*H*H), 2.04-1.88 (m, 2H, OCH_2CH_2), 1.78-1.63 (m, 1H, ArCH=CHCHCH*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ = 146.6, 145.4, 130.6, 129.4, 128.1, 120.3, 114.3, 108.3, 79.9, 68.1, 55.8, 32.4, 25.9 ppm.

HRMS (ESI+) *m/z* calculated for $C_{13}H_{16}O_3K$ $[M+K]^+$ 259.0737, found 259.0734

(E)-5-(4-Hydroxy-3-methoxystyryl)pyrrolidin-2-one (41)


41

Prepared according to GP-II, combining *(E)*-2-methoxy-4-(2-(phenylsulfonyl)vinyl)phenol (58.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (15.0 mg, 0.06 mmol, 30.0 mol%) in 2-pyrrolidone (10.0 mL, 0.02 M) for 108 h in front of a 36 W & 23 W household CFL bulb. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:9, R_f = 0.3) to afford the title compound **41** (24.5 mg, 52%, 94:6 *E:Z*) as yellow dense liquid.

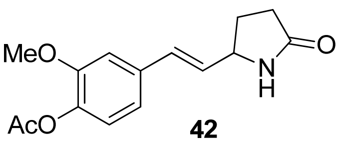
^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.88 (br. s, 1H, CH-aromatic), 6.87 (br. s, 2H, 2×CH-aromatic), 6.46 (d, *J* = 15.7 Hz, 1H, ArC*H*=CH), 5.96 (dd, *J* = 15.7, 7.6 Hz, 1H, ArCH=C*H*), 5.71 (s, 1H, OH), 5.66 (br. s, 1H, NH), 4.36-4.25 (m, 1H, C*H*NH), 3.91 (s, 3H, OCH_3), 2.48-2.31 (m, 3H, $COCH_2CH$H), 2.02-1.86 (m, 1H, C*H*HCHNH) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 177.9, 146.7, 145.9, 131.2, 128.5, 127.59, 120.4, 114.5, 108.3, 56.5, 55.9, 29.9, 28.7 ppm.

IR (Neat) ῡ = 1701, 1604 cm^{-1}.

HRMS (ESI+) *m/z* calculated for$C_{13}H_{15}NO_3Na$ $[M+Na]^+$ 256.0950, found 256.0951

(E)-2-Methoxy-4-(2-(5-oxopyrrolidin-2-yl)vinyl)phenyl acetate (42)


42

Prepared according to GP-II, combining *(E)*-2-methoxy-4-(2-(phenylsulfonyl)vinyl)phenyl acetate (310.0 mg, 0.93 mmol, 1.0 equiv), and Cat. **II** (43.0 mg, 0.19 mmol, 20.0 mol%) in 2-

pyrrolidone (47.0 mL, 0.02 M) for 46 h in front of a 36 W & 23 W household CFL bulb. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1.5, R_f = 0.4) to afford the title compound **42** (196.0 mg, 76%, 94:6 *E:Z*) as pale yellow colour solid.

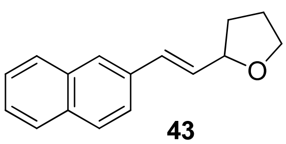
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.02-6.82 (m, 3H, 3×CH-aromatic), 6.49 (d, *J* = 15.8 Hz, 1H, ArC*H*=CH), 6.37 (br. s, 1H, NH), 6.07 (dd, *J* = 15.8, 7.3 Hz, 1H, ArCH=C*H*), 4.36-4.25 (m, 1H, C*H*NH), 3.83 (s, 3H, OCH_3), 2.46-2.32 (m, 3H, $COCH_2CH$H), 2.29 (s, 3H, $COCH_3$), 1.95-1.86 (m, 1H, C*H*HCHNH) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 178.3, 168.9, 151.1, 139.5, 135.1, 130.4, 130.2, 122.9, 119.1, 110.1, 56.2, 55.8, 29.8, 28.4, 20.6 ppm.

IR (Neat) ῡ = 3184, 1762, 1689 cm^{-1}.

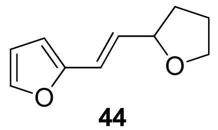
HRMS (ESI+) *m/z* calculated for $C_{15}H_{18}NO_4$ $[M+H]^+$ 276.1230, found 276.1210.

(E)-2-(2-(Naphthalen-2-yl)vinyl)tetrahydrofuran (43)


43

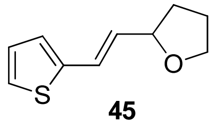
Prepared according to GP-I, combining *(E)*-2-(2-(phenylsulfonyl)vinyl)naphthalene (58.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 47 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.5) to afford the title compound **43** (33.6 mg, 75%, 82:18 *E:Z*) as pale yellow colour liquid. Spectroscopic data are in agreement with those previously reported.[7, 15]

(E)-2-(2-(Tetrahydrofuran-2-yl)vinyl)furan (44)


44

Prepared according to GP-I, combining *(E)*-2-(2-(phenylsulfonyl)vinyl)furan (46.8 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (15.0 mg, 0.06 mmol, 30.0 mol%) in THF (10.0 mL, 0.02 M) for 41 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.4) to afford the title compound **44** (26.7 mg, 81%, 94:6 *E:Z*) as pale yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[18]

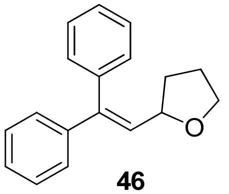
(E)-2-(2-(Thiophen-2-yl)vinyl)tetrahydrofuran (45)


45

Prepared according to GP-I, combining *(E)*-2-(2-(phenylsulfonyl)vinyl)thiophene (50.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 36 h.

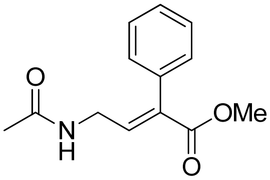
The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.35) to afford the title compound **45** (25.5 mg, 71%, 92:8 *E:Z*) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[15, 18]

2-(2,2-Diphenylvinyl)tetrahydrofuran (46)


46

Prepared according to GP-I, combining (2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene (64.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 18 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.4) to afford the title compound **46** (48.2 mg, 96%) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[19]

(E)-Methyl 4-acetamido-2-phenylbut-2-enoate (47)



47

Prepared according to GP-II, combining (Z)-methyl 2-phenyl-3-(phenylsulfonyl)acrylate (60.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in *N*-methylacetamide (10.0 mL, 0.02 M) for 23 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1.5:1, R_f = 0.3) to afford the title compound **47** (28.4 mg, 61% overall yield, 87:13 *E:Z*) as colourless liquid.

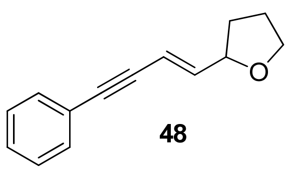
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45-7.24 (m, 8H, 3×CH-aromatic$_{\text{major,}}$ 5×CH-aromatic$_{\text{minor}}$), 7.20-7.13 (m, 2H, 2×CH-aromatic$_{\text{major}}$), 6.94 (t, *J* = 6.2 Hz, 1H, CH- alkene$_{\text{major}}$), 6.23 (t, *J* = 6.6 Hz, 2H, CH- alkene$_{\text{minor}}$, NH$_{\text{minor}}$), 5.94 (br. s, 1H, NH$_{\text{major}}$), 4.20 (t, *J* = 6.6 Hz, 2H, CH_2NH$_{\text{minor}}$), 3.90 (t, *J* = 6.2 Hz, 2H, CH_2NH$_{\text{major}}$), 3.80 (s, 3H, OCH$_{3\text{minor}}$), 3.74 (s, 3H, OCH$_{3\text{major}}$), 1.98 (s, 3H, CO$CH_{3\ \text{minor}}$), 1.92 (s, 3H, CO$CH_{3\ \text{major}}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.1, 170.1, 167.9, 167.1, 139.8, 137.0, 136.9, 136.4, 135.2, 134.1, 129.4, 128.3, 128.1, 128.1, 128.0, 127.5, 52.2, 52.0, 38.6, 38.4, 23.1, 22.9 ppm.

IR (Neat) $\bar{\upsilon}$ = 1717, 1674, 1604 cm^{-1}.

HRMS (ESI+) *m/z* calculated for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$ 256.0950, found 256.0952.

(E)-2-(4-Phenylbut-1-en-3-yn-1-yl)tetrahydrofuran (48)



48

Prepared according to GP-I, combining *(E)*-((4-phenylbut-1-en-3-yn-1-yl)sulfonyl)benzene (53.6 mg, 0.2 mmol, 1.0 equiv), and Cat.

II (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 60 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.3) to afford the title compound **48** as an inseparable mixture of stereoisomeric products (31.0 mg, 78%, 1.5:1 *E:Z*) as colourless liquid.

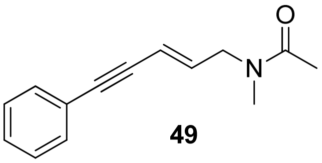
^{1}H NMR (300 MHz, Acetone-d_6) δ = 7.49-7.33 (m, 10H, 5×CH-aromatic$_{major}$, 5×CH-aromatic$_{minor}$), 6.23 (dd, *J* = 15.8, 5.7 Hz, 1H, ArCH=C*H*$_{major}$), 6.05 (dd, *J* = 10.9, 8.1 Hz, 1H, ArCH=C*H*$_{minor}$), 5.93 (dd, *J* = 15.8, 1.4 Hz, 1H, ArC*H*=CH$_{major}$), 5.78 (dd, *J* = 10.9, 1.1 Hz, 1H, ArC*H*=CH$_{minor}$), 4.90-4.80 (m, 1H, ArCH=CHC*H*O$_{minor}$), 4.38 (dq, *J* = 7.0, 1.3 Hz, 1H, ArCH=CHC*H*O$_{major}$), 3.92-3.81 (m, 2H, OC*H*H$_{major,}$ OC*H*H$_{minor}$), 3.78-3.68 (m, 2H, OCH*H*$_{major,}$ OCH*H*$_{minor}$), 2.28-2.16 (m, 1H, 1×CH-THF$_{minor}$), 2.16-2.08 (m, 1H, 1×CH-THF$_{minor}$), 2.00-1.85 (m, 4H, 3×CH-THF$_{major,}$ 1×CH-THF$_{minor}$), 1.71-1.56 (m, 2H, 1×CH-THF$_{major,}$ 1×CH-THF$_{minor}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.9, 143.9, 131.4, 131.4, 129.9, 128.2, 128.1, 127.6, 123.3, 123.2, 109.9, 109.7, 94.6, 89.8, 87.5, 85.4, 78.7, 77.0, 68.3, 68.2, 32.1, 32.0, 26.1, 25.6 ppm.

IR (Neat) ῡ = 2974, 2869, 2198, 1596 cm^{-1}.

HRMS (ESI+) *m/z* calculated for.$C_{14}H_{14}OK$ $[M+K]^+$ 237.0682, found 237.0679

***(E)-N*-Methyl-*N*-(5-phenylpent-2-en-4-yn-1-yl)acetamide (49)**



49

Prepared according to GP-II, combining *(E)*-((4-phenylbut-1-en-3-yn-1-yl)sulfonyl)benzene (53.6 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in DMA (10.0 mL, 0.02 M) for 45 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1.5, R_f = 0.5) to afford the title compound **49** as an inseparable mixture of rotamer in 1.2:1 ratio (35.9 mg, 84% overall yield, 1:1 *E:Z*) as pale yellow colour liquid.

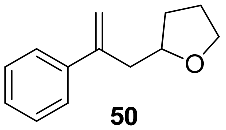
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42 (s, 4H, 2×CH-aromatic$_{rotamer1,}$ 2×CH-aromatic$_{rotamer2}$), 7.31 (s, 6H, 3×CH-aromatic$_{rotamer1,}$ 3×CH-aromatic$_{rotamer2}$), 6.20-6.05 (m, 2H, ArCH=C*H*$_{rotamer1}$, ArCH=C*H*$_{rotamer2}$), 5.80 (d, *J* = 15.9 Hz, 2H, ArC*H*=CH$_{rotamer1}$, ArC*H*=CH$_{rotamer2}$), 4.08 (d, *J* = 6.2 Hz, 2H, *CH$_2$*NMe $_{rotamer1}$), 4.00 (d, *J* = 5.0 Hz, 2H, *CH$_2$*NMe $_{rotamer2}$), 2.98 (s, 3H, N*CH$_3$* $_{rotamer1}$), 2.94 (s, 3H, N*CH$_3$* $_{rotamer2}$), 2.11 (s, 6H, CO*CH$_3$* $_{rotamer1,}$ CO*CH$_3$* $_{rotamer2}$) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) δ = 170.7, 170.5, 137.9, 136.9, 131.5, 131.4, 128.4, 128.3, 128.3, 128.2, 123.1, 122.8, 112.4, 111.9, 90.7, 89.91, 87.0, 86.5, 52.3, 48.9, 35.6, 33.6, 21.7, 21.1 ppm.

IR (Neat) ῡ = 2201, 1648 cm^{-1}.

HRMS (ESI+) *m/z* calculated for $C_{14}H_{15}NONa$ [M+Na]$^+$ 236.1051, found 236.1053.

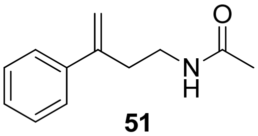
2-(2-Phenylallyl)tetrahydrofuran (**50**)



50

Prepared according to GP-I, combining ((2-phenylallyl)sulfonyl)benzene (48.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 48 h. The crude material was purified by column chromatography (SiO$_2$, Hexane:EtOAc = 19:1, R$_f$ = 0.4) to afford the title compound **50** (27.9 mg, 74%) as colourless liquid. The Spectroscopic data are in good agreement with the previously reported values.[20]

N-(3-Phenylbut-3-en-1-yl)acetamide (**51**)



51

Prepared according to GP-II, combining ((2-phenylallyl)sulfonyl)benzene (48.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in *N*-methylacetamide (10.0 mL, 0.02 M) for 40 h. The crude material was purified by column chromatography (SiO$_2$, Hexane:EtOAc = 1.5:1, R$_f$ = 0.3) to afford the title compound **51** (20.1 mg, 54%) as colourless liquid.

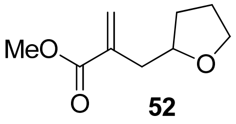
^{1}H NMR (300 MHz, CDCl$_3$) δ = 7.44-7.32 (m, 3H, 3×CH-aromatic), 7.32-7.25 (m, 2H, 2×CH-aromatic), 5.47 (br. s, 1H, NH), 5.38 (d, *J* = 1.1 Hz, 1H, CH-olefin), 5.12 (d, *J* = 1.1 Hz, 1H, CH-olefin), 3.37 (dd, *J* = 12.6, 6.6 Hz, 2H, *CH$_2$*NH), 2.73 (dt, *J* = 6.6, 1.1 Hz, 2H, *CH$_2$*CH$_2$NH), 1.92 (s, 3H, CO*CH$_3$*) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) δ = 169.9, 145.5, 140.2, 128.5, 127.8, 126.0, 114.2, 38.2, 35.0, 23.2 ppm.

IR (Neat) ῡ = 1669, 1518 cm^{-1}.

HRMS (ESI+) *m/z* calculated for $C_{12}H_{15}NONa$ [M+Na]$^+$ 212.1051, found 212.1050.

Methyl 2-((tetrahydrofuran-2-yl)methyl)acrylate (**52**)

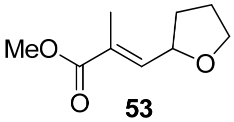


52

Prepared according to GP-I, combining methyl 2-((phenylsulfonyl)methyl)acrylate (58.8 mg, 0.2 mmol, 1.0 equiv), and

Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 12 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 9:1, R_f = 0.3) to afford the title compound **52** (17.7 mg, 46%, 76% NMR yield using mesitylene as internal standard) as pale yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[21]

***(E)*-Methyl 2-methyl-3-(tetrahydrofuran-2-yl)acrylate** (**53**)

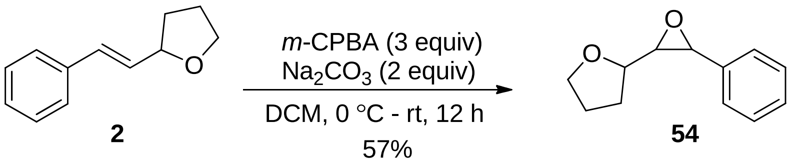


53

Prepared according to GP-I, combining *(E)*-methyl 2-methyl-3-(phenylsulfonyl)acrylate (48.0 mg, 0.2 mmol, 1.0 equiv), and Cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) for 15 h. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 9:1, R_f = 0.4) to afford the title compound **53** (29.3 mg, 86%, 97:3 *E:Z*) as pale yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[22]

Synthetic Application of the C-H Vinylation Reaction:

Synthesis of (±) 2-(3-Phenyloxiran-2-yl)tetrahydrofuran (54) via olefin epoxidation:



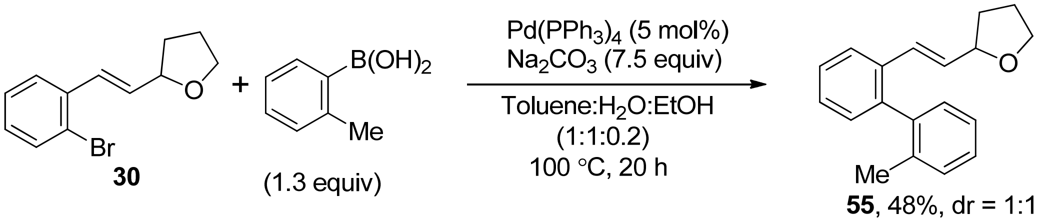
To an oven dried schlenck round bottom flask, **2** (34.8 mg, 0.2 mmol, 1.0 equiv), Na_2CO_3 (42.3 mg, 0.4 mmol, 2.0 equiv) and DCM (2.0 mL, 0.1 M) were added. The reaction mixture was cooled to 0 °C. To this cold solution, *m*-CPBA (77%; 138.0 mg, 0.6 mmol, 3.0 equiv) was added in portion wise and allowed to stir at room temperature for 12 h. Then the reaction mixture was neutralized with saturated $NaHCO_3$ solution (2.0 mL) and diluted with distilled water (4.0 mL). The organic layer was extracted with ethyl acetate (3 x 5.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.3$) to afford the title compound (±) **54** (21.6 mg, 57%, dr = 1:1) as colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37-7.24 (m, 5H, 5×CH-aromatic), 4.06-3.96 (m, 1H, *CH*O-THF), 3.95-3.74 (m, 3H, *CH₂*O-THF, O*CH*Ph), 3.05 (dt, *J* = 4.2, 4.1, 2.1 Hz, 1H, *CH*OCHPh), 2.14-2.03 (m, 1H, C*H*H-THF), 2.01-1.80 (m, 3H, CH*HCH₂*-THF) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.2, 137.0, 128.4 (2C), 128.1, 128.0, 125.6 (2C), 78.1, 77.3, 68.9, 68.7, 64.5, 63.5, 56.8, 55.7, 28.6, 28.0, 25.9, 25.7 ppm.

HRMS (ESI+) *m/z* calculated for $C_{12}H_{14}O_2Na$ $[M+Na]^+$ 213.0892, found 213.0893

Synthesis of (±) *(E)*-2-(2-(2'-Methyl-[1,1'-biphenyl]-2-yl)vinyl)tetrahydrofuran (55) via Suzuki cross-coupling reaction:



To a solution of 2-Methylphenylboronic acid (18.0 mg, 0.13 mmol, 1.3 equiv) in Toluene (300.0 μL), H_2O (300.0 μL), ethanol (57.0 μL), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 5.0 mol%),

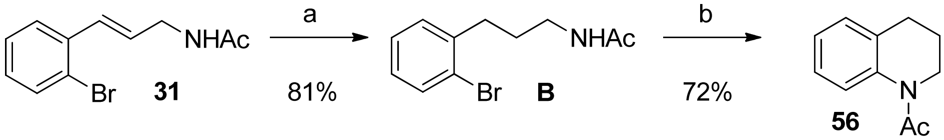
Na_2CO_3 (80.9 mg, 0.76 mmol, 7.5 equiv) and **30** (25.8 mg, 0.10 mmol, 1.0 equiv) were added under argon atmosphere. The reaction mixture was allowed to stir at 100 °C for 20 h, and then cooled to room temperature. Saturated NH_4Cl solution (2.0 mL) was added and the aqueous mixture was extracted with EtOAc (3 x 5.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, R_f = 0.5) to afford the title compound (±) **55** (12.6 mg, 48%, dr = 1:1) as colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.62 (dd, *J* = 7.5, 1.5 Hz, 1H, 1×CH-aromatic), 7.37-7.18 (m, 5H, 5×CH-aromatic), 7.15-7.08 (m, 2H, 2×CH-aromatic), 6.24 (d, *J* = 15.9 Hz, 1H, Ar*CH*=CH), 6.08 (ddd, *J* = 15.9, 6.9, 0.9 Hz, 1H, ArCH=*CH*), 4.26 (dq, *J* = 6.9, 2.3 Hz, 1H, *CH*O-THF), 3.89-3.79 (m, 1H, C*H*HOCH-THF), 3.78-3.68 (m, 1H, CH*H*OCH-THF), 2.04 (s, 3H, CH_3), 2.01-1.92 (m, 1H, OCHC*H*H-THF), 1.92-1.81 (m, 2H, OCH_2*CH_2*-THF), 1.66-1.61 (m, 1H, OCHCH*H*-THF) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.7, 140.7, 140.6, 136.4, 136.1, 135.1, 135.0, 131.3, 131.3, 131.3, 130.0, 129.9, 129.9, 129.7, 129.7, 128.9, 127.3, 127.3, 127.2, 127.1, 125.4, 125.3, 125.2, 79.9, 79.8, 68.0, 68.0, 32.3, 32.3, 25.8, 25.7, 20.1, 20.0 ppm.

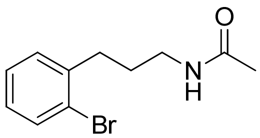
HRMS (ESI+) *m/z* calculated for $C_{19}H_{20}ONa$ $[M+Na]^+$ 287.1412, found 287.1414.

Synthesis of 1-(3,4-dihydroquinolin-1(2H)-yl)ethanone (56) via olefin hydrogenation followed by C-N coupling:



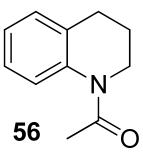
Reaction conditions: a) Pd/C (10 mol%), H_2 (1 atm), MeOH (0.12 M), rt, 1 h. b) $Pd(OAc)_2$ (3 mol%), (±)-BINAP (5 mol%), Cs_2CO_3 (1.4 equiv), Toluene (0.3 M), 100 °C, 38 h.

N-(3-(2-bromophenyl)propyl)acetamide (B)



To a dry 5.0 mL round bottom flask containing a magnetic stir bar, **31** (60.1 mg, 0.24 mmol, 1.0 equiv), Pd-C (10%) (6.0 mg), MeOH (2.0 mL, 0.12 M) were added. The reaction mixture was then fitted with a H_2 balloon (1 atm) and allowed to stir at room temperature for 1 hr. After completion of reaction confirmed by TLC analysis, the reaction mixture was filtered through celite and washed with EtOAc (8.0 mL). The combined organic part was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1, R_f = 0.4) to afford the title compound **B** (49.2 mg, 81%) as pale yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[23]

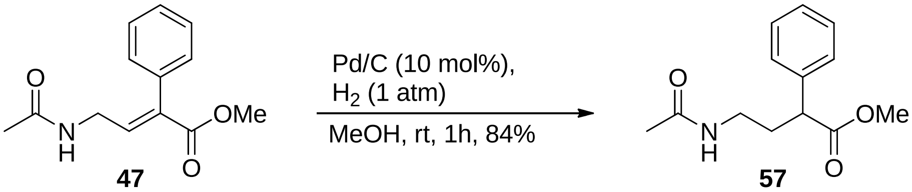
1-(3,4-dihydroquinolin-1(2H)-yl)ethanone (56)



56

Prepared according to the literature procedure.[24] A dry 10.0 mL Schlenk tube was charged with $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 3.3 mol%) and (*rac*)-BINAP (4.9 mg, 0.008 mmol, 5.0 mol%). The reaction vessel was evacuated and flushed with argon. A solution of *N*-(3-(2-bromophenyl)propyl)acetamide (40.0 mg, 0.16 mmol, 1.0 equiv) in toluene (0.4 mL) was added via cannula. The mixture was heated under argon at 100 °C for 2 min to dissolve the solids. The reaction vessel was removed from the oil bath, charged quickly with Cs_2CO_3 (71.2 mg, 0.22 mmol, 1.4 equiv) and toluene (0.2 mL), sealed properly, and heated at 100 °C until the aryl bromide was consumed completely (38 h). The reaction mixture was cooled to room temperature, filtered through a short plug of SiO_2, and concentrated. The residue was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1.5, R_f = 0.6) to afford the title compound **56** (20.1 mg, 72%) as pale yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[24]

Synthesis of (±) methyl 4-acetamido-2-phenylbutanoate (57) via olefin hydrogenation:



To a dry 5.0 mL round bottom flask containing a magnetic stir bar, **47** (16.8 mg, 0.07 mmol, 1.0 equiv), Pd-C (10%) (1.6 mg), MeOH (1.4 mL, 0.05 M) were added. The reaction mixture was then fitted with a H_2 balloon (1 atm) and allowed to stir at room temperature for 1 hr. After completion of reaction confirmed by TLC analysis, the reaction mixture was filtered through celite and washed with EtOAc (5.0 mL). The combined organic part was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1.5, R_f = 0.4) to afford the title compound (±) **57** (14.2 mg, 84%) as colourless liquid.

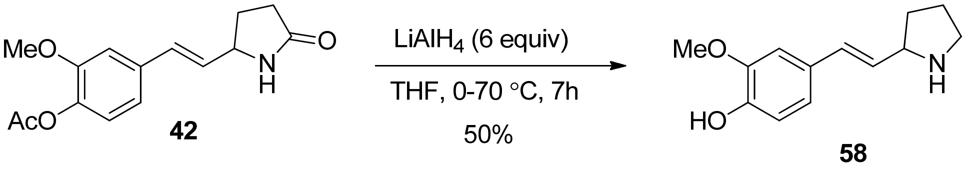
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38-7.22 (m, 5H, 5×CH-aromatic), 5.64 (br. s, 1H, NH), 3.66 (s, 3H, OCH_3), 3.61 (t, *J* = 7.5 Hz, 1H, *CH*CO_2Me), 3.31-3.13 (m, 2H, *CH_2*NH), 2.38-2.22 (m, 1H, C*H*HCH_2NH), 2.06-1.94 (m, 1H, CH*H*CH_2NH), 1.91 (s, 3H, CO*CH_3*) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ = 174.1, 170.1, 138.3, 128.8, 127.8, 127.5, 52.1, 49.3, 37.9, 33.0, 23.1 ppm.

IR (KBr) ῡ = 1734, 1674 cm^{-1}.

HRMS (ESI+) *m/z* calculated for $C_{13}H_{17}NO_3Na$ $[M+Na]^+$ 258.1106, found 258.1103.

Synthesis of *(E)*-2-Methoxy-4-(2-(pyrrolidin-2-yl)vinyl)phenol [(±)-Norruspoline] (58) via amide reduction:



To an oven dried schlenck round bottom flask, **42** (38.0 mg, 0.14 mmol, 1.0 equiv) and THF (5.0 mL, 0.027 M) were added and cooled to 0 °C. To this cold solution, $LiAlH_4$ (32.0 mg, 0.84 mmol, 6.0 equiv) was added in portion wise and allowed to stir at 70 °C for 7 h. After completion of reaction confirmed by TLC, reaction mixture was quenched with saturated Rochelle solution (3.0 mL). The organic layer was extracted with ethyl acetate (3 x 5.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, DCM:MeOH:NH_3 = 92:8:2, R_f = 0.4) to afford the title compound (±) **58** (15.1 mg, 50%) as yellow colour liquid. The Spectroscopic data are in good agreement with the previously reported values.[25]

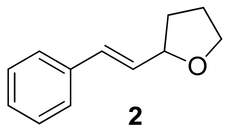
^{1}H NMR (300 MHz, CD_3OD) δ = 6.98 (s, 1H, CH-aromatic), 6.83 (d, *J* = 8.1 Hz, 1H, CH-aromatic), 6.76 (br s, 1H, OH), 6.72 (d, *J* = 8.1 Hz, 1H, CH-aromatic), 6.48 (d, *J* = 15.7 Hz, 1H, CH-olefin), 6.04 (dd, *J* = 15.7, 7.7 Hz, 1H, CH-olefin), 3.85 (s, 3H, OCH_3), 3.73-3.61 (m, 1H, C*H*NHCH_2), 3.57 (br. s, 1H, NH), 3.15-3.01 (m, 1H, NHCH*H*), 2.98-2.84 (m, 1H, NHC*H*H), 2.12-1.96 (m, 1H, NHCH_2CH*H*), 1.96-1.71 (m, 3H, NHCH_2C*H*H*CH_2*) ppm.

^{13}C NMR (100 MHz, CD_3OD) δ = 149.2, 147.9, 132.7, 130.4, 128.4, 121.1, 116.3, 110.5, 62.7, 46.8, 33.4, 30.2, 26.1 ppm.

HRMS (ESI+) *m/z* calculated for $C_{13}H_{18}NO_2$ $[M+H]^+$ 220.1332, found 220.1330.

Gram Scale Experiment:

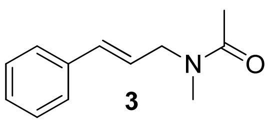
(E)-2-styryltetrahydrofuran (2)



2

To an oven dried 1 L round bottom flask equipped with a magnetic stir bar, charged with *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (2.5 g, 10.2 mmol, 1.0 equiv) and Cat. **II** (514.0 mg, 2.0 mmol, 20.0 mol%) followed by THF (511 mL, 0.02 M). The resultant reaction mixture was placed in front of two 36 W household CFL bulb and allowed to stir for 52 h at 40 ºC. After complete consumption of the starting material (confirmed by TLC analysis), unreacted THF was distilled out. The reaction mixture was neutralized with saturated aqueous solution of $NaHCO_3$ (10.0 mL) and diluted with distilled water (20.0 mL). The organic layer was extracted with ethyl acetate (3 x 25.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 19:1, $R_f = 0.7$) to afford the title compound **2** (1.47 g, 83%, 98:3 *E:Z*) as colourless liquid. All spectroscopic data is in agreement with those previously reported.[7] [8]

N-cinnamyl-*N*-methylacetamide (3)



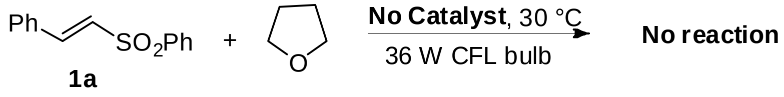
3

To an oven dried 500 mL round bottom flask equipped with a magnetic stir bar, charged with *(E)*-(2-(phenylsulfonyl)vinyl)benzene (**1a**) (1.0 g, 4.1 mmol, 1.0 equiv) and Cat. **II** (205.5 mg, 0.2 mmol, 20.0 mol%) followed by DMA (204 mL, 0.02 M). The resultant reaction mixture was placed in front of two 36 W household CFL bulb and allowed to stir for 64 h at 40 ºC. After complete consumption of the starting material (confirmed by TLC analysis), unreacted DMA was distilled out. The reaction mixture was diluted with distilled water (50.0 mL) and the organic layer was extracted with ethyl acetate (5 x 25.0 mL). The combined organic layer was washed with distilled water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, Hexane:EtOAc = 1:1.5, $R_f = 0.4$) to afford the title compound **3** as an inseparable mixture of rotamer in 1:1 ratio (621.0 mg, 80% overall yield, 96:4 *E:Z*) as pale yellow colour liquid. All spectroscopic data is in agreement with those previously reported.[11]

Mechanistic Investigation:

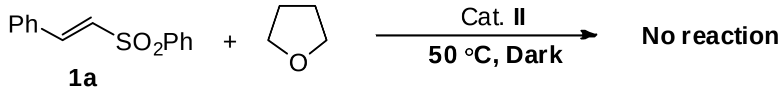
a) Control experiments:

To gain insights into the reaction mechanism, a series of control experiments was carried out. Accordingly, the reaction was performed in absence of both catalyst and visible light, which gave no desired product formation (Eq. S1 and S2). This indicates that the reaction may proceed via visible light photocatalysis. The reaction also failed to provide the expected vinylated ether when it was stirred in dark at 50 °C with or without a catalyst suggesting the requirement of visible light for the success of the reaction (Eq. S3 and S4). Furthermore, performing the reaction in absence of vinyl sulfone resulted in decomposition of the catalyst. This result suggests that the sulfinyl radical may play a key role in catalyst regeneration process of the proposed catalytic cycle (Eq. S5).

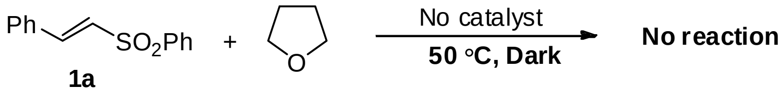


Eq. S1

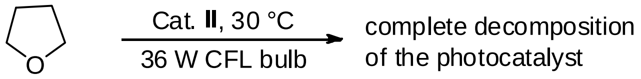
Eq. S2



Eq. S3



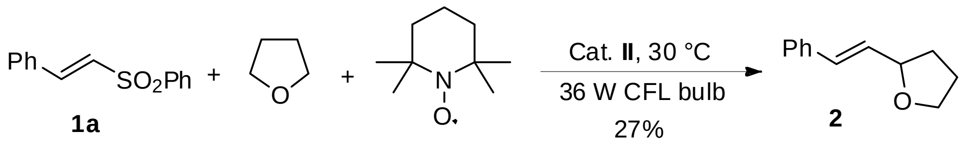
Eq. S4



Eq. S5

Reaction conditions: a solution of cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) in THF (10.0 mL, 0.02 M) was allowed to stir for 36 h in front of a 36 W household CFL bulb for 18 h.

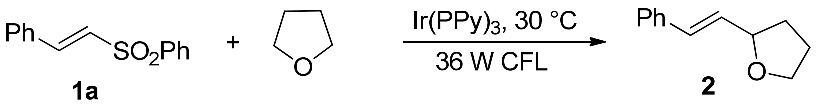
Additionally, a very sluggish reactivity for the catalytic direct C-H vinylation reaction was realized in the presence of a radical inhibitor like TEMPO under otherwise optimal reaction conditions, delivering the desired product **2** in 27% yield (Eq. S6). The formation of TEMPO-THF adduct was confirmed by GCMS analysis. This result indicates that the reaction most likely proceeds via a radical mechanism.



Eq. S6

Reaction conditions: a solution of **1a** (48.8 mg, 0.2 mmol, 1.0 equiv), cat. **II** (10.0 mg, 0.04 mmol, 20.0 mol%) and TEMPO (15.6 mg, 0.10 mmol, 50.0 mol%) in THF (10.0 mL, 0.02 M) was allowed to stir for 20 h in front of a 36 W CFL bulb, yield refer to the isolated product.

When the reaction was performed using 2.0 mol% of visible light photocatalyst Ir(PPy)$_3$ instead of catalyst **II**. The desired product **2** was obtained in 25% yield (Eq. S7). This result may suggest that photoexcited iridium-catalyst could produce phenyl sulfinyl radical via single electron transfer (SET) process. The in situ generated phenyl sulfinyl radical may initiate the radical chain reaction by producing α-alkoxyl radical through homolytic activation of C(sp3)-H bond of ether.

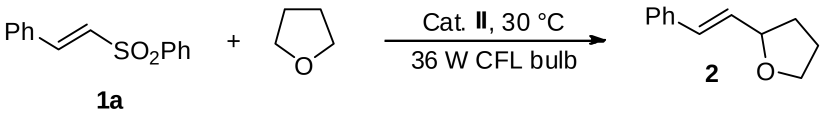


Eq. S7

Reaction conditions: a solution of **1a** (48.8 mg, 0.2 mmol, 1.0 equiv), Ir(PPy)$_3$ (2.6 mg, 0.004 mmol, 2.0 mol%) in THF (10.0 mL, 0.02 M) was allowed to stir for 21 h in front of a 36 W CFL bulb, yield refer to the isolated product.

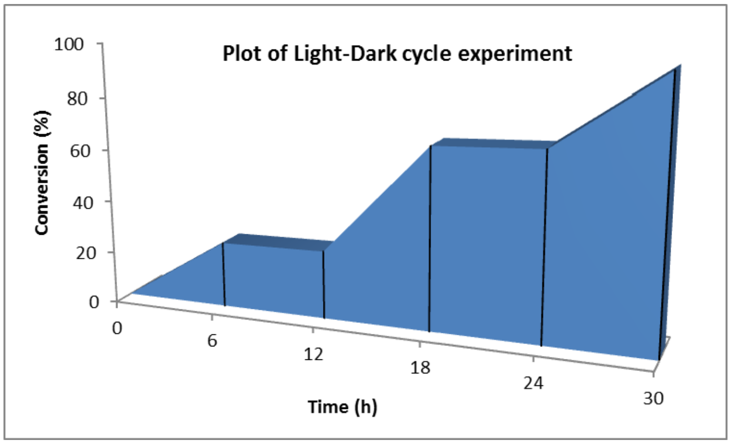
b) Light-dark cycle experiment:

The necessity of visible light for the reaction was further established by performing a light-dark cycle experiment. It was found that by turning light on and off the reaction can be switched on and off.

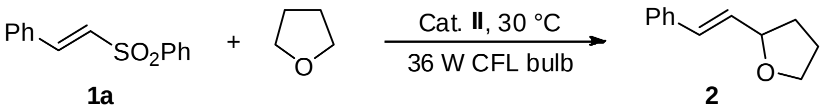


Condition	Time (h)	Conv. %
Light	6	25
Dark	6	26
Light	6	69
Dark	6	71
Light	6	100

[a]Reaction conditions: a solution of **1a** (0.2 mmol, 1.0 equiv) and cat. **II** (20.0 mol%) in THF (10 mL, 0.02 M) was allowed to stir in front of a 36 W CFL bulb; conversion was determined by GC analysis.



Catalyst Recycle Experiment:

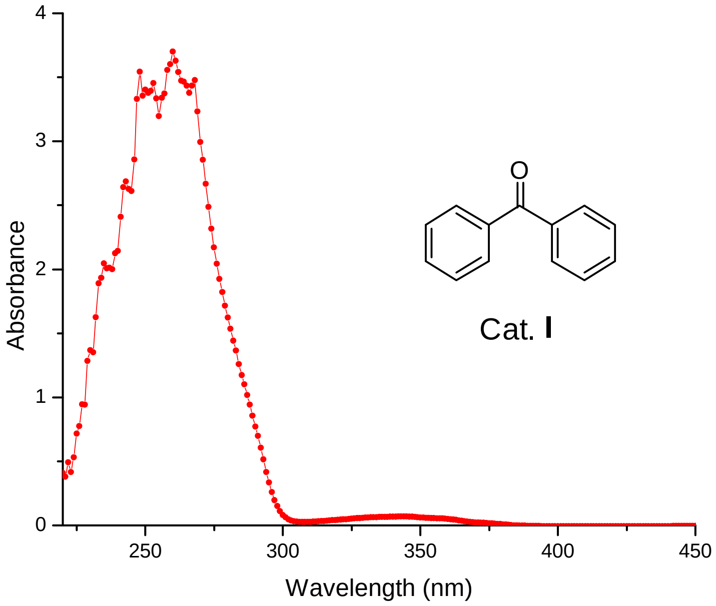


No. of recycle	**1a** (mmol)	Time (h)	Yield (%)	Cat. **II** Recovered (%)
1	1.00	18	86	78
2	0.77	17	83	68
3	0.53	16	85	66
4	0.35	16	78	36
5	0.12	15	80	73

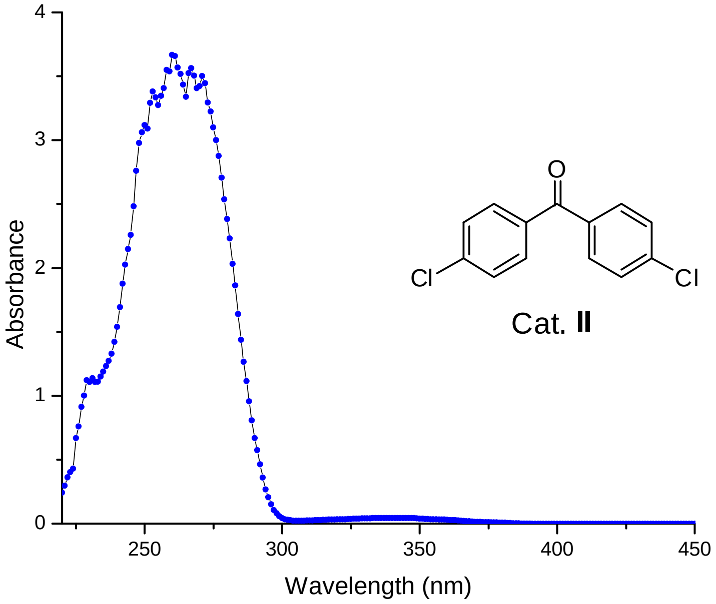
[a] Reaction conditions: a solution of **1a** (1.0 equiv) and cat. **II** (20.0 mol%) in THF (0.02 M) was allowed to stir in front of a 36 W CFL bulb; yields refer to the isolated product.

In the control experiment, it was found that sulfinyl radical played a key role in catalyst regeneration process, as complete decomposition of the catalyst was observed in absence of vinyl sulfone. We therefore envisaged that the catalyst recycle experiments need to be performed in the presence of sulfone. Accordingly, every set of catalyst recycle experiment was stopped at around 95% consumption of the starting vinyl sulfone. As presented above, the catalyst could indeed be recovered and reused up to five cycles without realizing significant loss of its catalytic activity.

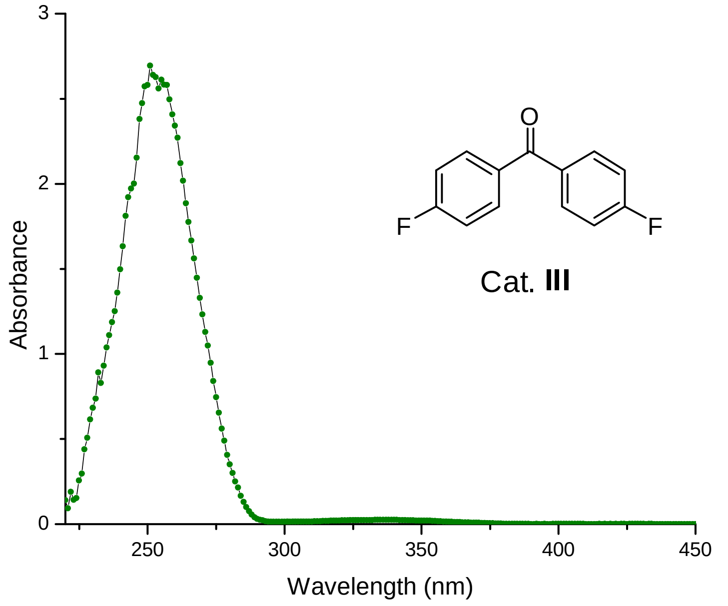
UV-Visible Spectra of Photocatalysts (I-IX)



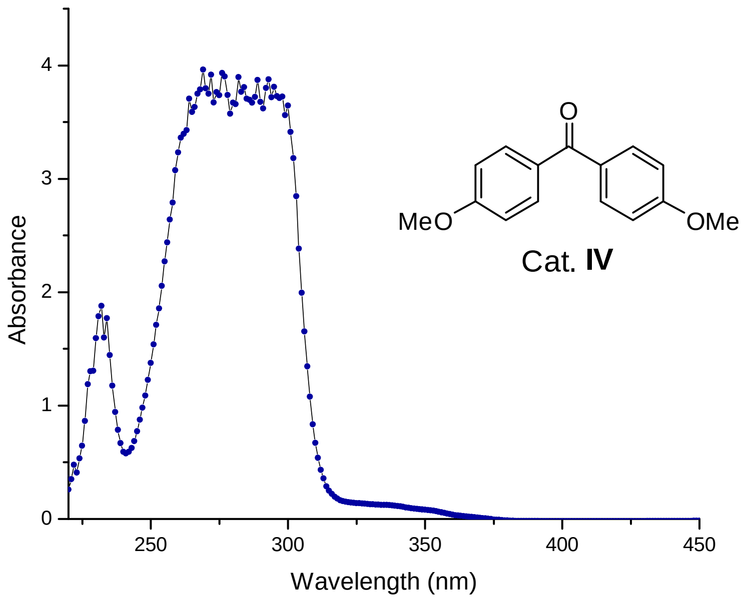
UV-Visible spectrum of Cat. **I** in THF



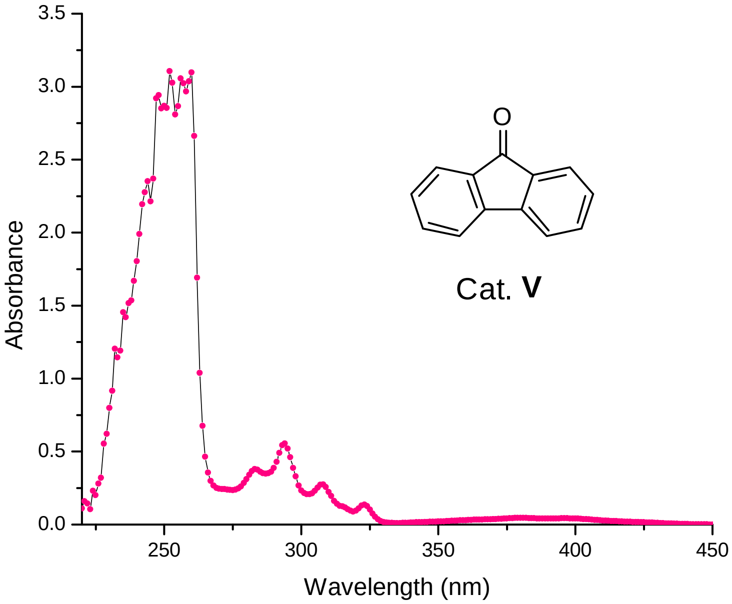
UV-Visible spectrum of Cat. **II** in THF



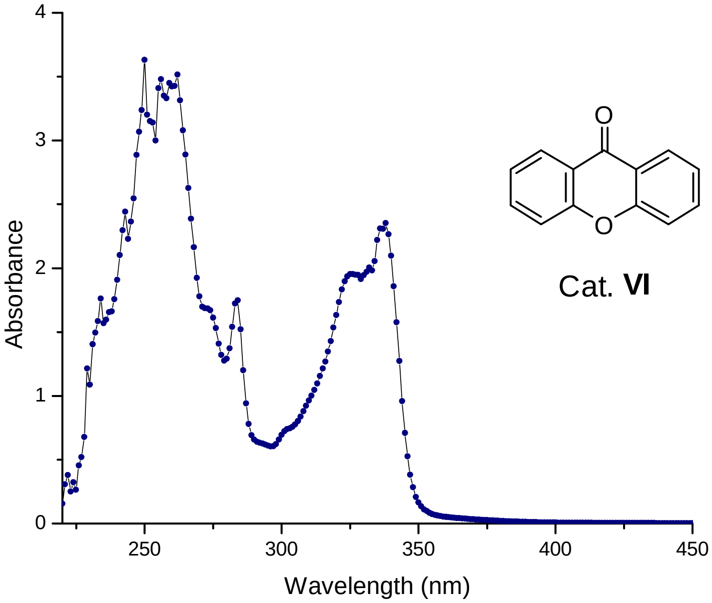
UV-Visible spectrum of Cat. **III** in THF



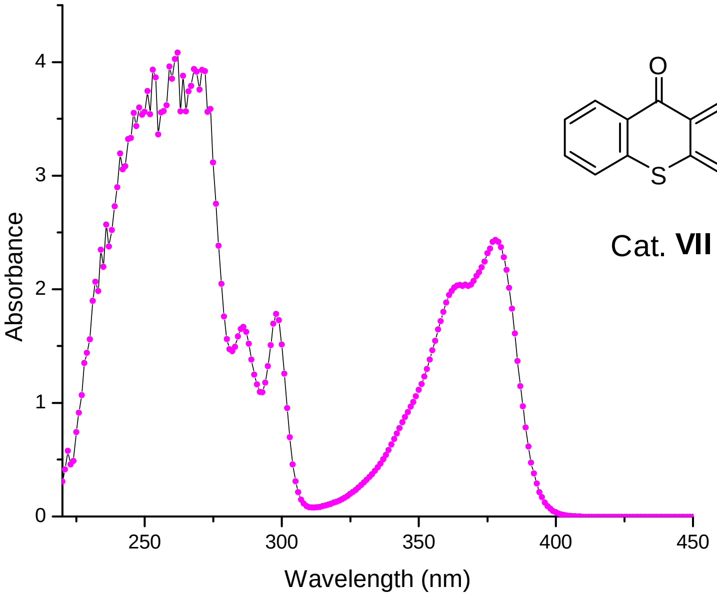
UV-Visible spectrum of Cat. **IV** in THF



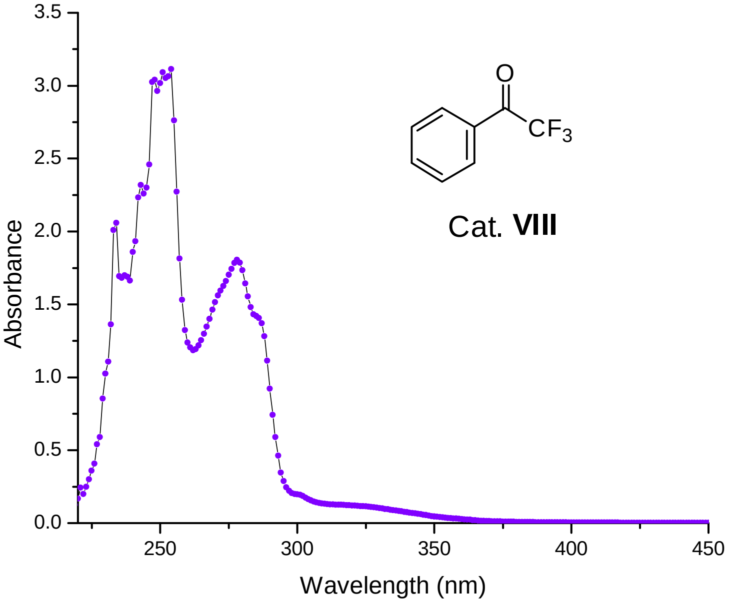
UV-Visible spectrum of Cat. **V** in THF



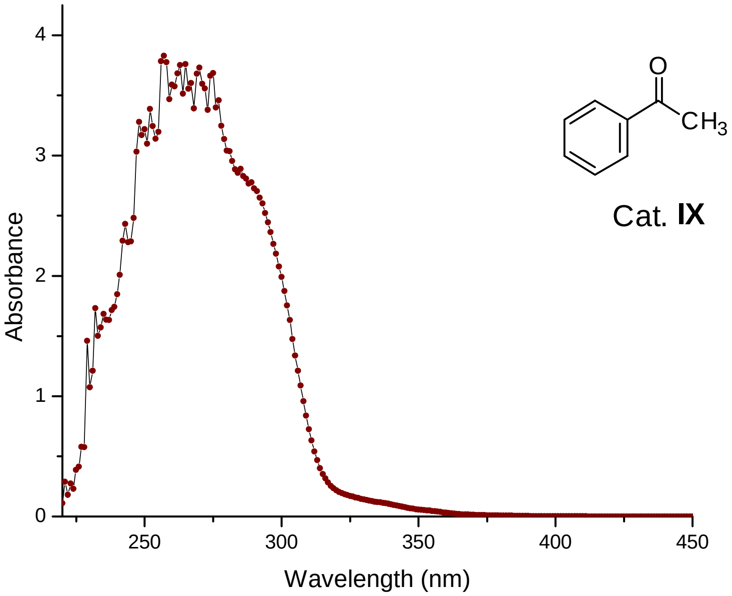
UV-Visible spectrum of Cat. **VI** in THF



UV-Visible spectrum of Cat. **VII** in THF

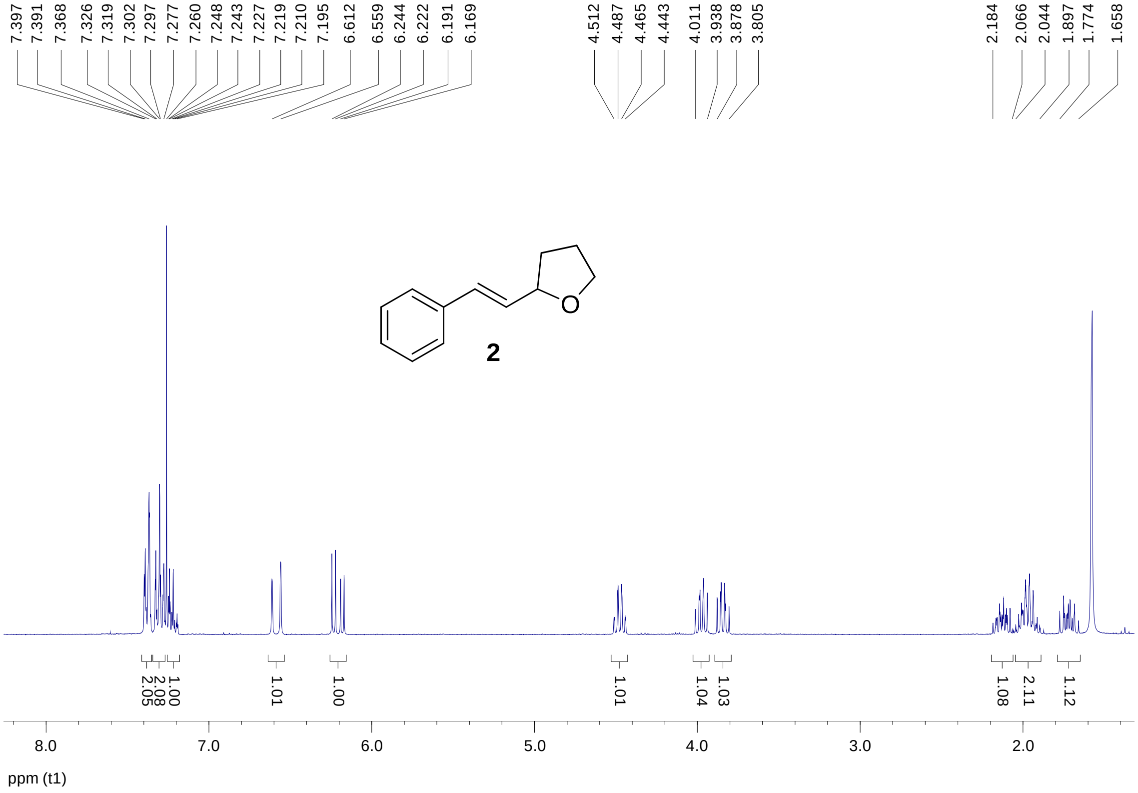


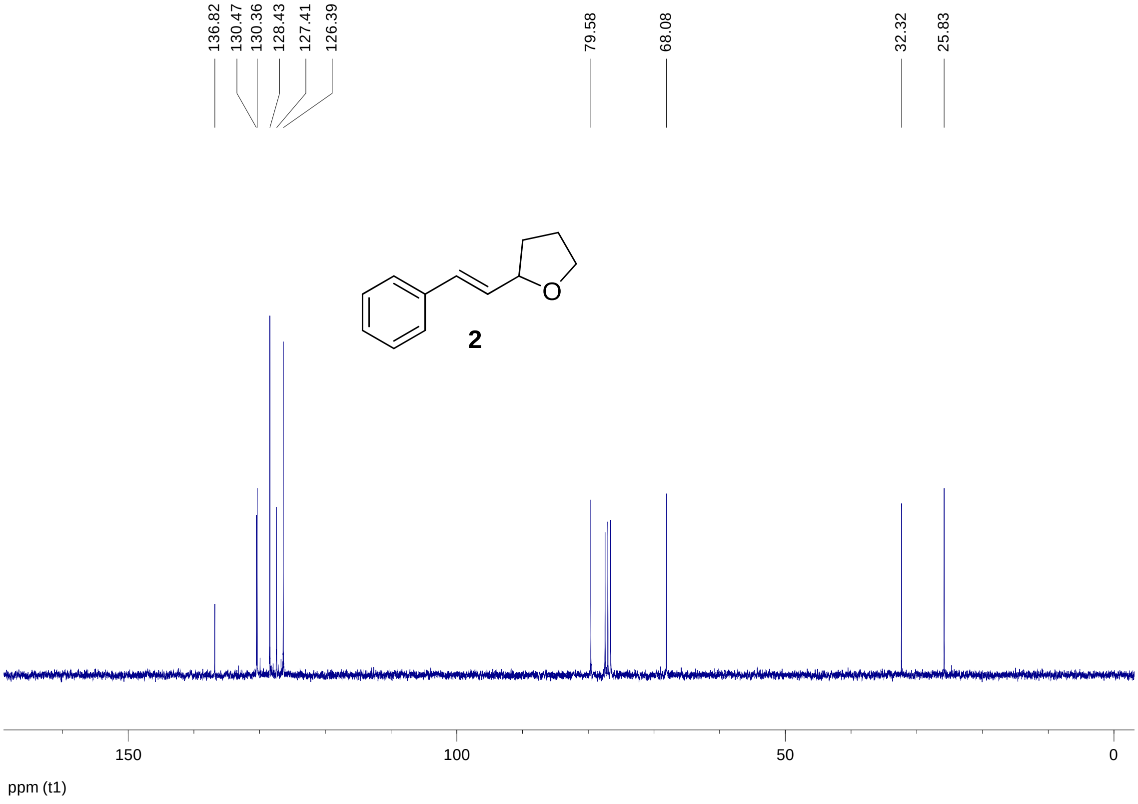
UV-Visible spectrum of Cat. **VIII** in THF

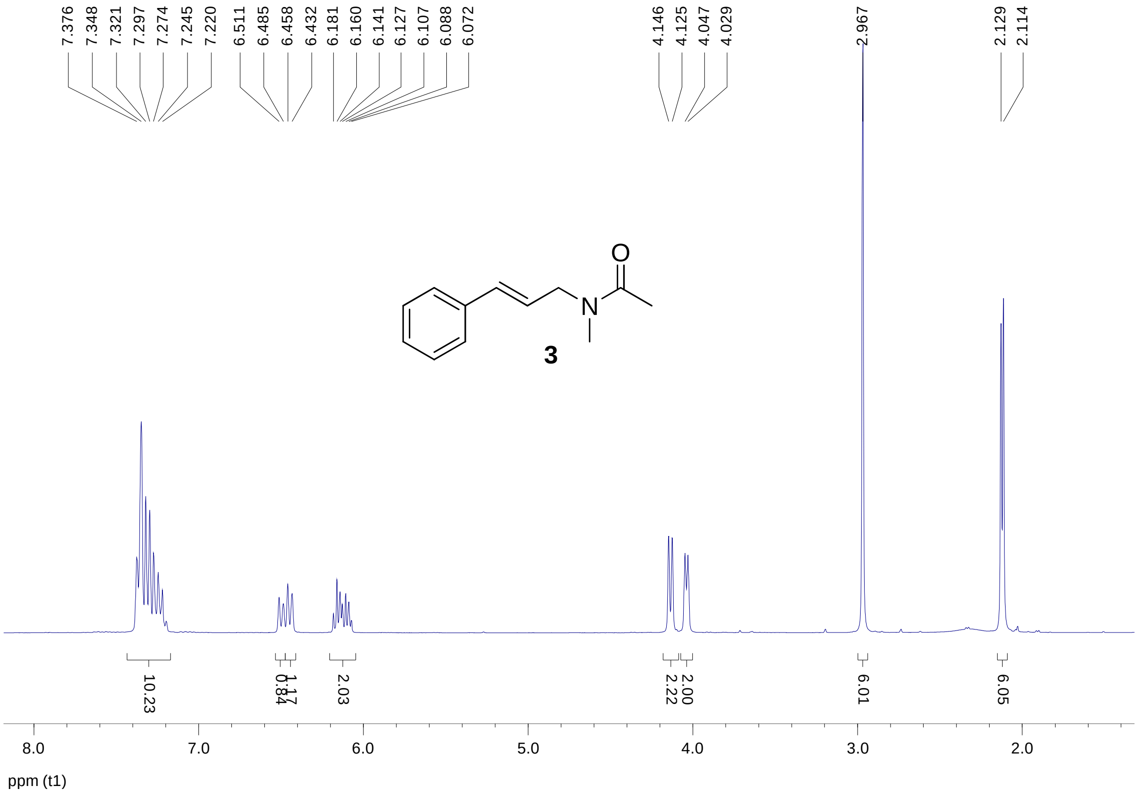


UV-Visible spectrum of Cat. **IX** in THF

^{1}H and ^{13}C NMR Spectra



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6.160
6.141
6.127
6.107
6.088
6.072
4.146
4.125
4.047
4.029
2.967
2.129
2.114
O
N
3
10.23
0.84
1.17
2.03
2.22
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6.05
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7.0
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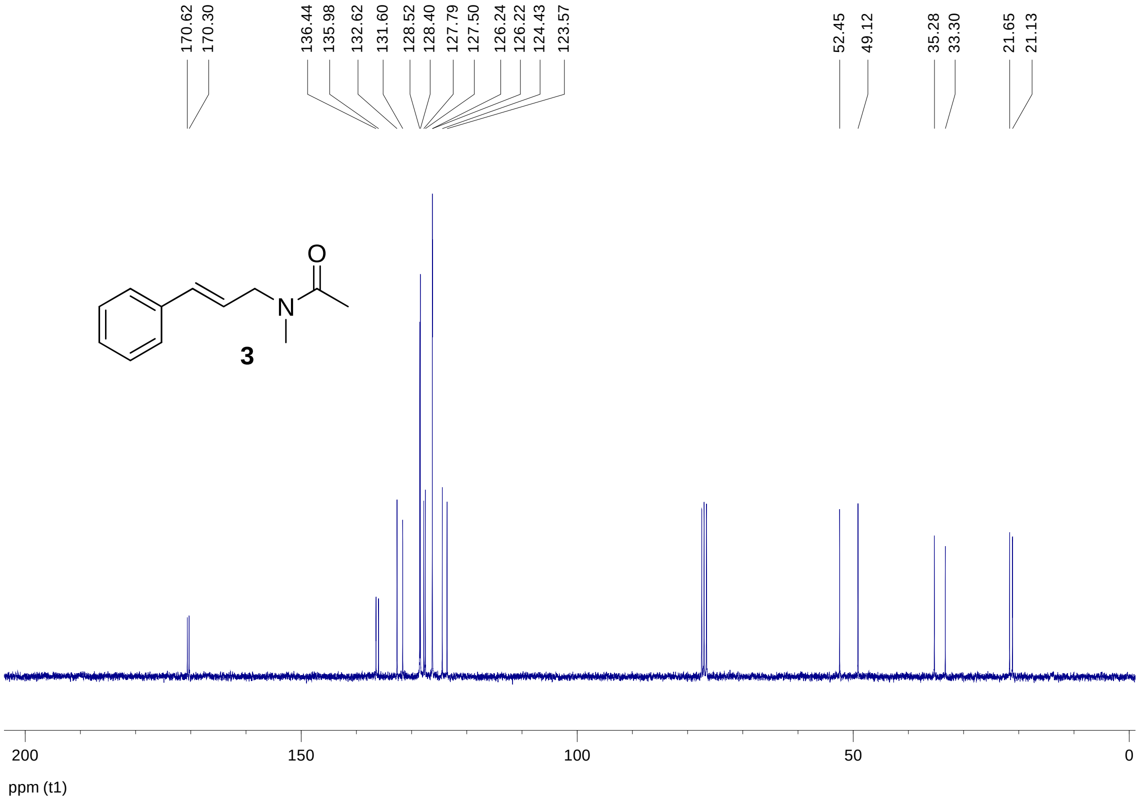
4.0
3.0
2.0
ppm (t1)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170.30
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128.52
128.40
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127.50
126.24
126.22
124.43
123.57
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33.30
21.65
21.13
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N
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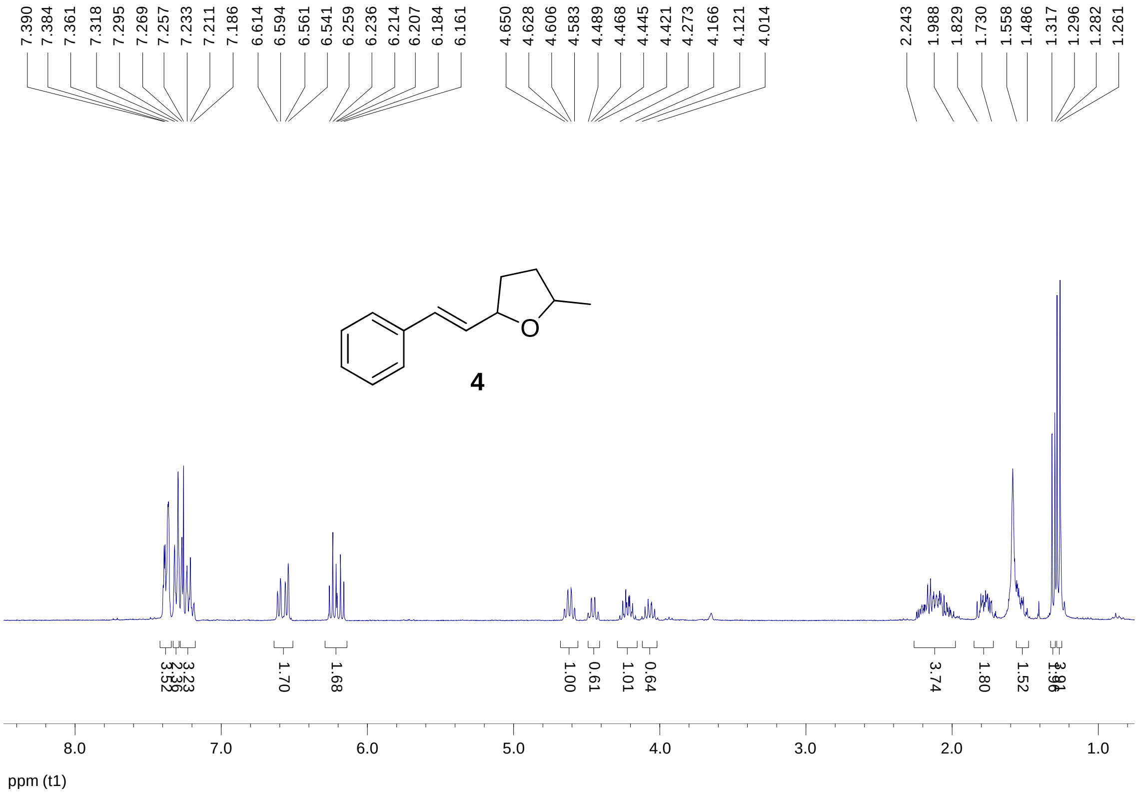
100
50
0
ppm (t1)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6.561
6.541
6.259
6.236
6.214
6.207
6.184
6.161
4.650
4.628
4.606
4.583
4.489
4.468
4.445
4.421
4.273
4.166
4.121
4.014
2.243
1.988
1.829
1.730
1.558
1.486
1.317
1.296
1.282
1.261
O
4
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2.36
3.23
1.70
1.68
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1.01
0.64
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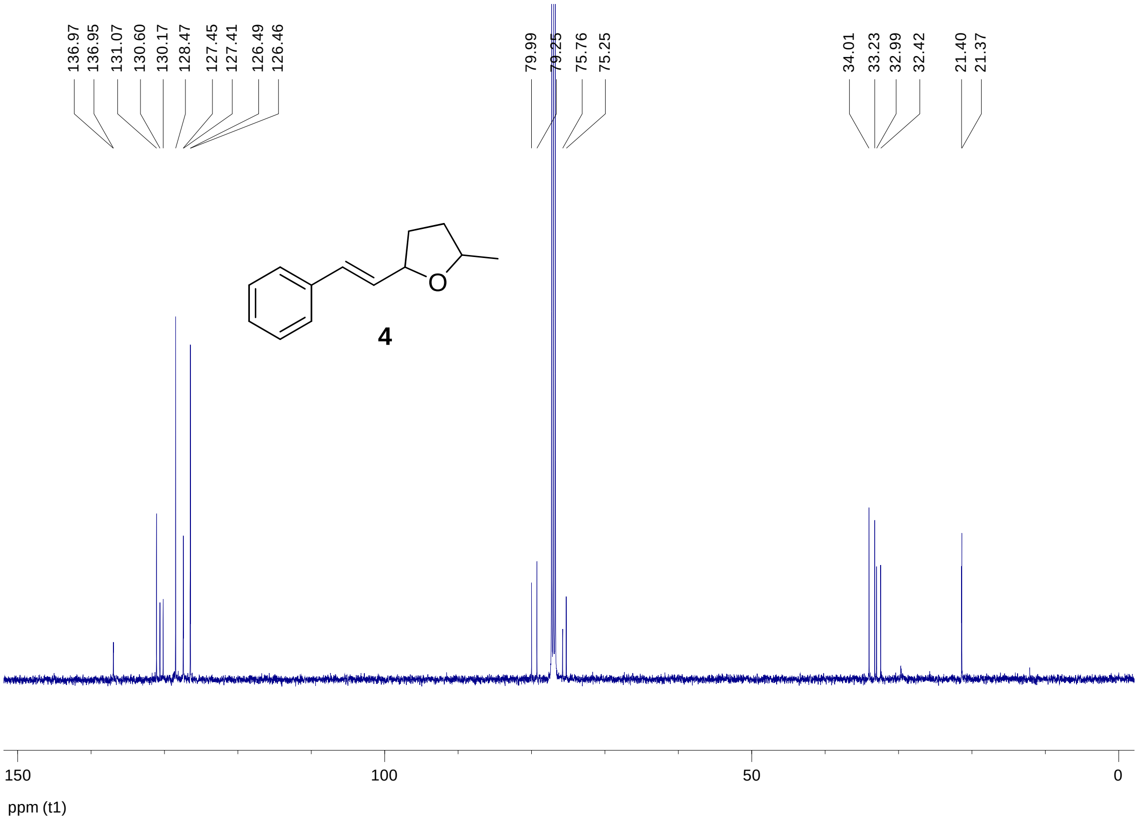
1.0
ppm (t1)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127.41
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126.46
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79.25
75.76
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32.99
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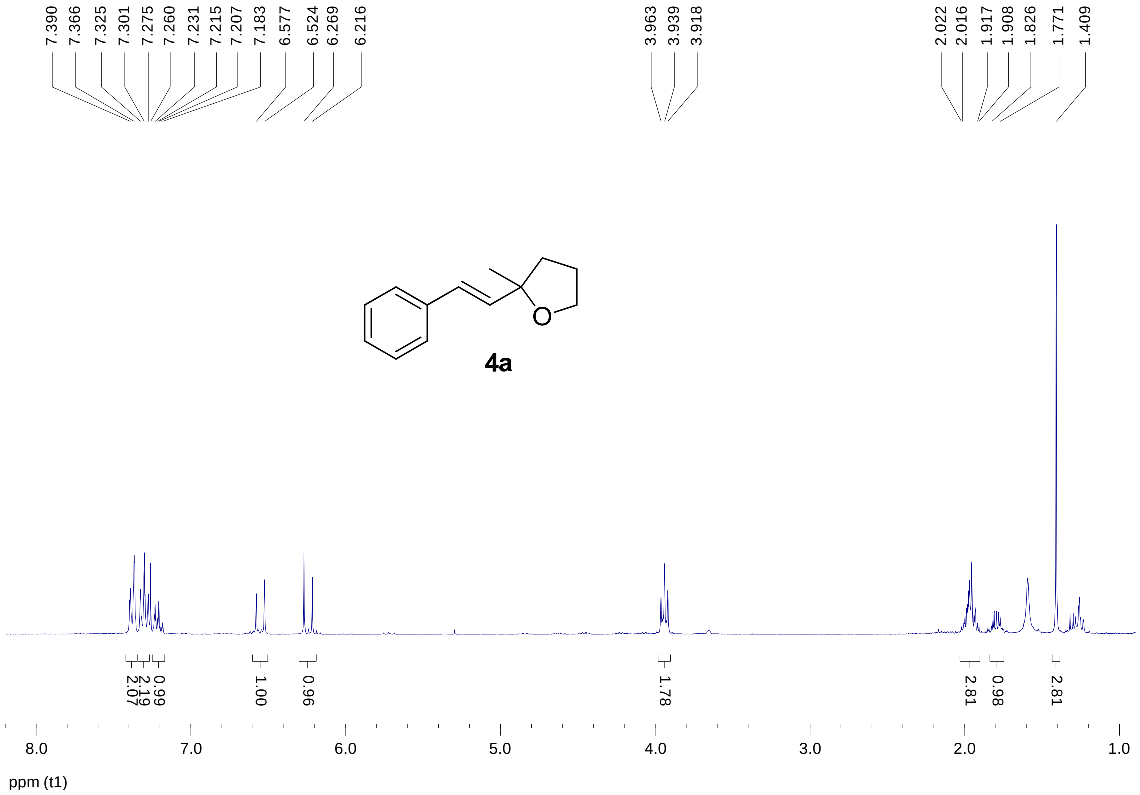
100
50
0
ppm (t1)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7.183
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6.269
6.216
3.963
3.939
3.918
2.022
2.016
1.917
1.908
1.826
1.771
1.409
O
4a
2.07
2.19
0.99
1.00
0.96
1.78
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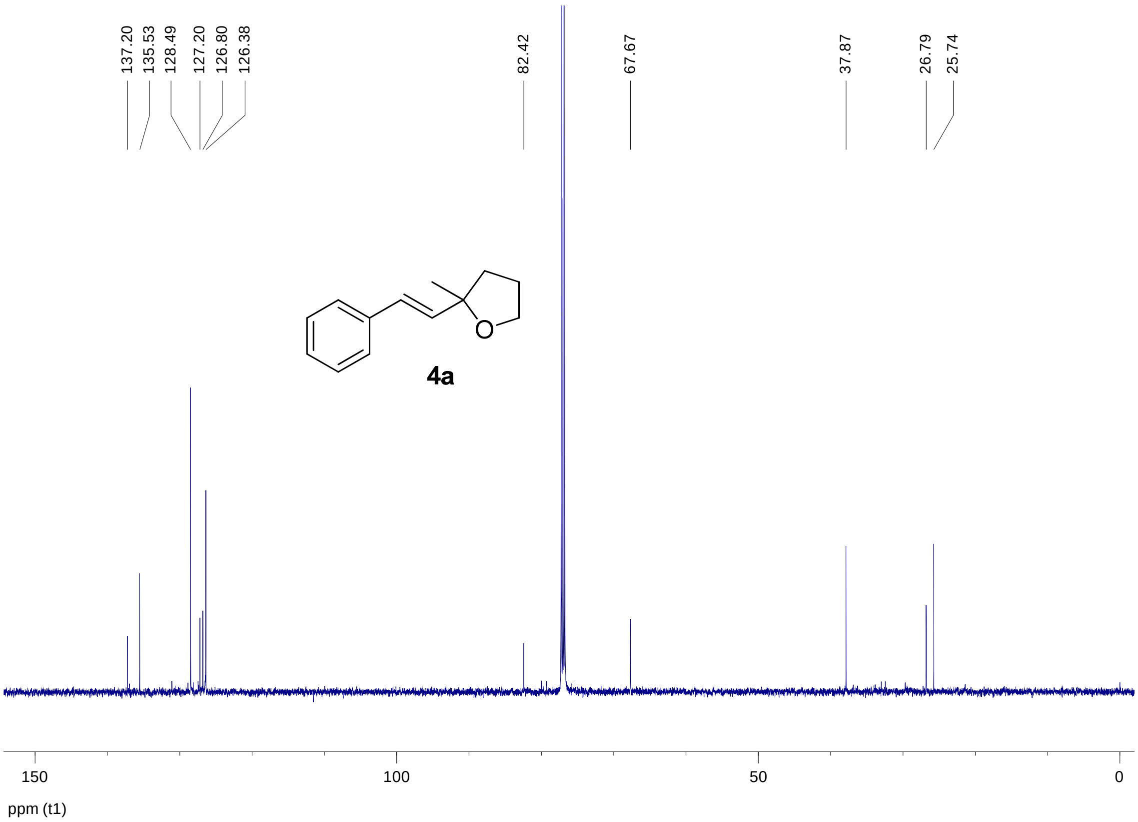
1.0
ppm (t1)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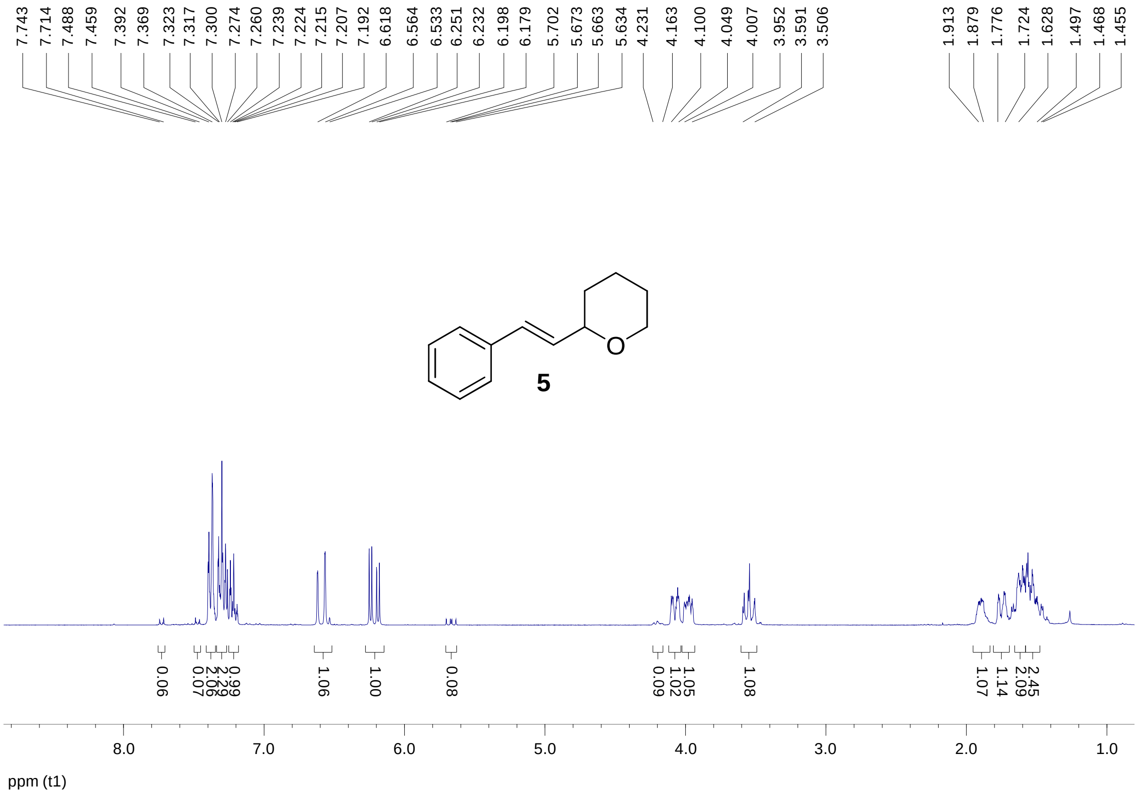
150
100
50
0
ppm (t1)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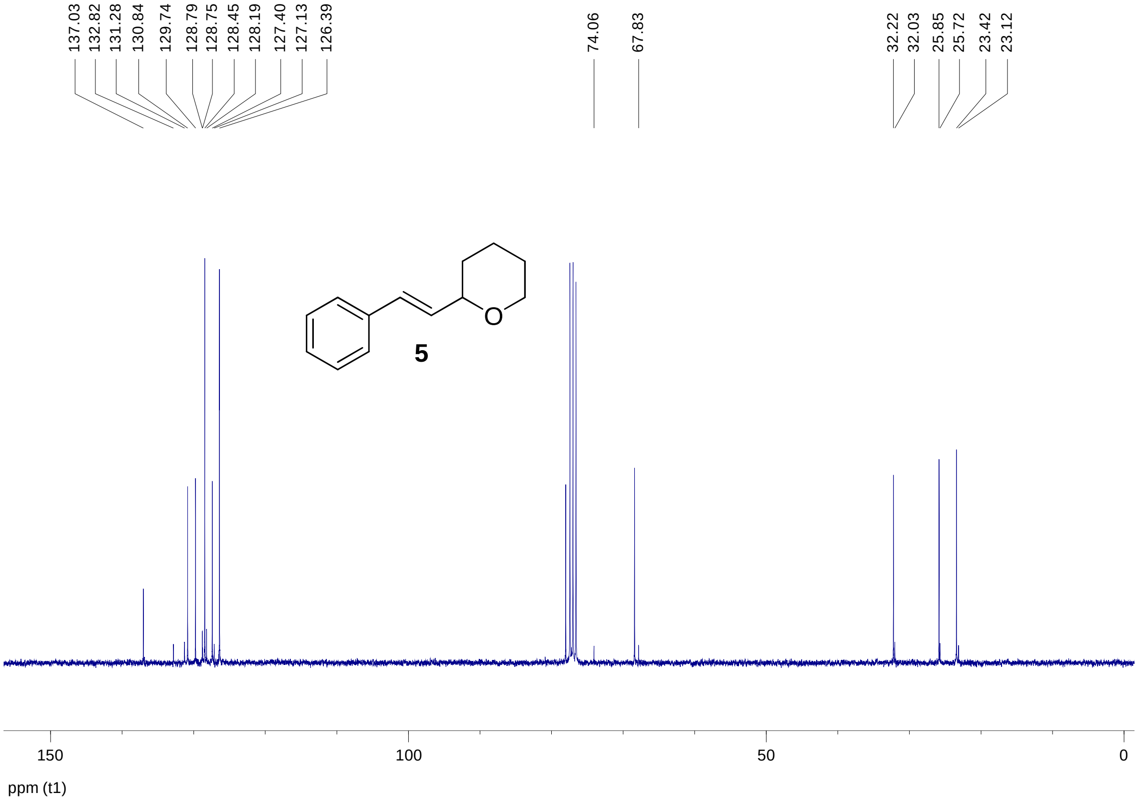
1.913 1.879 1.776 1.724 1.628 1.497 1.468 1.455
O
5
0.06 0.07 2.06 2.29 0.99 1.06 1.00 0.08 0.09 1.02 1.05 1.08 1.07 1.14 2.09 2.45
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (t1)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74.06 67.83
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O
5
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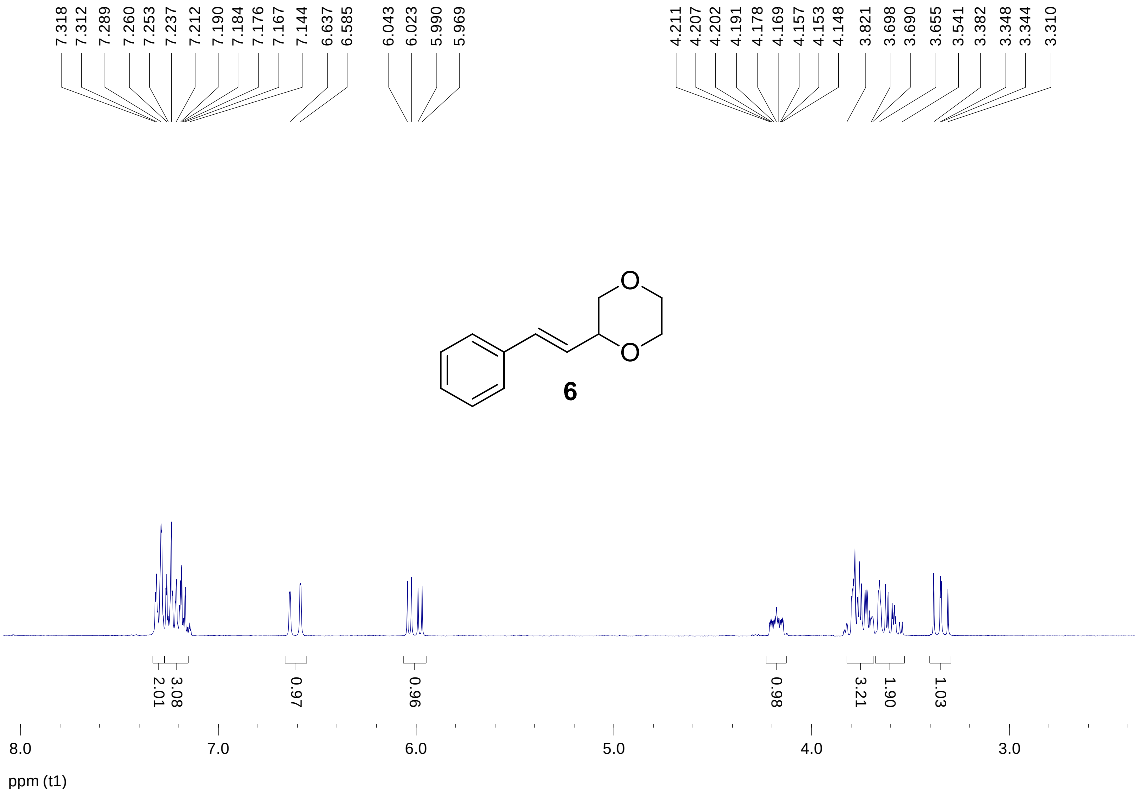
ppm (t1)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4.202
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3.344
3.310
O
O
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3.08
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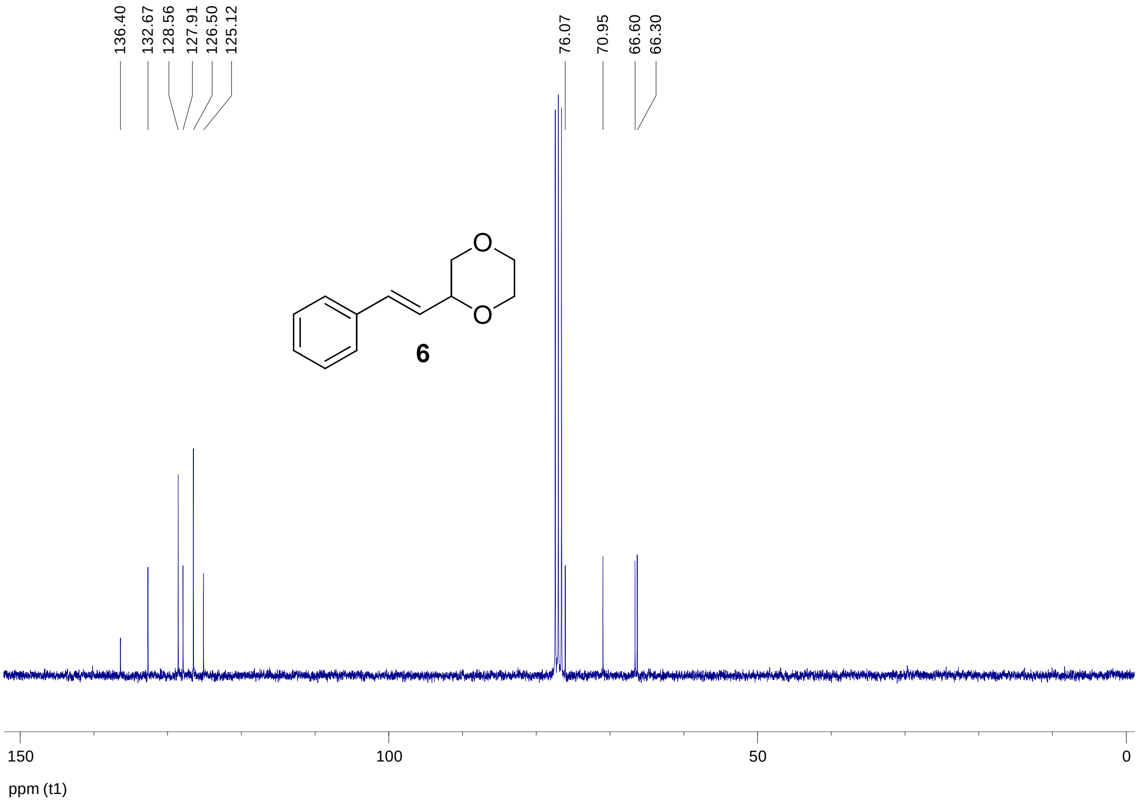
3.0
ppm (t1)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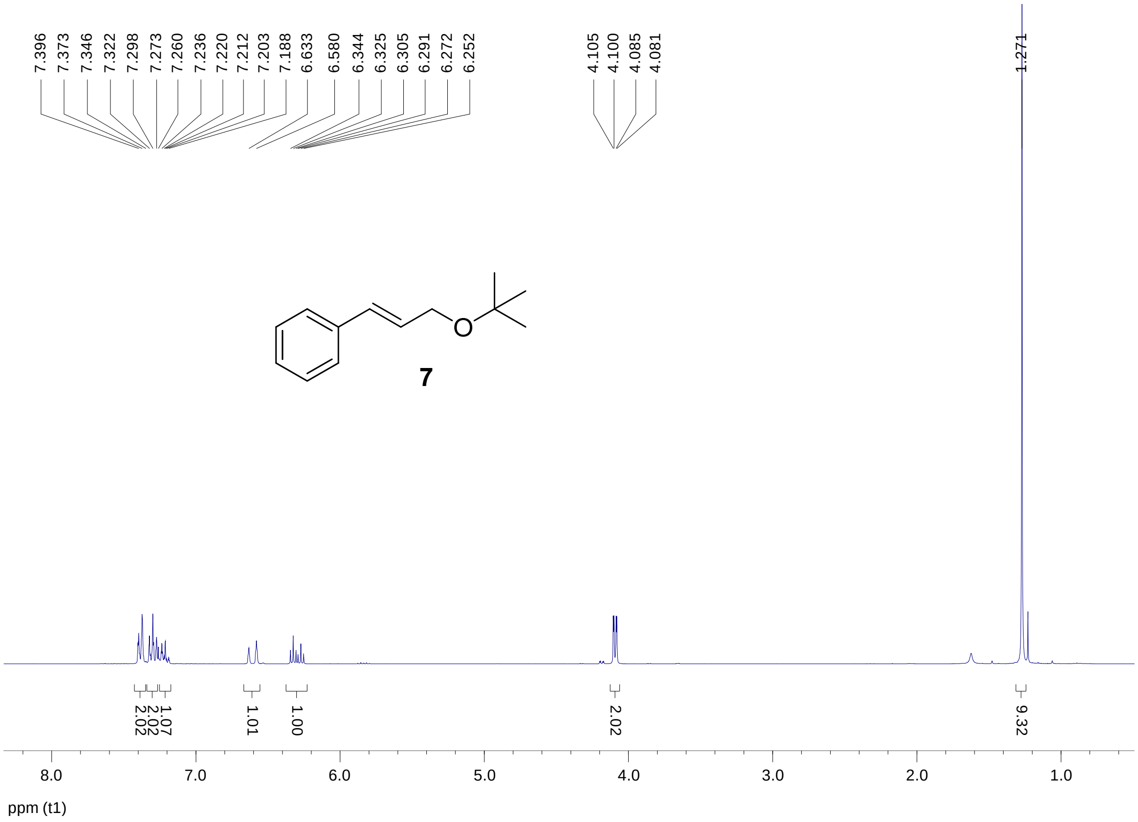
ppm (t1)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6.580
6.344
6.325
6.305
6.291
6.272
6.252
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4.100
4.085
4.081
1.271
O
7
2.02
2.02
1.07
1.01
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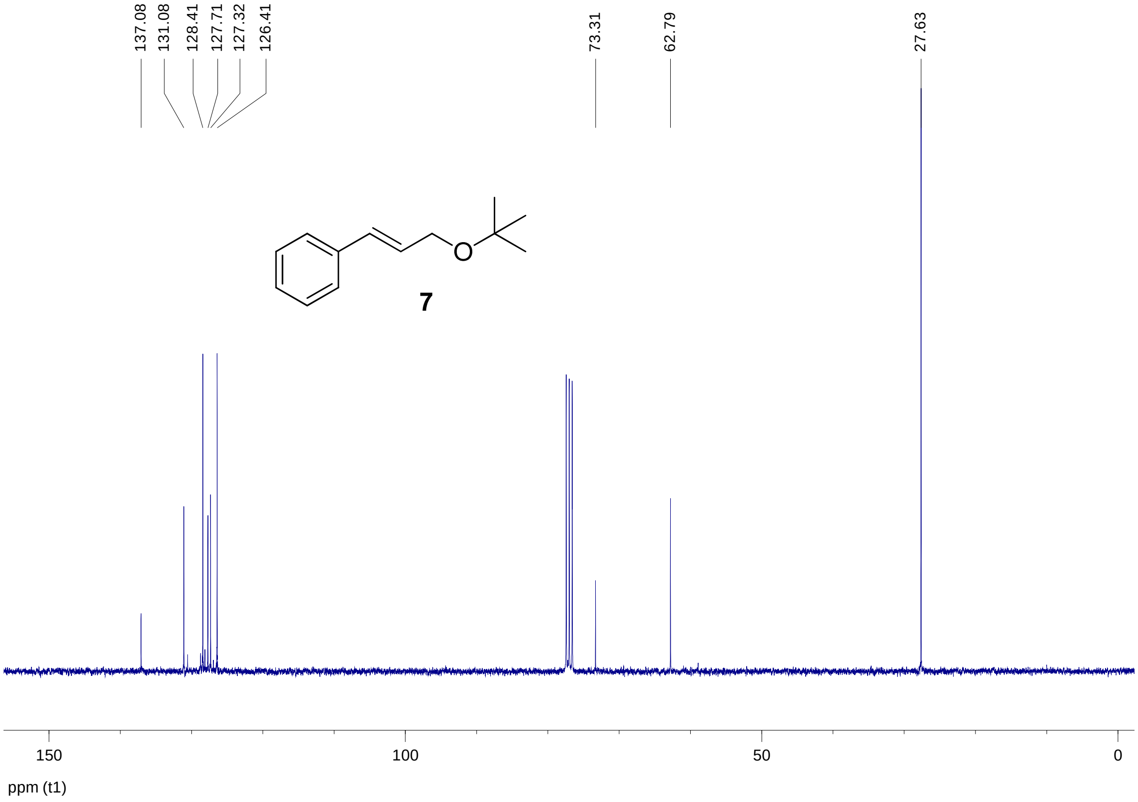
1.0
ppm (t1)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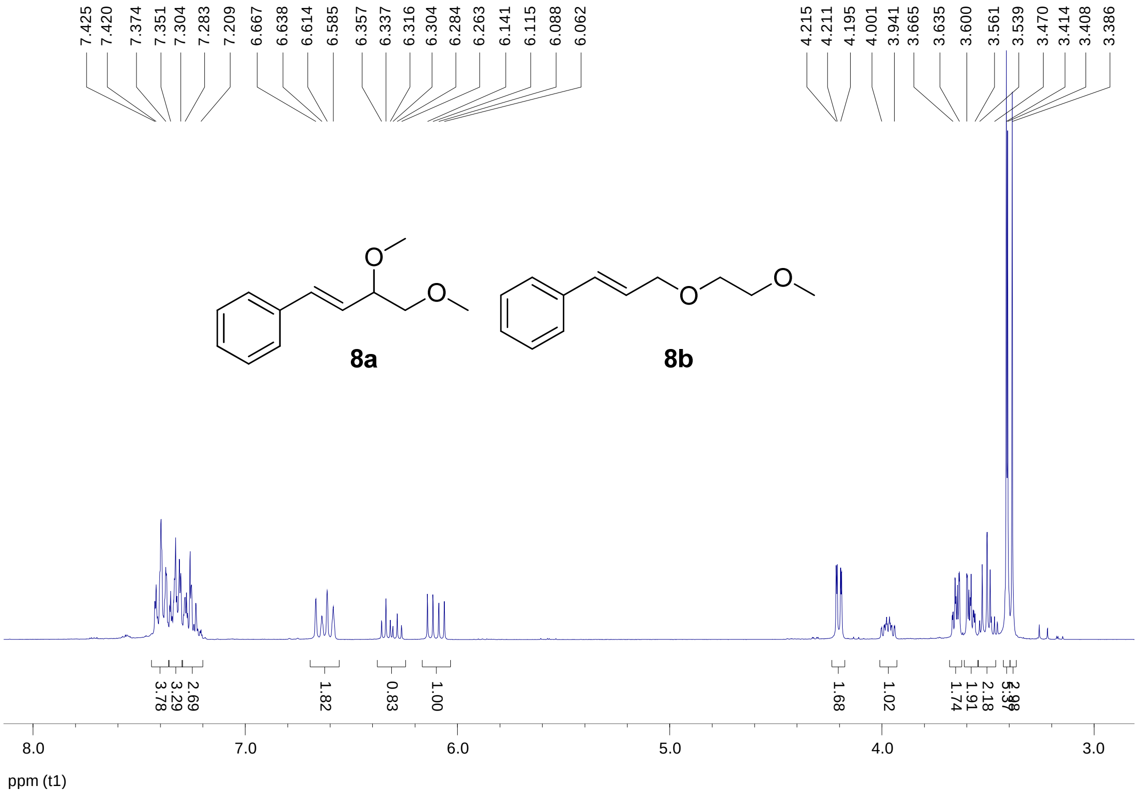
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6.088
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4.211
4.195
4.001
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3.665
3.635
3.600
3.561
3.539
3.470
3.414
3.408
3.386
O
O
8a
O
O
8b
3.78
3.29
2.69
1.82
0.83
1.00
1.68
1.02
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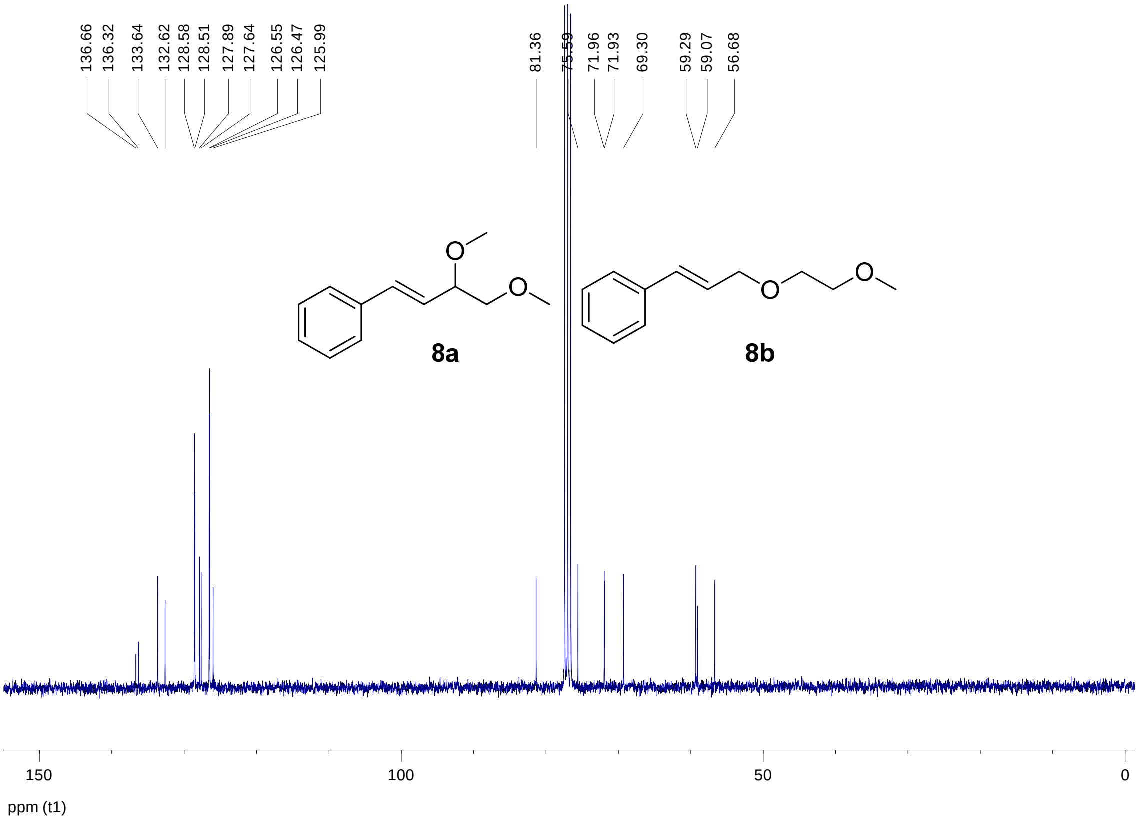
ppm (t1)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71.96
71.93
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59.07
56.68
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O
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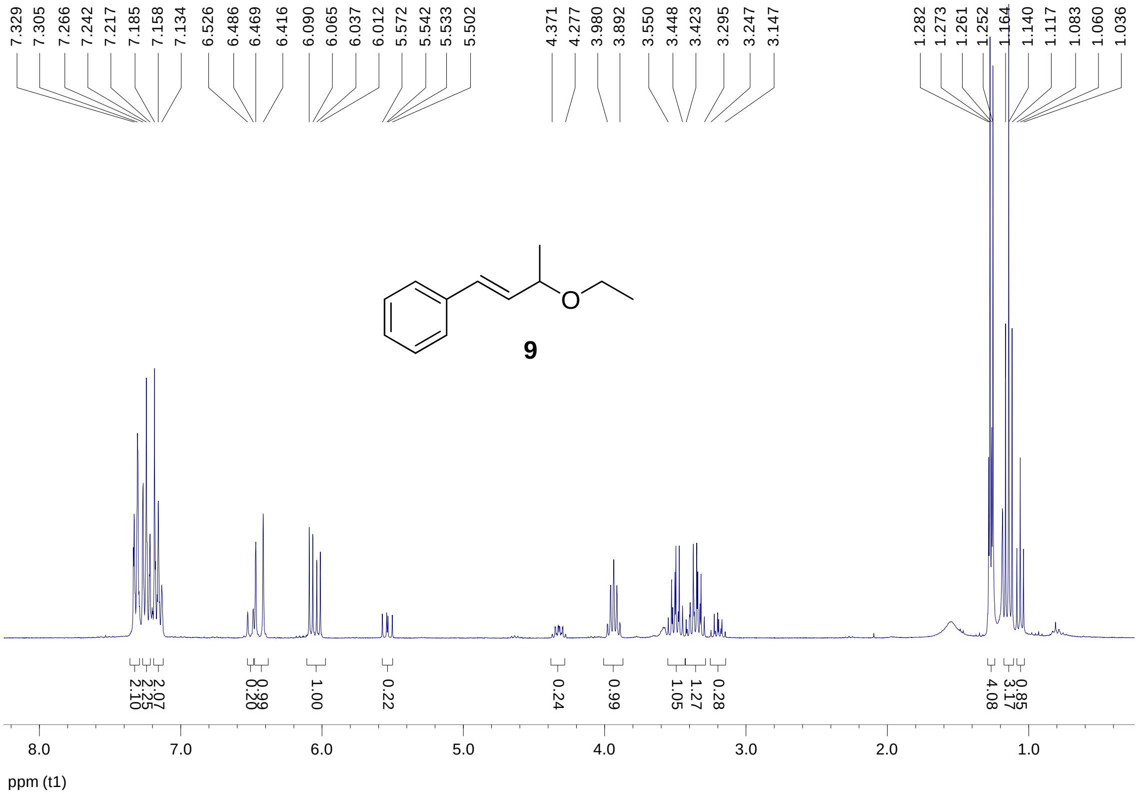
O
O
8b
150
100
50
0
ppm (t1)



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1.060
1.036
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9
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2.25
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0.20
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1.00
0.22
0.24
0.99
1.05
1.27
0.28
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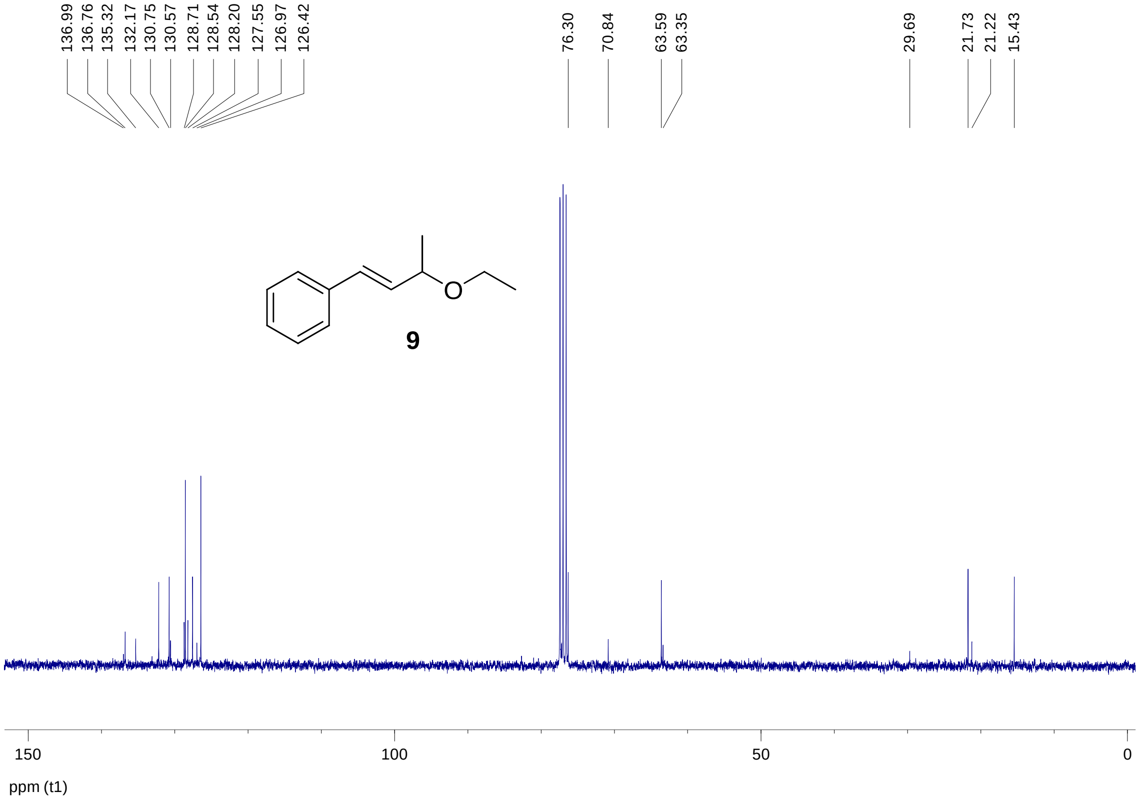
ppm (t1)



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128.20
127.55
126.97
126.42
76.30
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63.59
63.35
29.69
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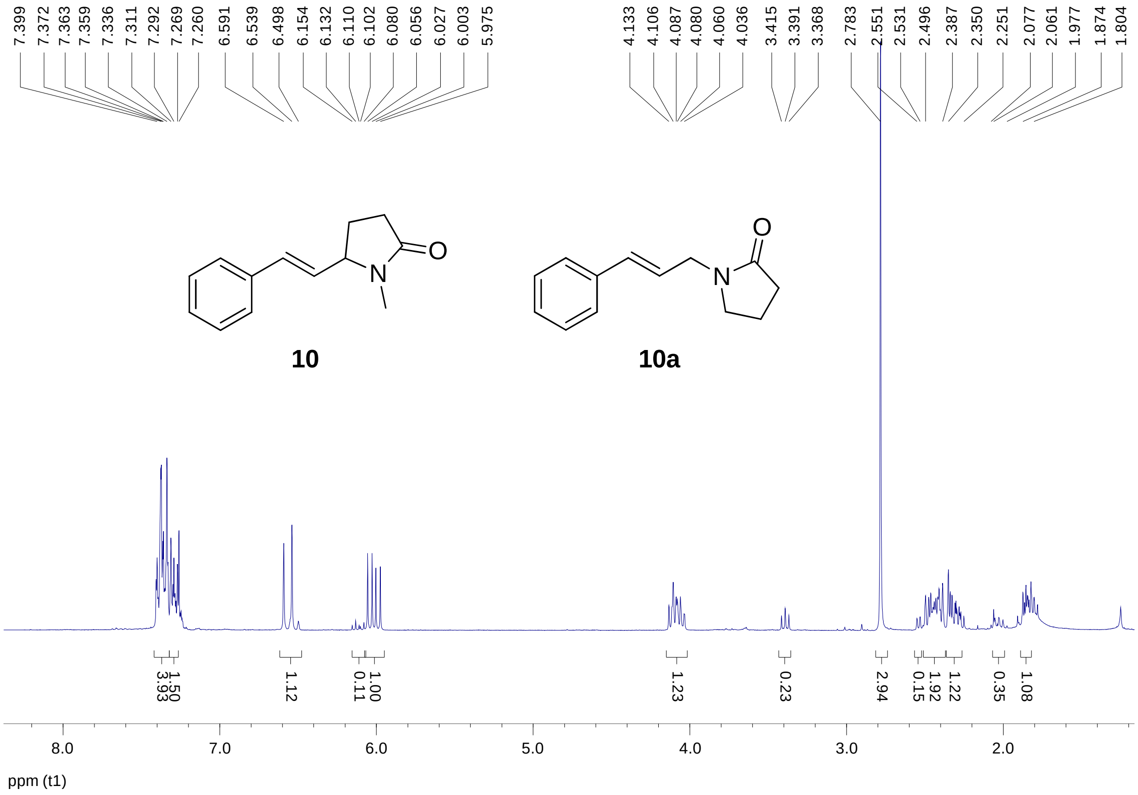
21.22
15.43
O
9
150
100
50
0
ppm (t1)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4.133 4.106 4.087 4.080 4.060 4.036 3.415 3.391 3.368 2.783 2.551 2.531 2.496 2.387 2.350 2.251 2.077 2.061 1.977 1.874 1.804
N
O
10
10a
3.93 1.50 1.12 0.11 1.00 1.23 0.23 2.94 0.15 1.92 1.22 0.35 1.08
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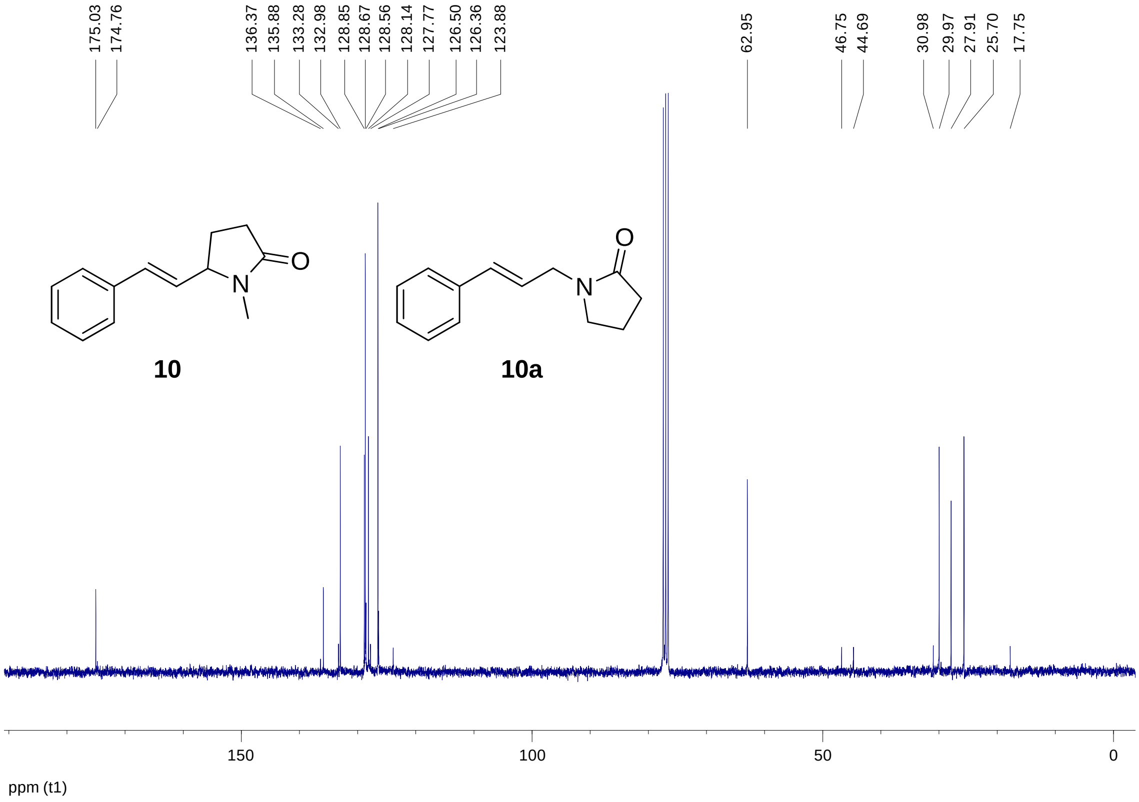
ppm (t1)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10a
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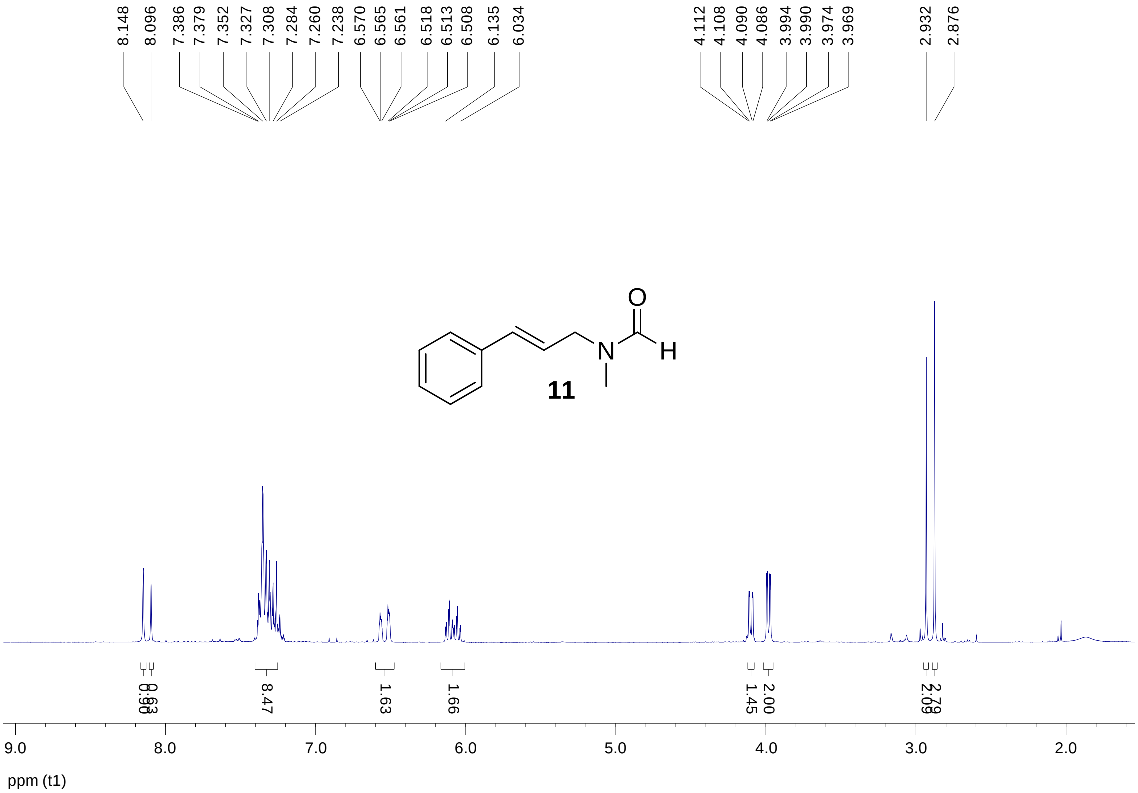
ppm (t1)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4.086
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2.876
O
N
H
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1.63
1.66
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2.09
2.79
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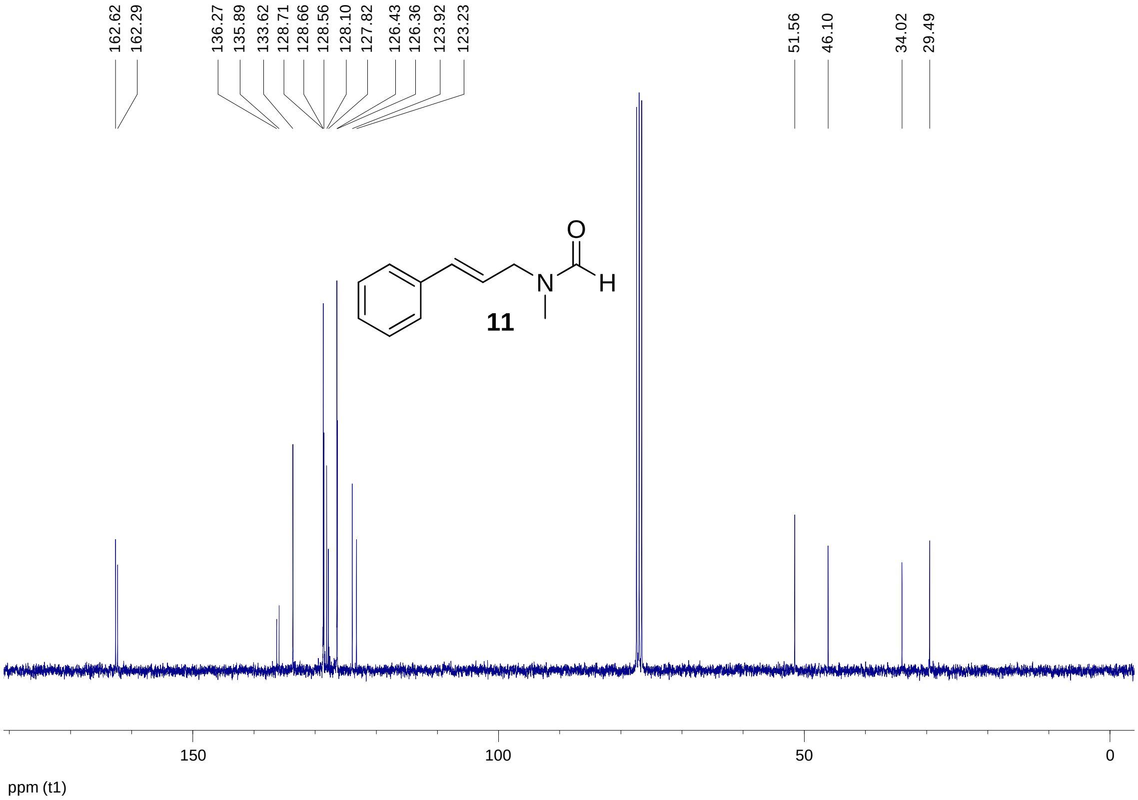
6.0
5.0
4.0
3.0
2.0
ppm (t1)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162.29
136.27
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133.62
128.71
128.66
128.56
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127.82
126.43
126.36
123.92
123.23
51.56
46.10
34.02
29.49
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N
H
11
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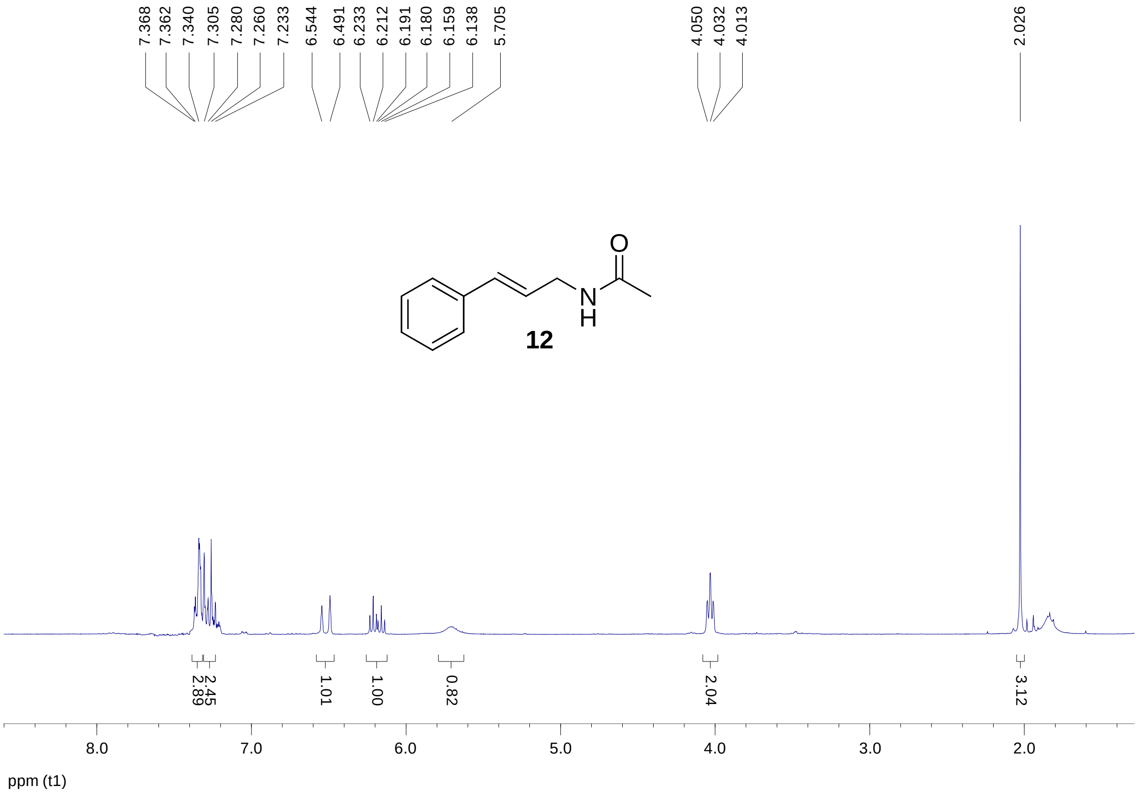
100
50
0
ppm (t1)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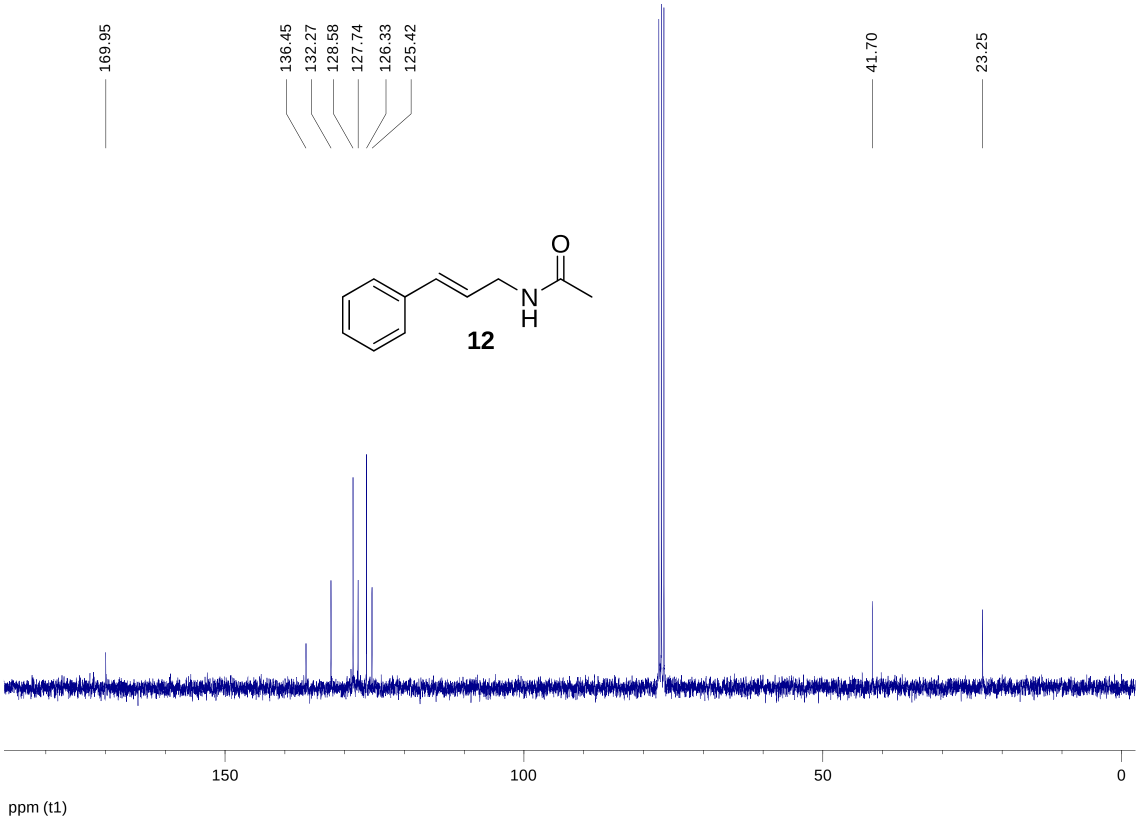
7.305
7.280
7.260
7.233
6.544
6.491
6.233
6.212
6.191
6.180
6.159
6.138
5.705
4.050
4.032
4.013
2.026
O
N
H
12
2.89
2.45
1.01
1.00
0.82
2.04
3.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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136.45
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H
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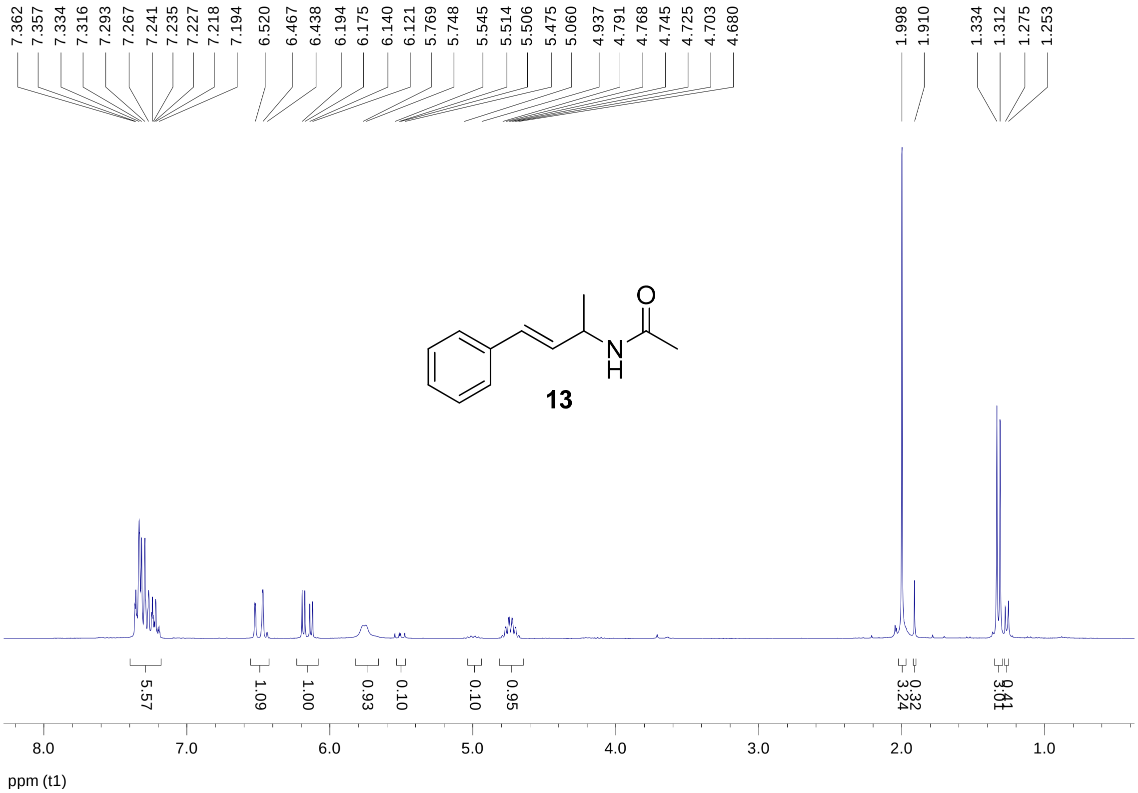
100
50
0
ppm (t1)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7.293
7.267
7.241
7.235
7.227
7.218
7.194
6.520
6.467
6.438
6.194
6.175
6.140
6.121
5.769
5.748
5.545
5.514
5.506
5.475
5.060
4.937
4.791
4.768
4.745
4.725
4.703
4.680
1.998
1.910
1.334
1.312
1.275
1.253
O
N
H
13
5.57
1.09
1.00
0.93
0.10
0.10
0.95
3.24
0.32
3.01
0.41
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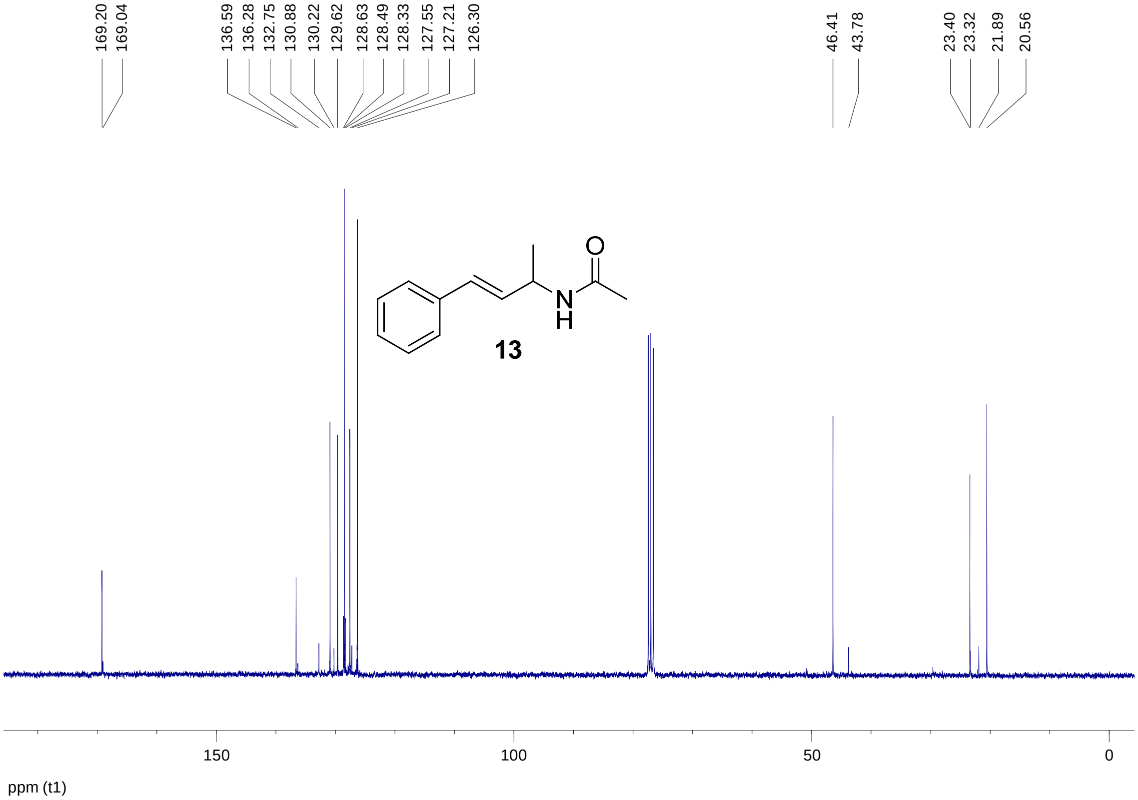
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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129.62
128.63
128.49
128.33
127.55
127.21
126.30
46.41
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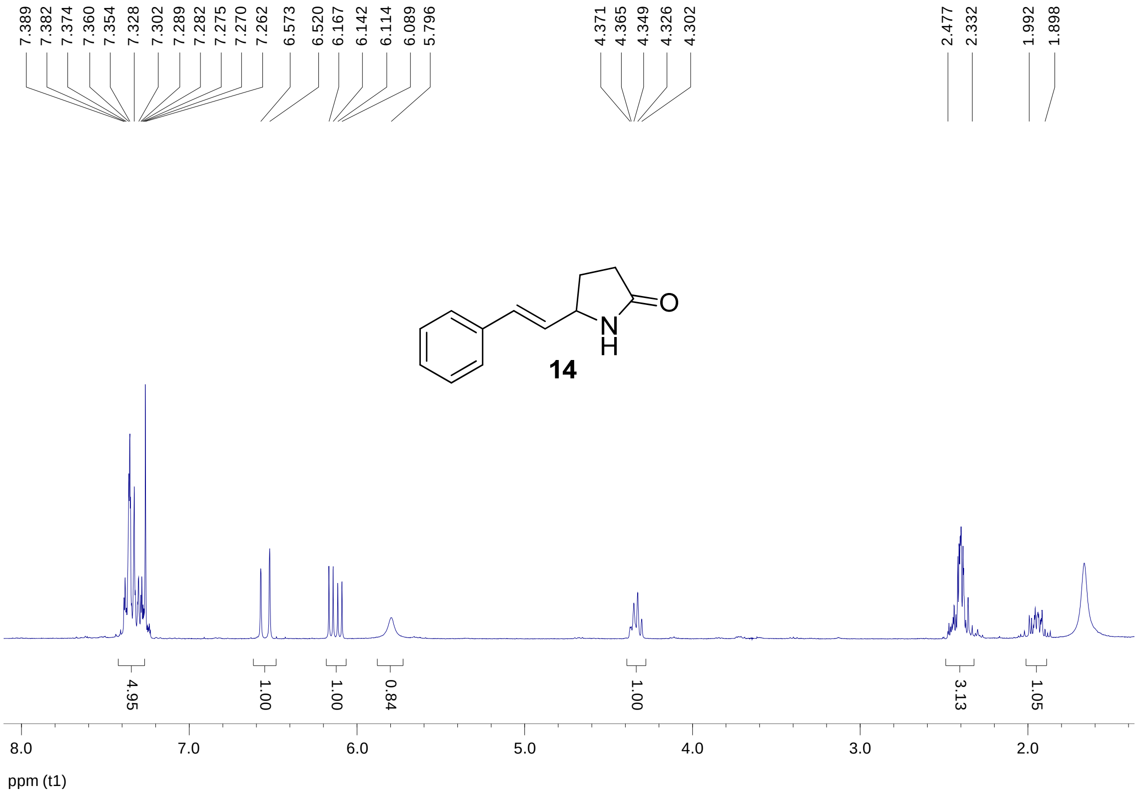
23.40
23.32
21.89
20.56
O
N
H
13
150
100
50
0
ppm (t1)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7.289
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7.275
7.270
7.262
6.573
6.520
6.167
6.142
6.114
6.089
5.796
4.371
4.365
4.349
4.326
4.302
2.477
2.332
1.992
1.898
NH
O
14
4.95
1.00
1.00
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1.05
8.0
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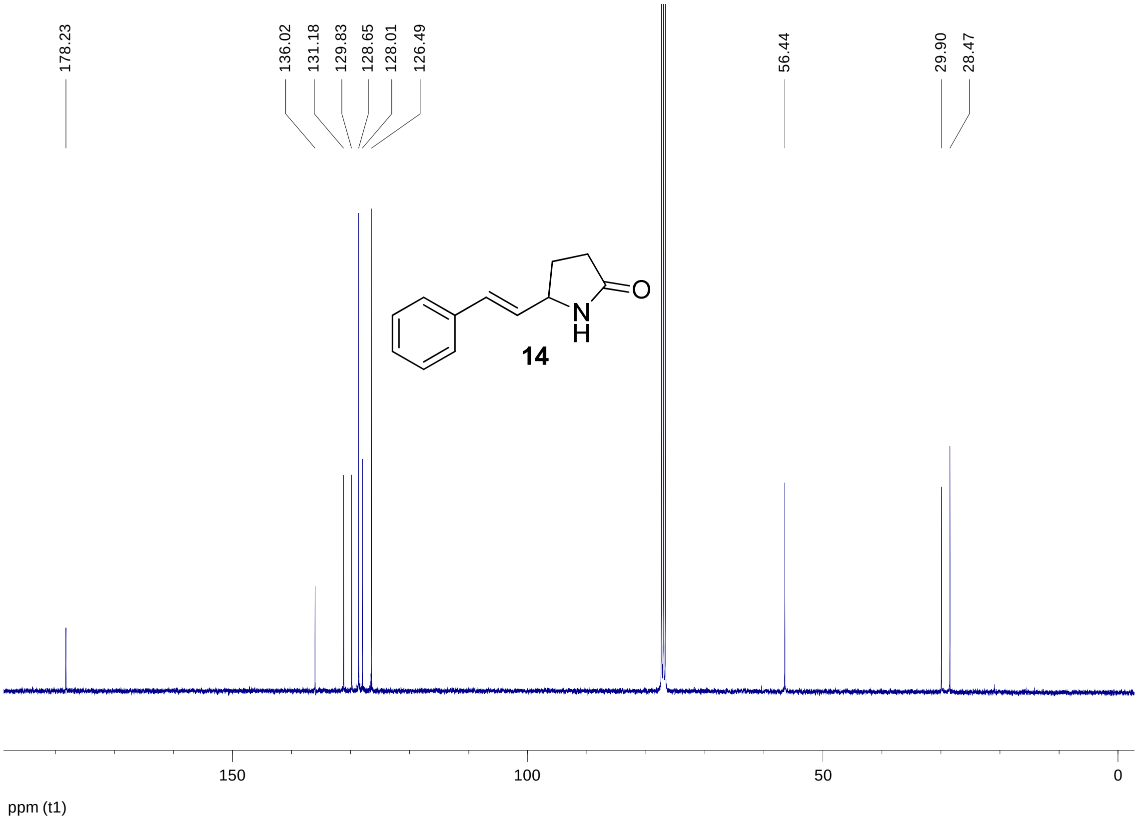
4.0
3.0
2.0
ppm (t1)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131.18
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126.49
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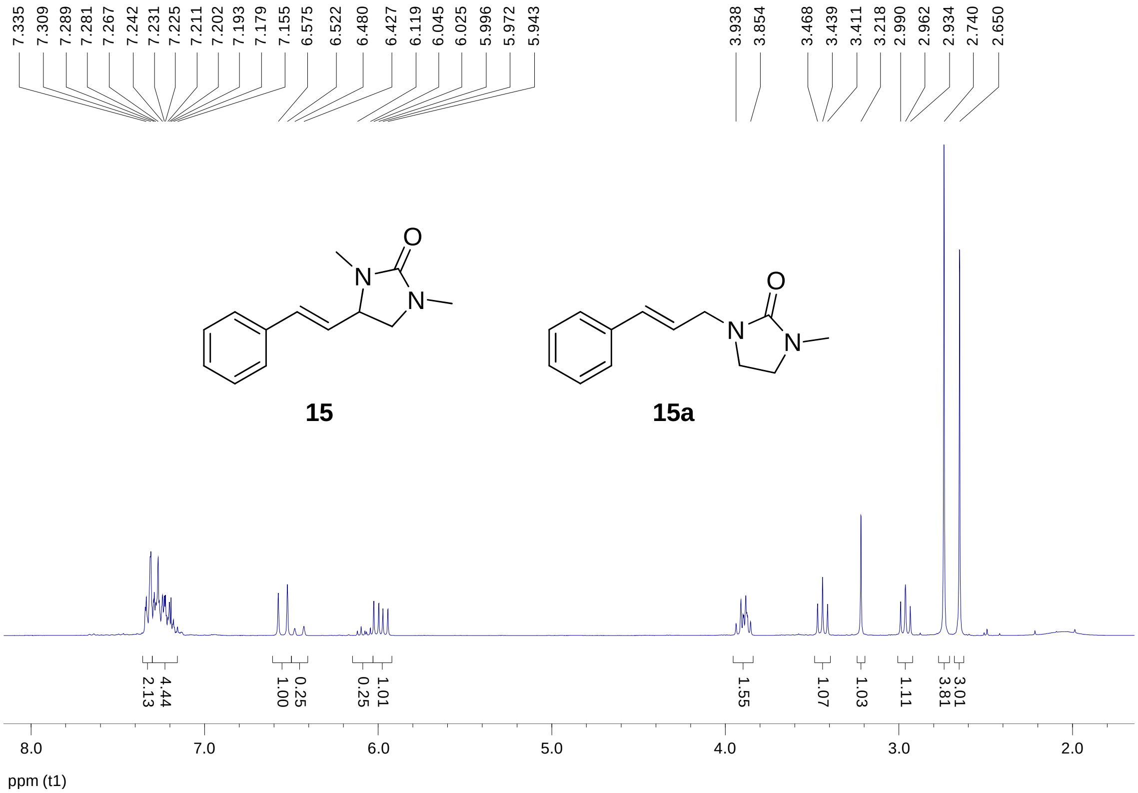
50
0
ppm (t1)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7.289
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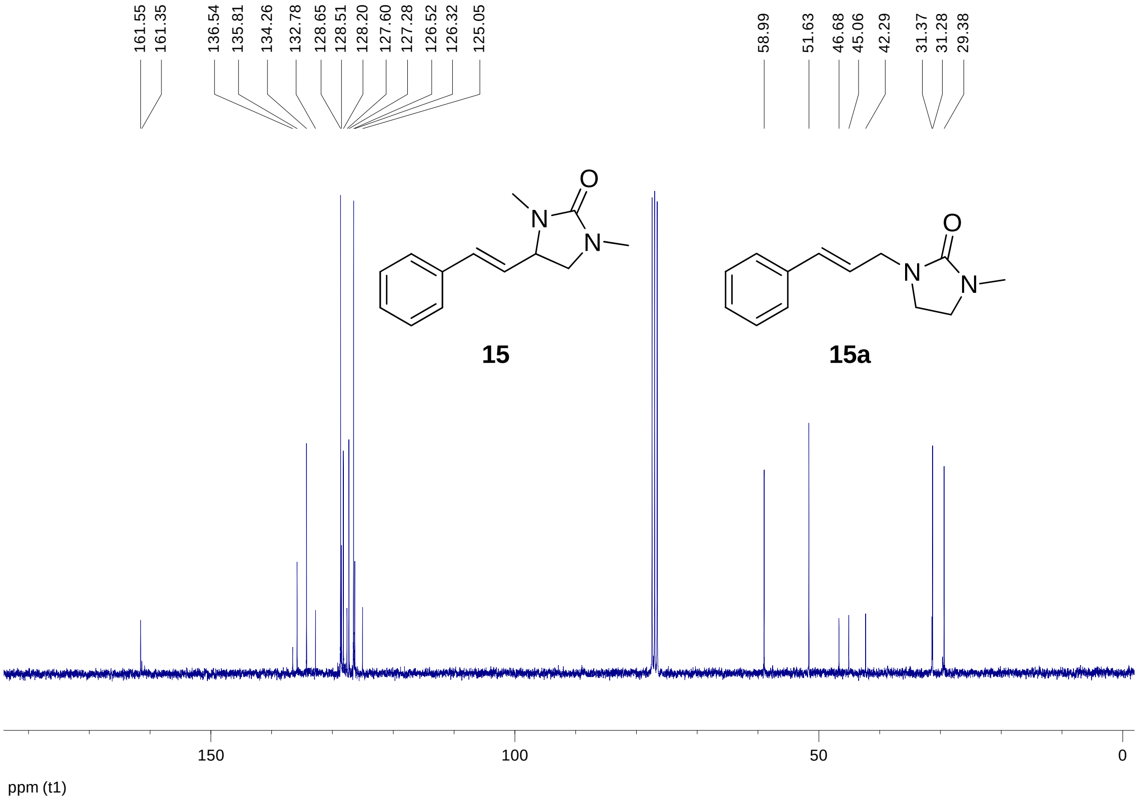
7.267
7.242
7.231
7.225
7.211
7.202
7.193
7.179
7.155
6.575
6.522
6.480
6.427
6.119
6.045
6.025
5.996
5.972
5.943
3.938
3.854
3.468
3.439
3.411
3.218
2.990
2.962
2.934
2.740
2.650
O
N
N
15
O
N
N
15a
2.13
4.44
1.00
0.25
0.25
1.01
1.55
1.07
1.03
1.11
3.81
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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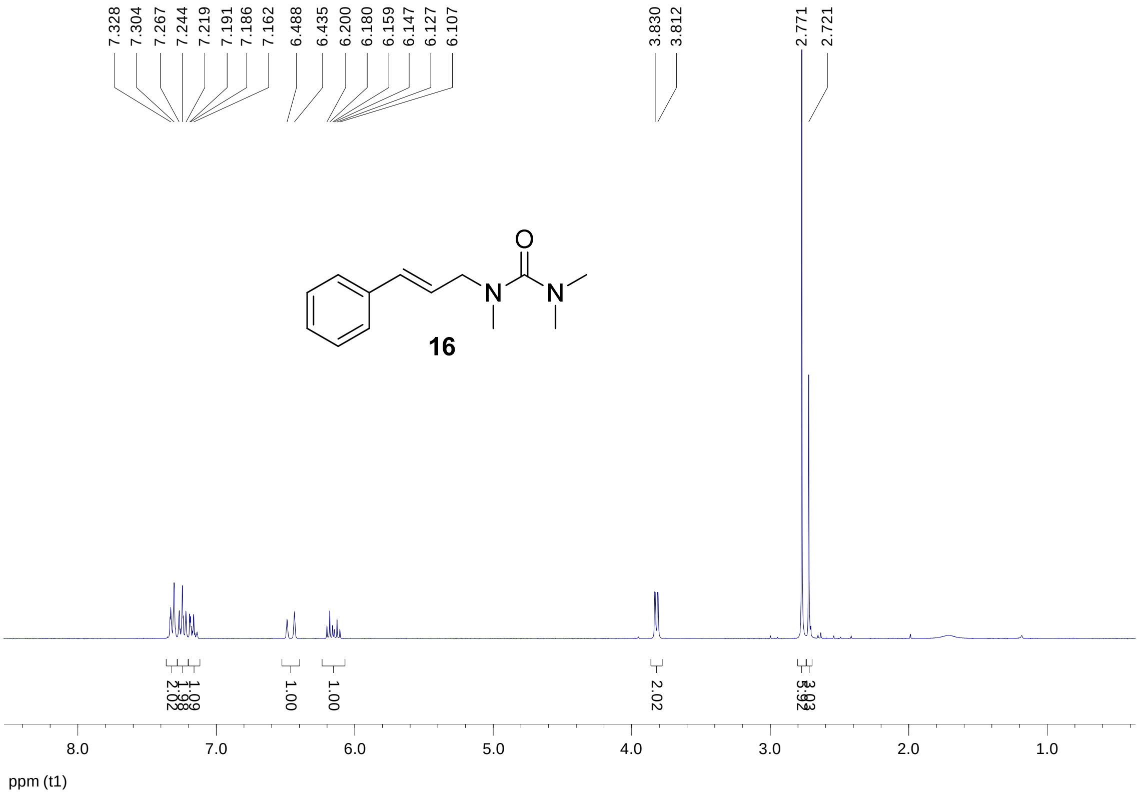
161.35
136.54
135.81
134.26
132.78
128.65
128.51
128.20
127.60
127.28
126.52
126.32
125.05
58.99
51.63
46.68
45.06
42.29
31.37
31.28
29.38
O
N
N
15
O
N
N
15a
150
100
50
0
ppm (t1)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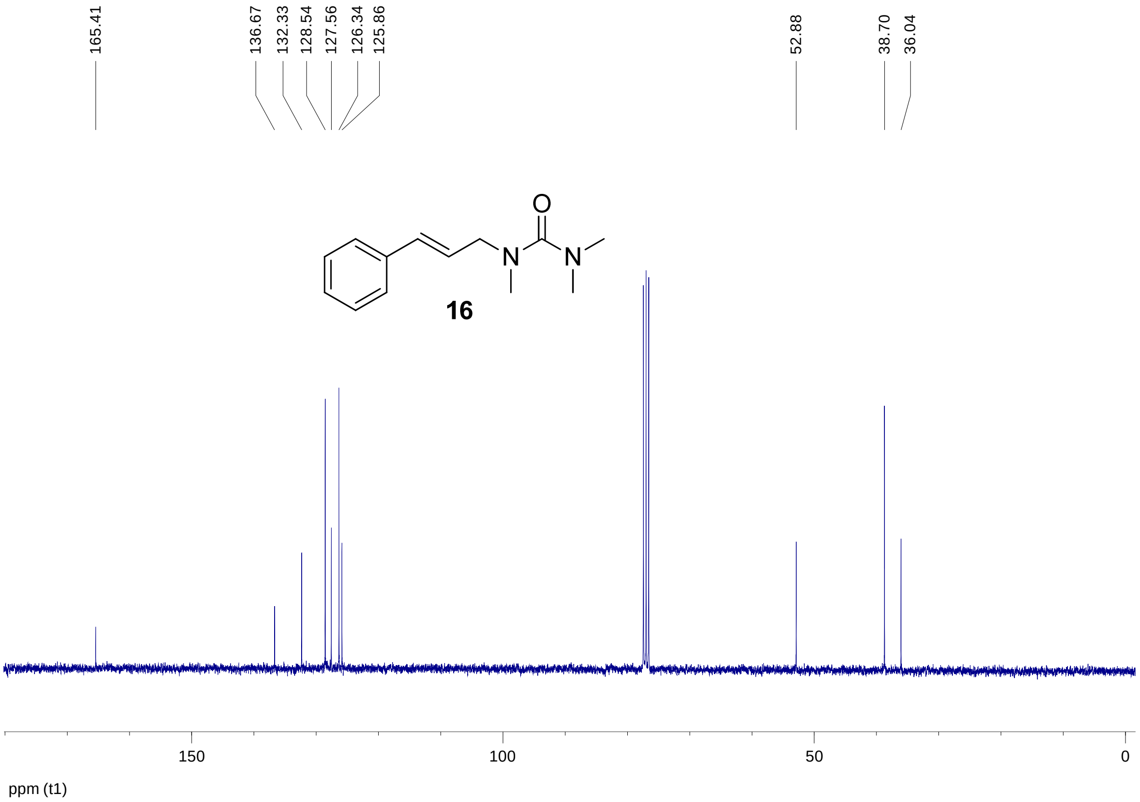
7.267
7.244
7.219
7.191
7.186
7.162
6.488
6.435
6.200
6.180
6.159
6.147
6.127
6.107
3.830
3.812
2.771
2.721
O
N
N
16
2.02
1.98
1.09
1.00
1.00
2.02
5.92
3.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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136.67
132.33
128.54
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126.34
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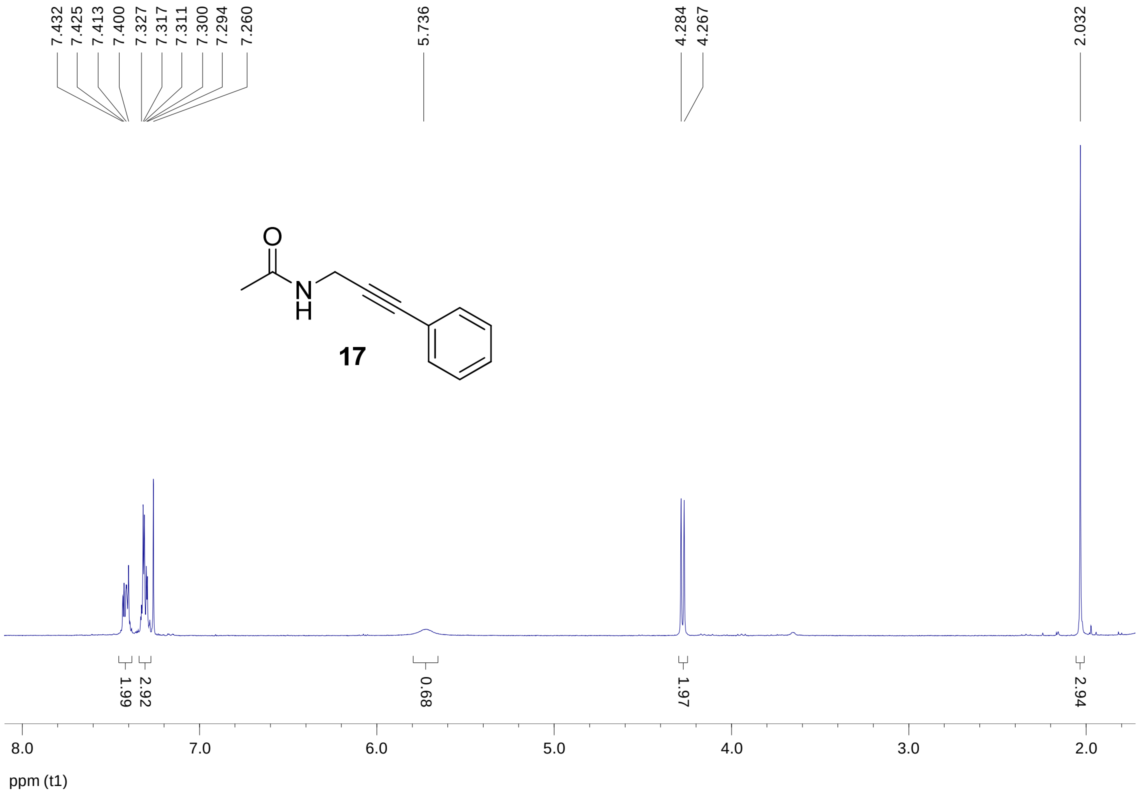
52.88
38.70
36.04
O
N
N
16
150
100
50
0
ppm (t1)


17

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7.425
7.413
7.400
7.327
7.317
7.311
7.300
7.294
7.260
5.736
4.284
4.267
2.032
O
N
H
1.99
2.92
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2.94
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7.0
6.0
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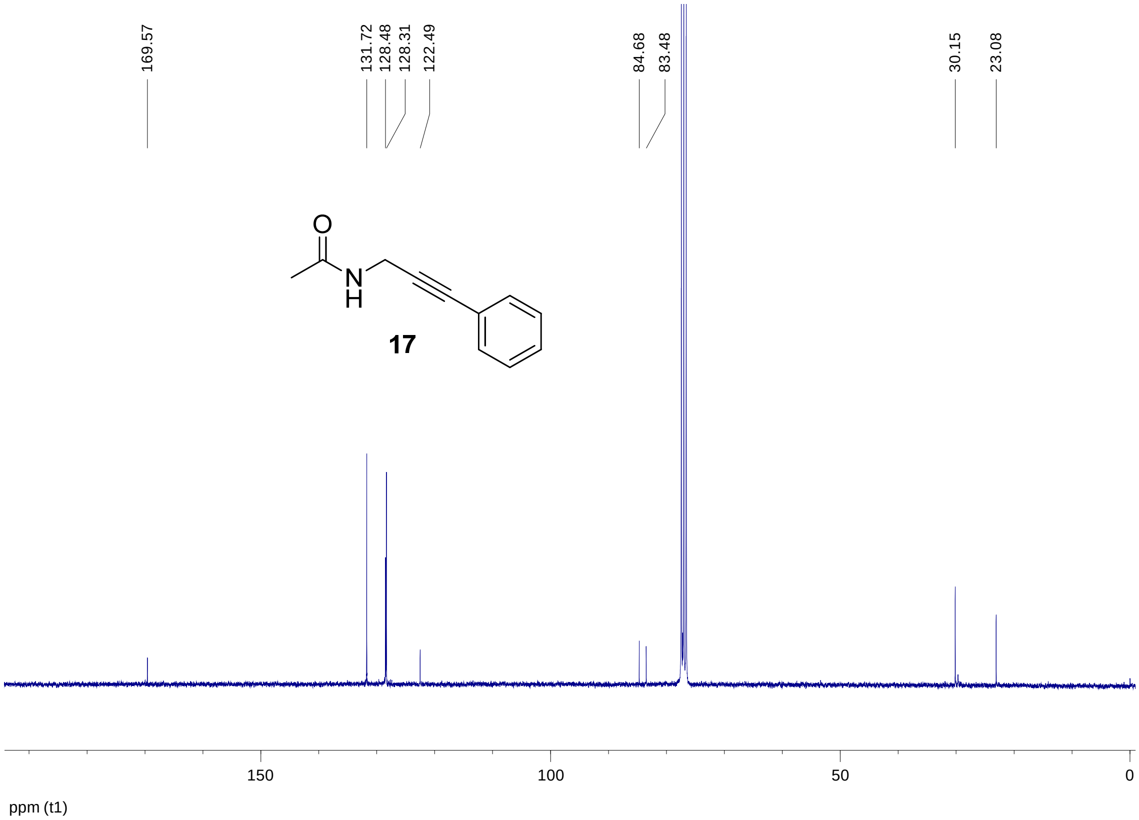
4.0
3.0
2.0
ppm (t1)


17

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131.72
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128.31
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83.48
30.15
23.08
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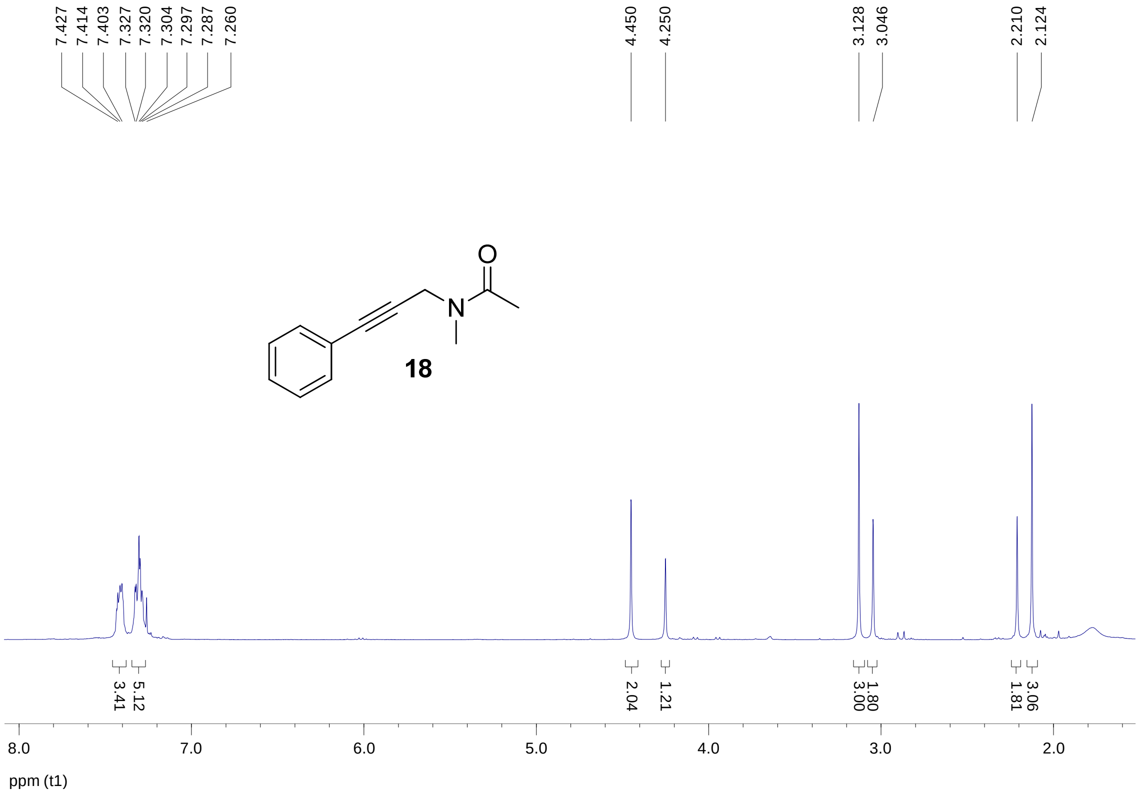
N
H
150
100
50
0
ppm (t1)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7.320
7.304
7.297
7.287
7.260
4.450
4.250
3.128
3.046
2.210
2.124
O
N
18
3.41
5.12
2.04
1.21
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3.06
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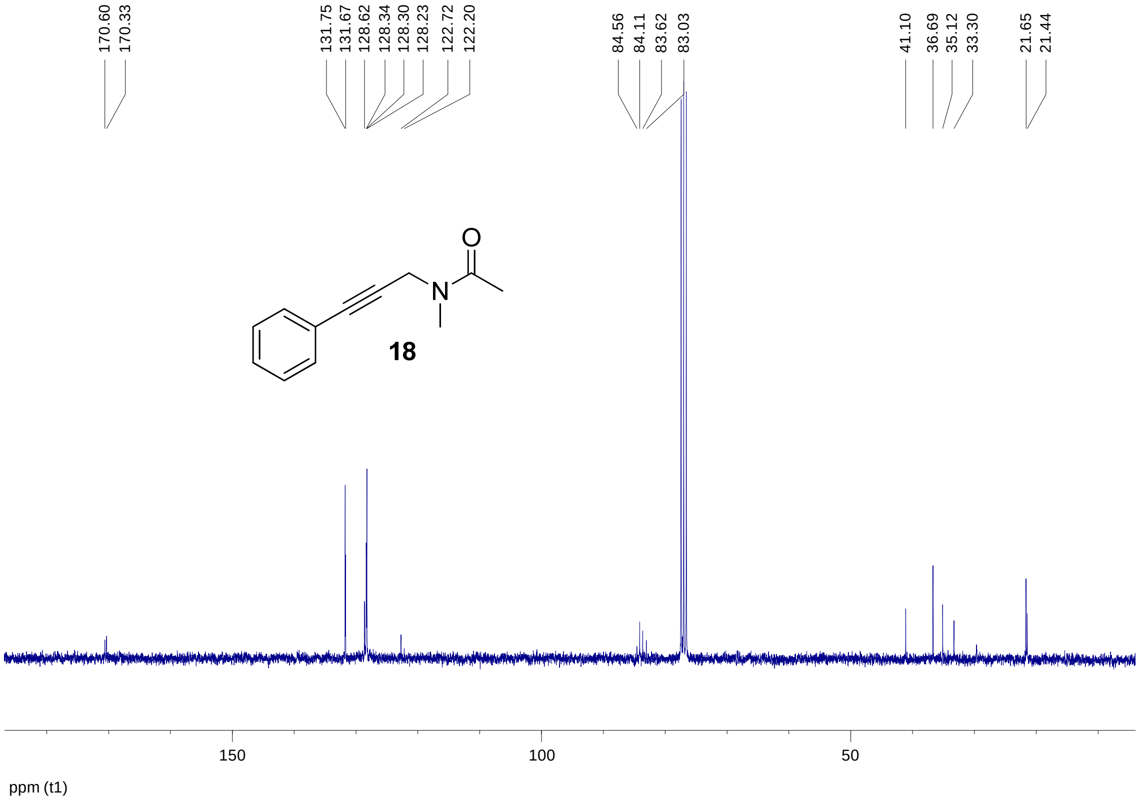
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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170.33
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128.62
128.34
128.30
128.23
122.72
122.20
84.56
84.11
83.62
83.03
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35.12
33.30
21.65
21.44
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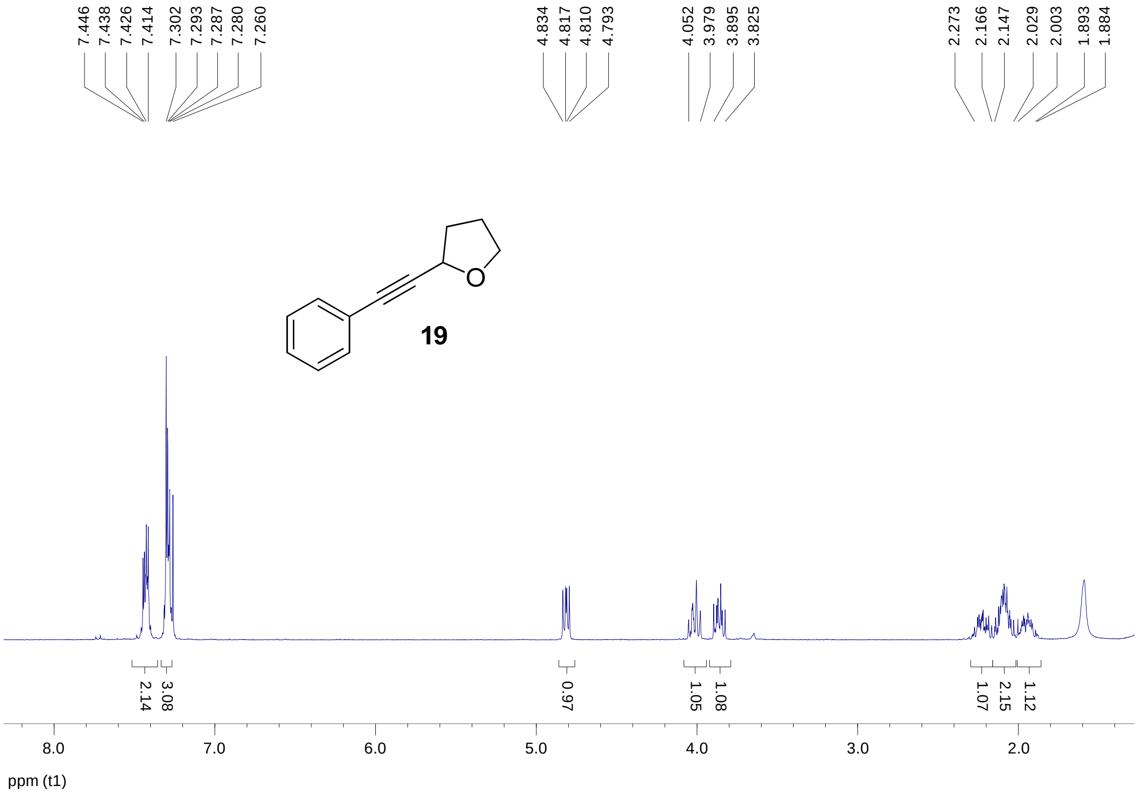
N
18
150
100
50
ppm (t1)


7.446
7.438
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7.414
7.302
7.293
7.287
7.280
7.260
4.834
4.817
4.810
4.793
4.052
3.979
3.895
3.825
2.273
2.166
2.147
2.029
2.003
1.893
1.884
O
19
2.14
3.08
0.97
1.05
1.08
1.07
2.15
1.12
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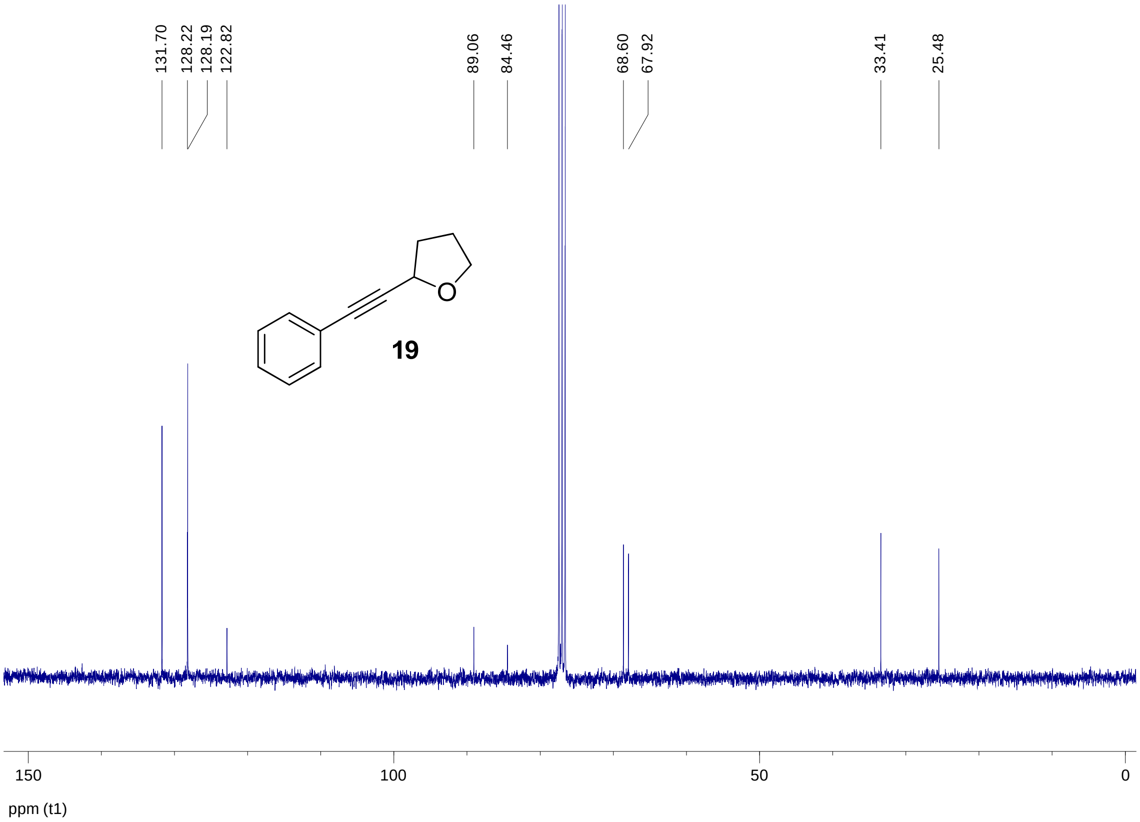
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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128.22
128.19
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89.06
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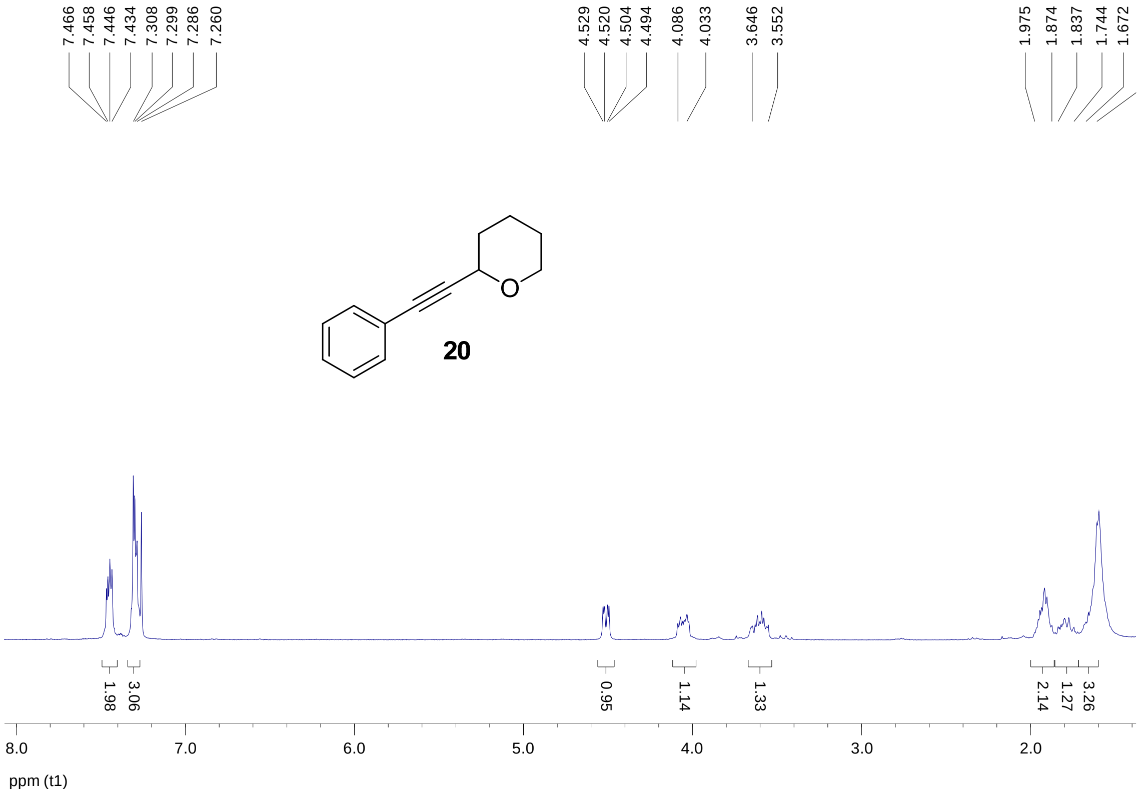
68.60
67.92
33.41
25.48
O
19
150
100
50
0
ppm (t1)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7.458
7.446
7.434
7.308
7.299
7.286
7.260
4.529
4.520
4.504
4.494
4.086
4.033
3.646
3.552
1.975
1.874
1.837
1.744
1.672
O
20
1.98
3.06
0.95
1.14
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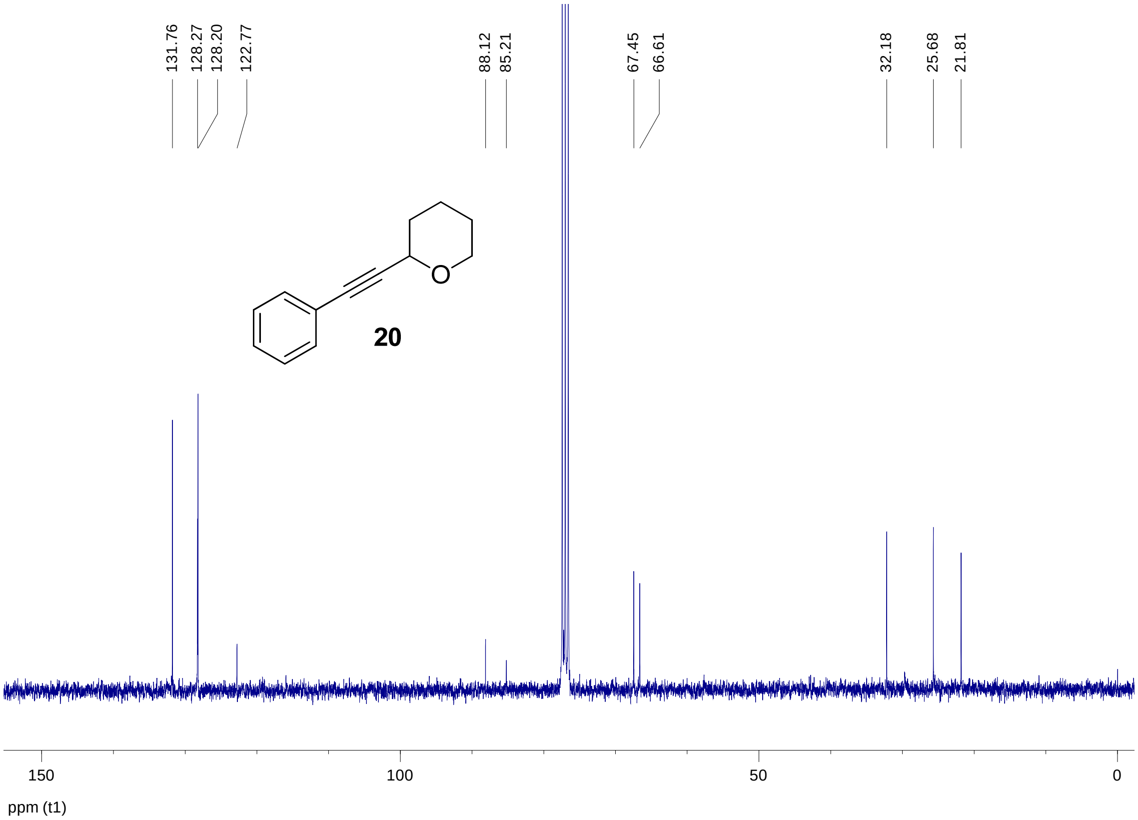
6.0
5.0
4.0
3.0
2.0
ppm (t1)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21.81
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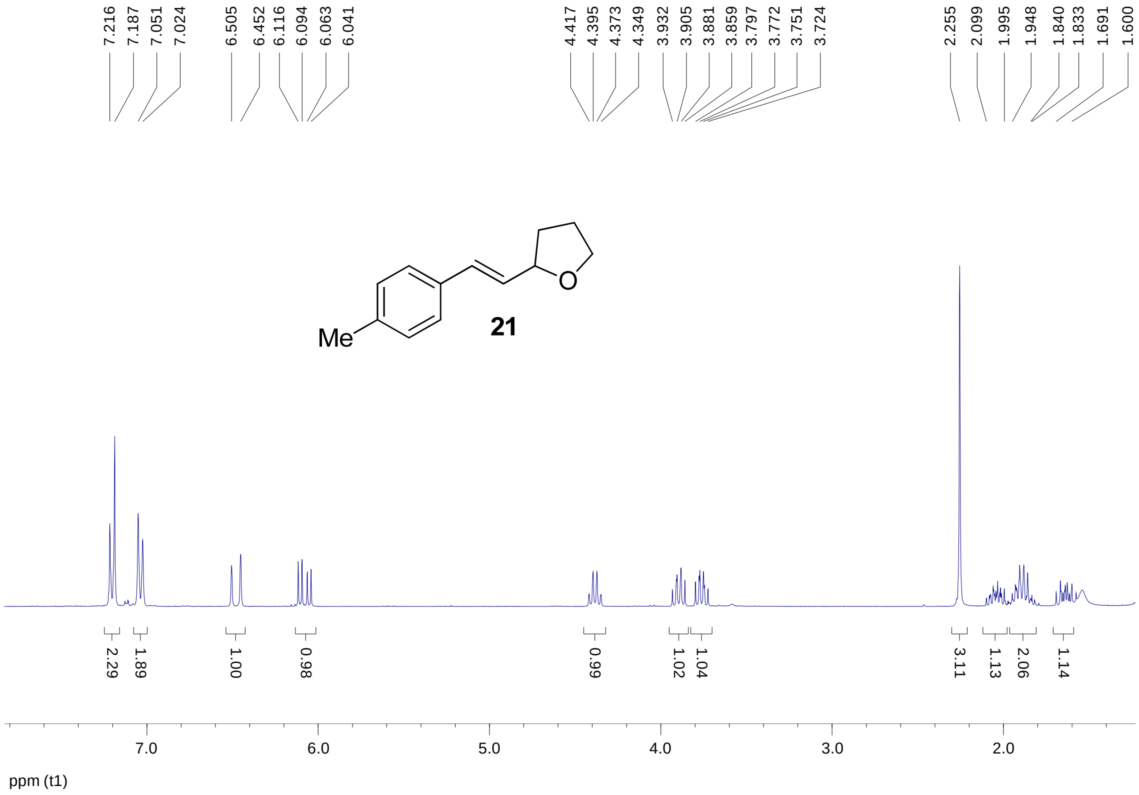
100
50
0
ppm (t1)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7.024
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6.452
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6.094
6.063
6.041
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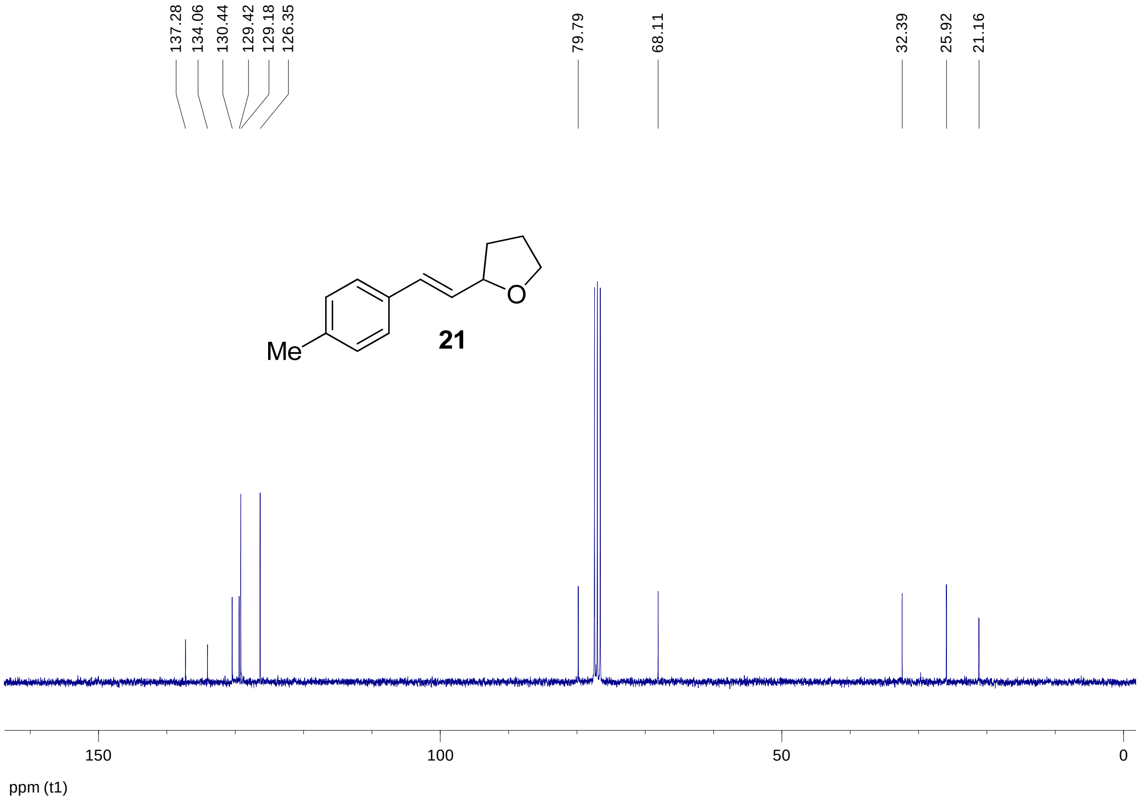
4.395
4.373
4.349
3.932
3.905
3.881
3.859
3.797
3.772
3.751
3.724
2.255
2.099
1.995
1.948
1.840
1.833
1.691
1.600
Me
O
21
2.29
1.89
1.00
0.98
0.99
1.02
1.04
3.11
1.13
2.06
1.14
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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129.42
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68.11
32.39
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21.16
Me
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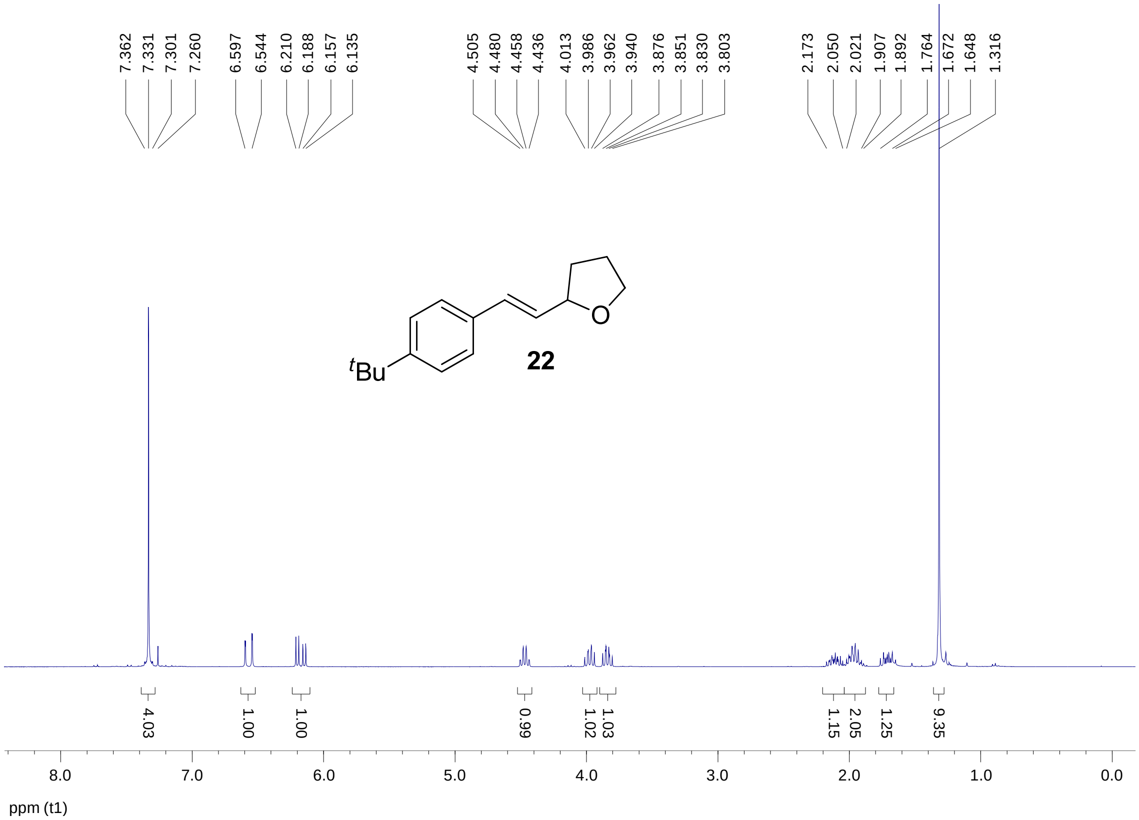
100
50
0
ppm (t1)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7.301
7.260
6.597
6.544
6.210
6.188
6.157
6.135
4.505
4.480
4.458
4.436
4.013
3.986
3.962
3.940
3.876
3.851
3.830
3.803
2.173
2.050
2.021
1.907
1.892
1.764
1.672
1.648
1.316
^tBu
O
22
4.03
1.00
1.00
0.99
1.02
1.03
1.15
2.05
1.25
9.35
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7.0
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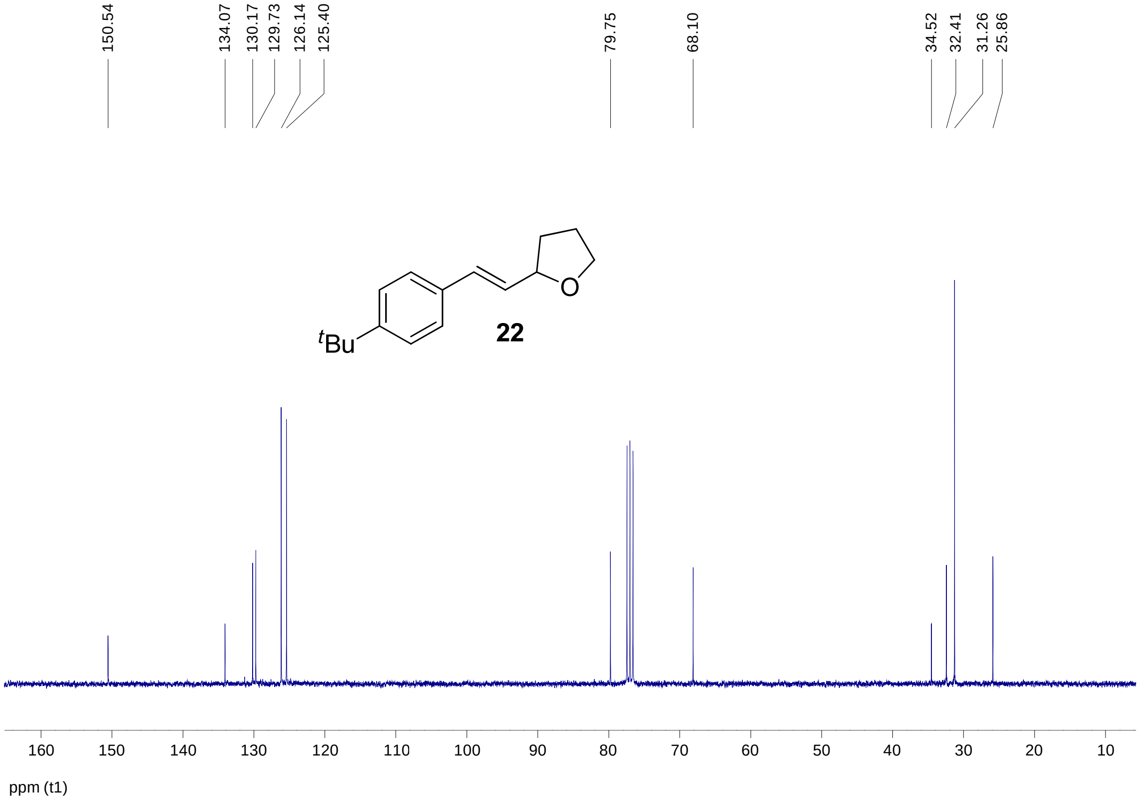
3.0
2.0
1.0
0.0
ppm (t1)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126.14
125.40
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68.10
34.52
32.41
31.26
25.86
tBu
O
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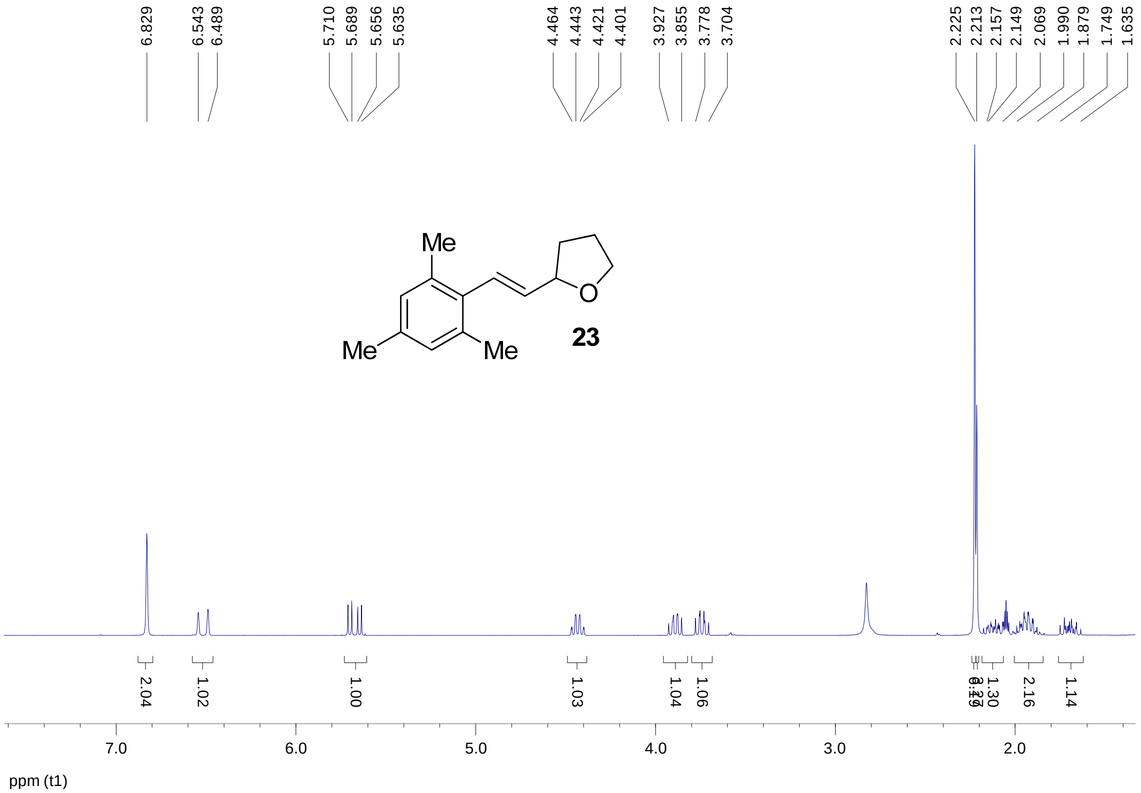
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)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5.689
5.656
5.635
4.464
4.443
4.421
4.401
3.927
3.855
3.778
3.704
2.225
2.213
2.157
2.149
2.069
1.990
1.879
1.749
1.635
Me
Me
Me
O
23
2.04
1.02
1.00
1.03
1.04
1.06
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2.16
1.14
7.0
6.0
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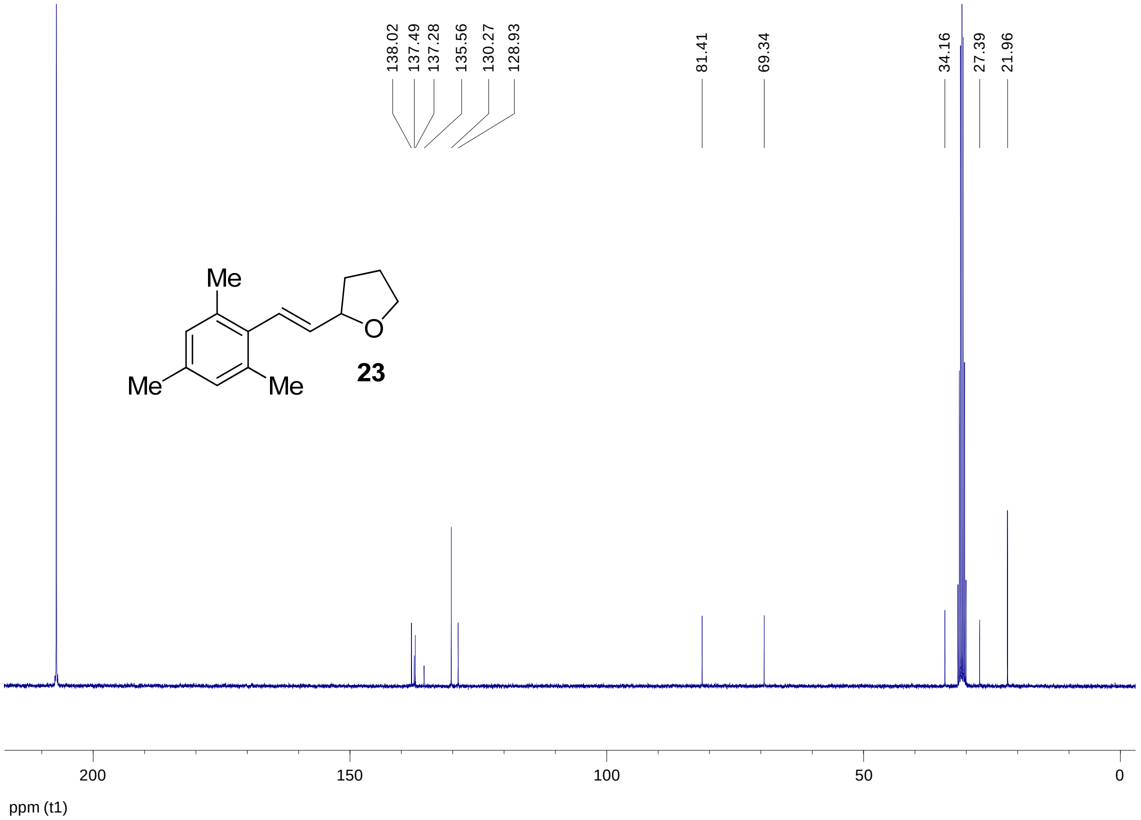
3.0
2.0
ppm (t1)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Me
Me
Me
O
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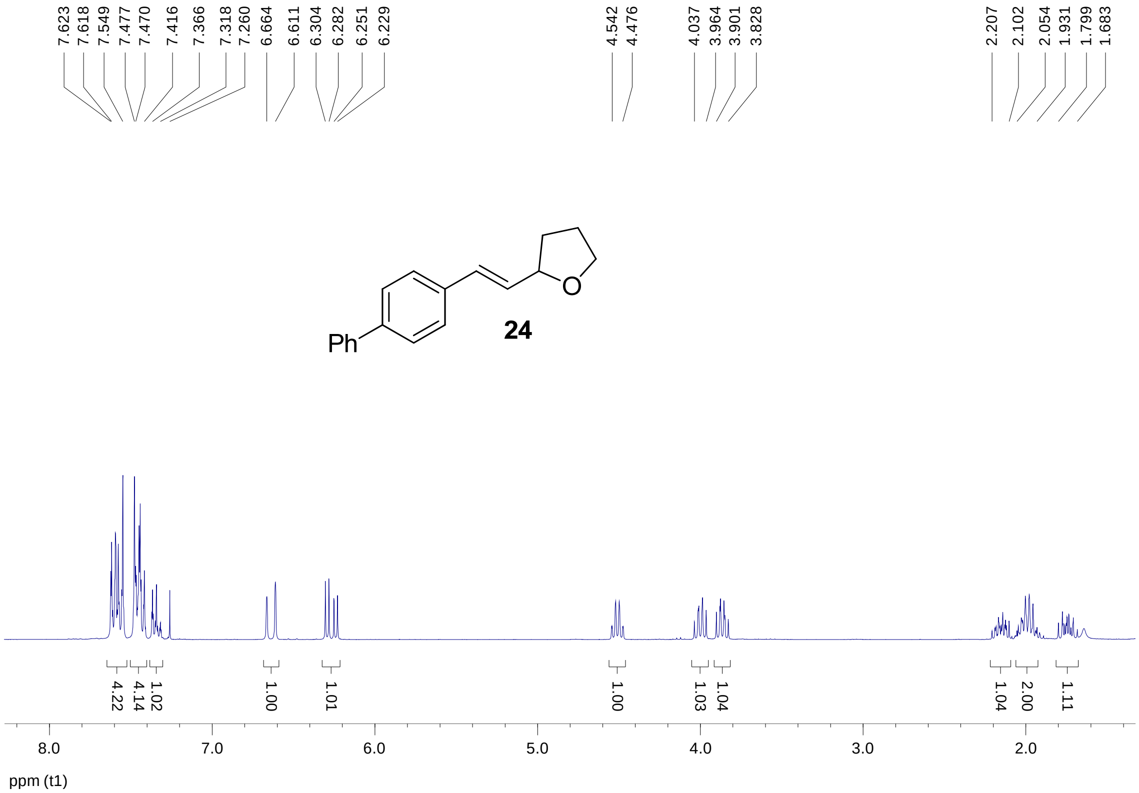
150
100
50
0
ppm (t1)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7.318
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6.304
6.282
6.251
6.229
4.542
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4.037
3.964
3.901
3.828
2.207
2.102
2.054
1.931
1.799
1.683
Ph
O
24
4.22
4.14
1.02
1.00
1.01
1.00
1.03
1.04
1.04
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1.11
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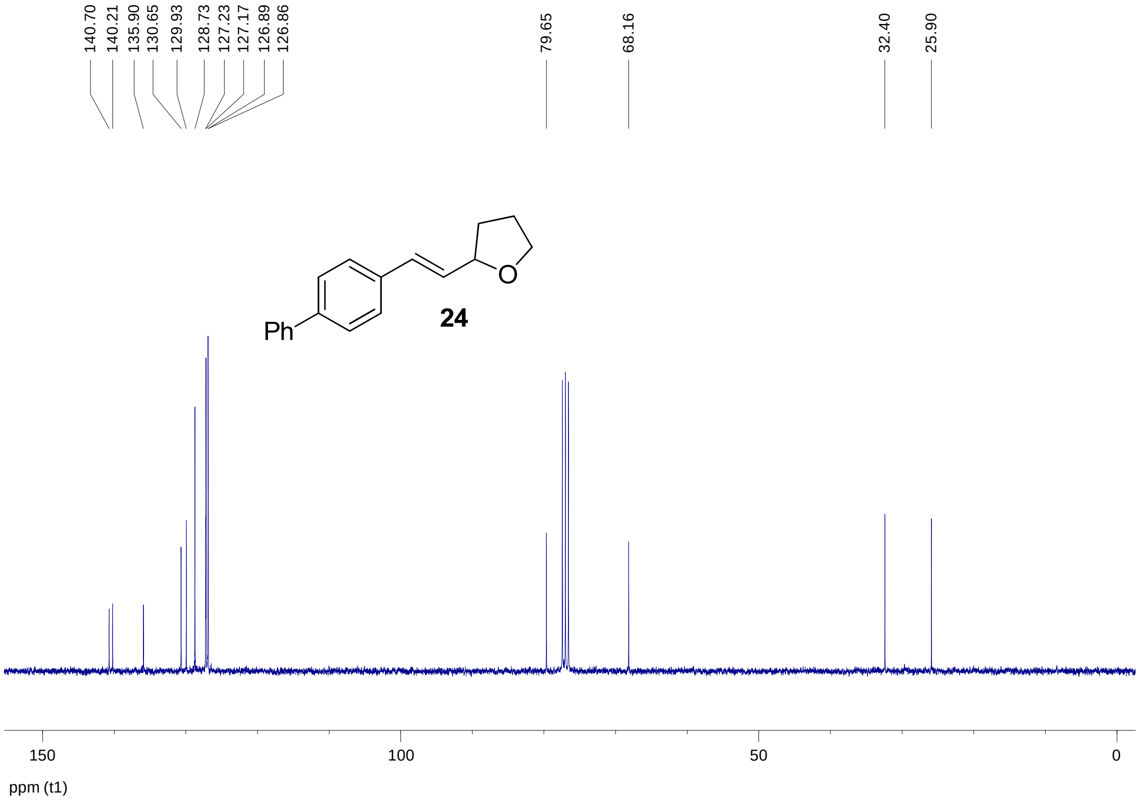
3.0
2.0
ppm (t1)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128.73
127.23
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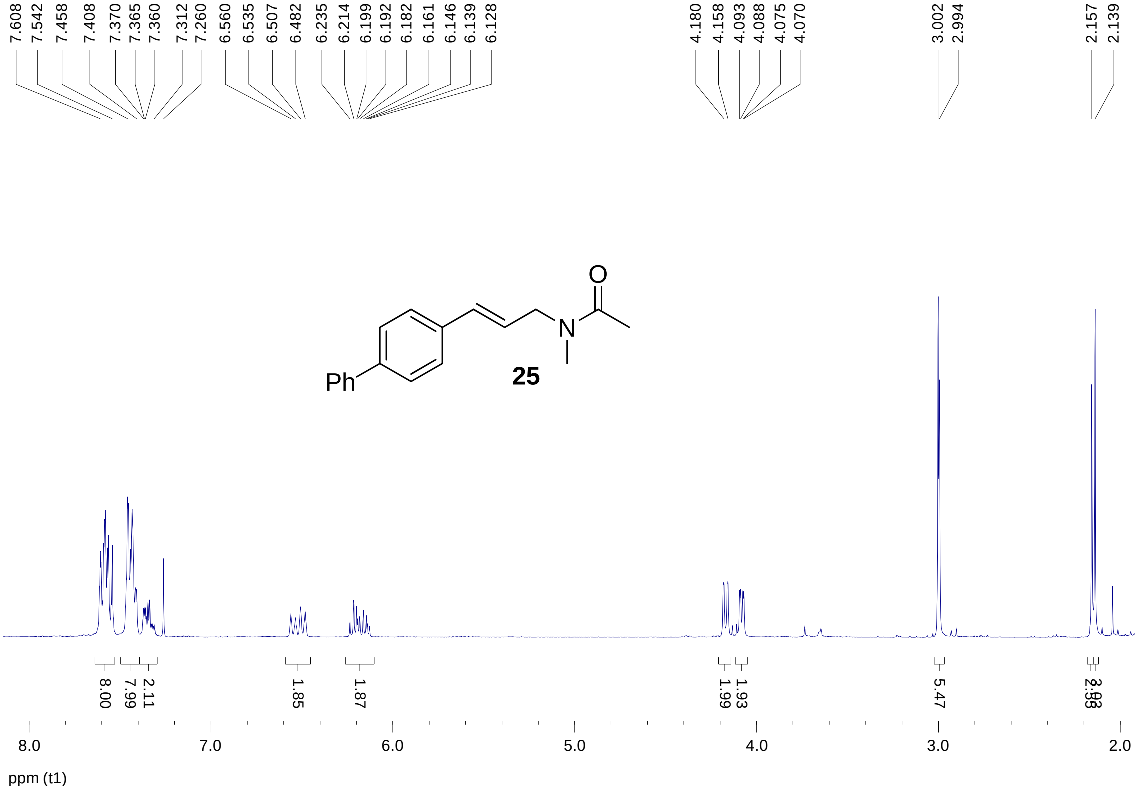
Ph
O
24
150
100
50
0
ppm (t1)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7.408
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7.260
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6.535
6.507
6.482
6.235
6.214
6.199
6.192
6.182
6.161
6.146
6.139
6.128
4.180
4.158
4.093
4.088
4.075
4.070
3.002
2.994
2.157
2.139
O
N
Ph
8.00
7.99
2.11
1.85
1.87
1.99
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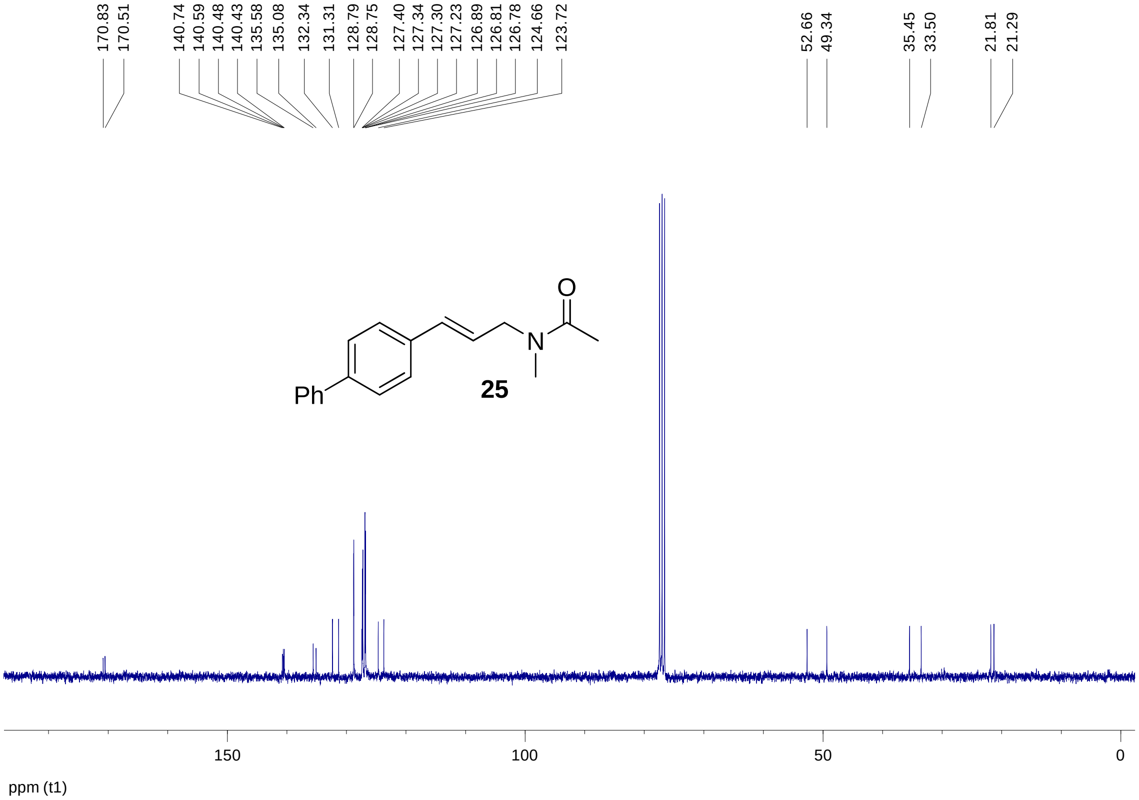
6.0
5.0
4.0
3.0
2.0
ppm (t1)

25


170.83
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135.08
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127.40
127.34
127.30
127.23
126.89
126.81
126.78
124.66
123.72
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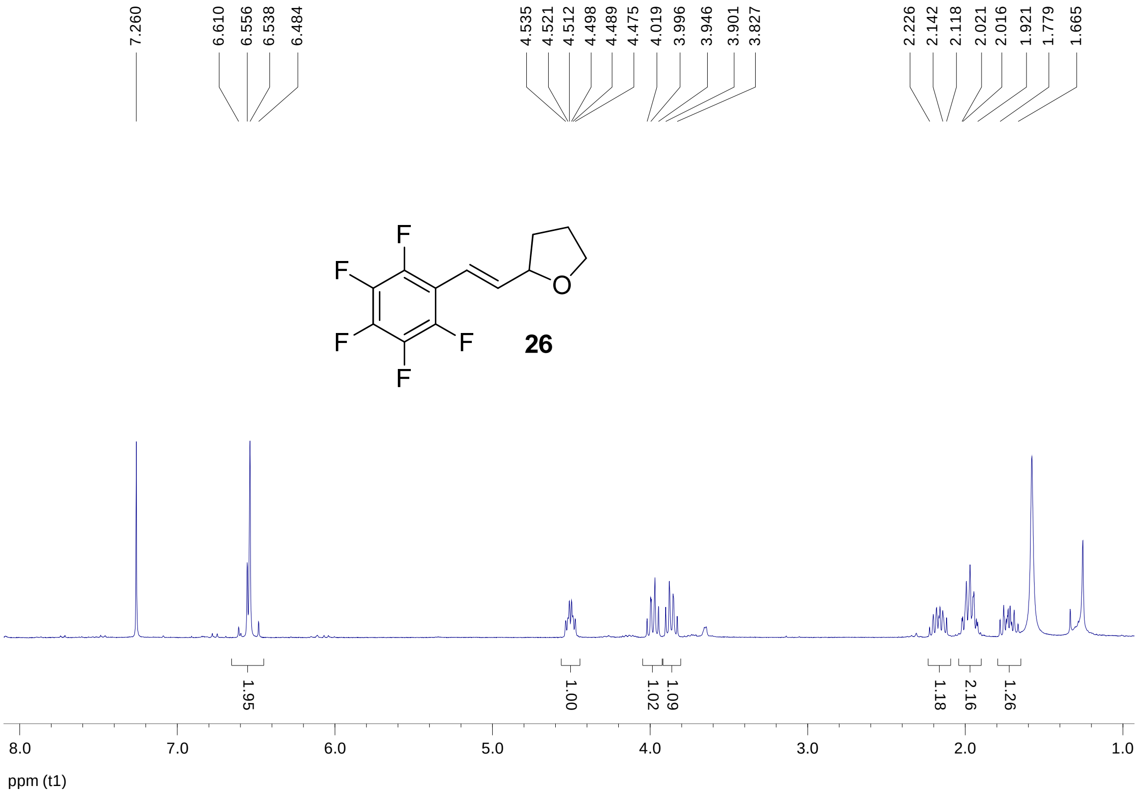
49.34
35.45
33.50
21.81
21.29
O
N
Ph
150
100
50
0
ppm (t1)

25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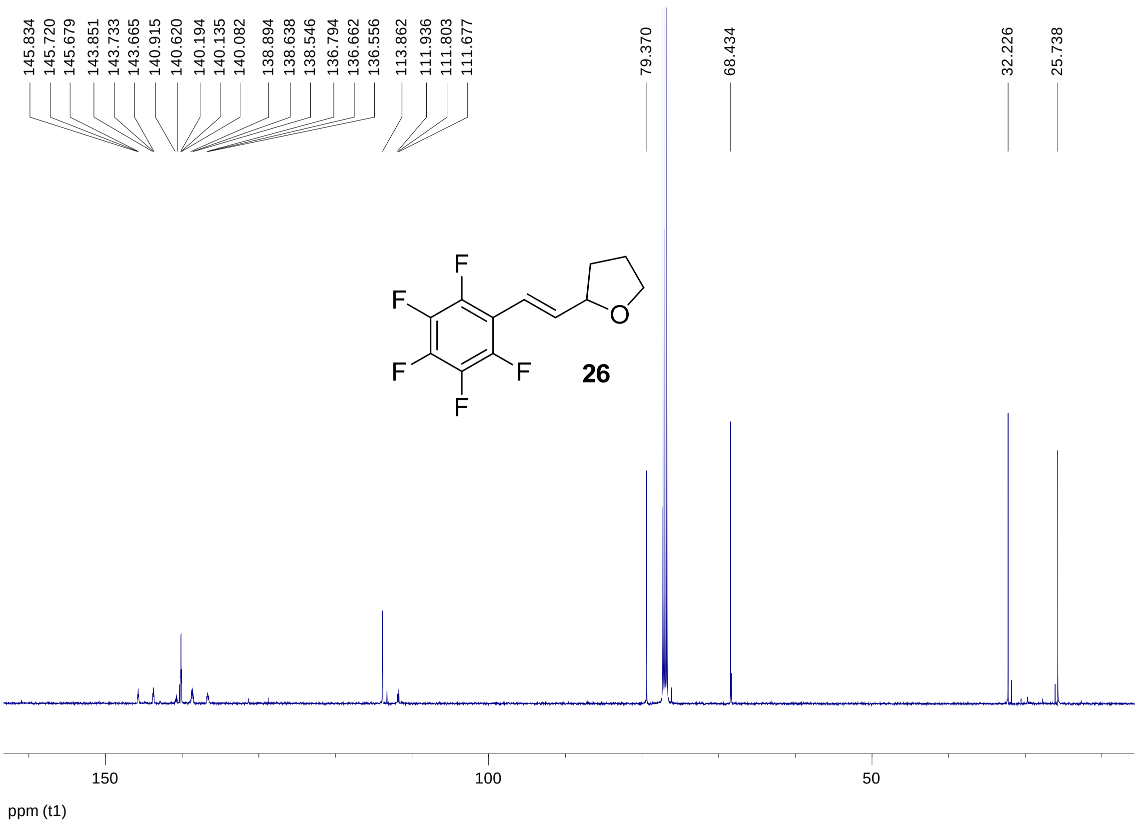
4.475
4.019
3.996
3.946
3.901
3.827
2.226
2.142
2.118
2.021
2.016
1.921
1.779
1.665
F
F
F
F
F
O
26
1.95
1.00
1.02
1.09
1.18
2.16
1.26
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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140.135
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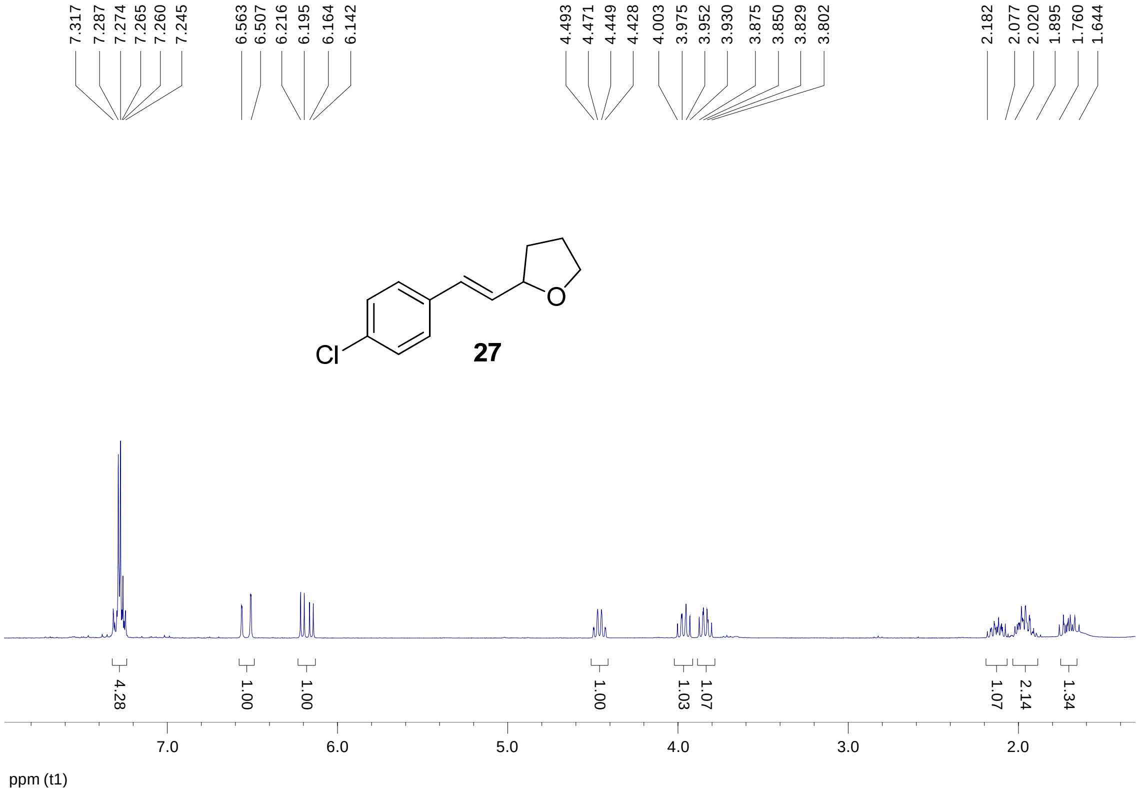
138.894
138.638
138.546
136.794
136.662
136.556
113.862
111.936
111.803
111.677
79.370
68.434
32.226
25.738
F
F
F
F
F
O
26
150
100
50
ppm (t1)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6.164
6.142
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4.471
4.449
4.428
4.003
3.975
3.952
3.930
3.875
3.850
3.829
3.802
2.182
2.077
2.020
1.895
1.760
1.644
Cl
O
27
4.28
1.00
1.00
1.00
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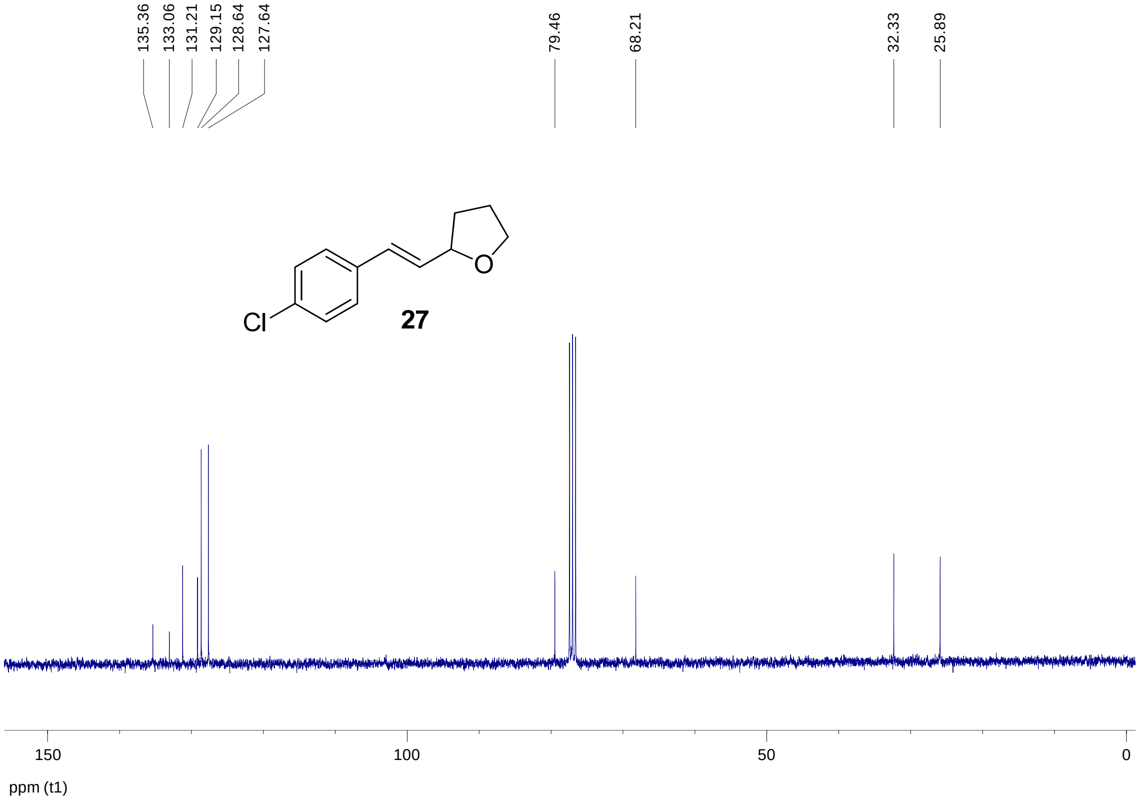
3.0
2.0
ppm (t1)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131.21
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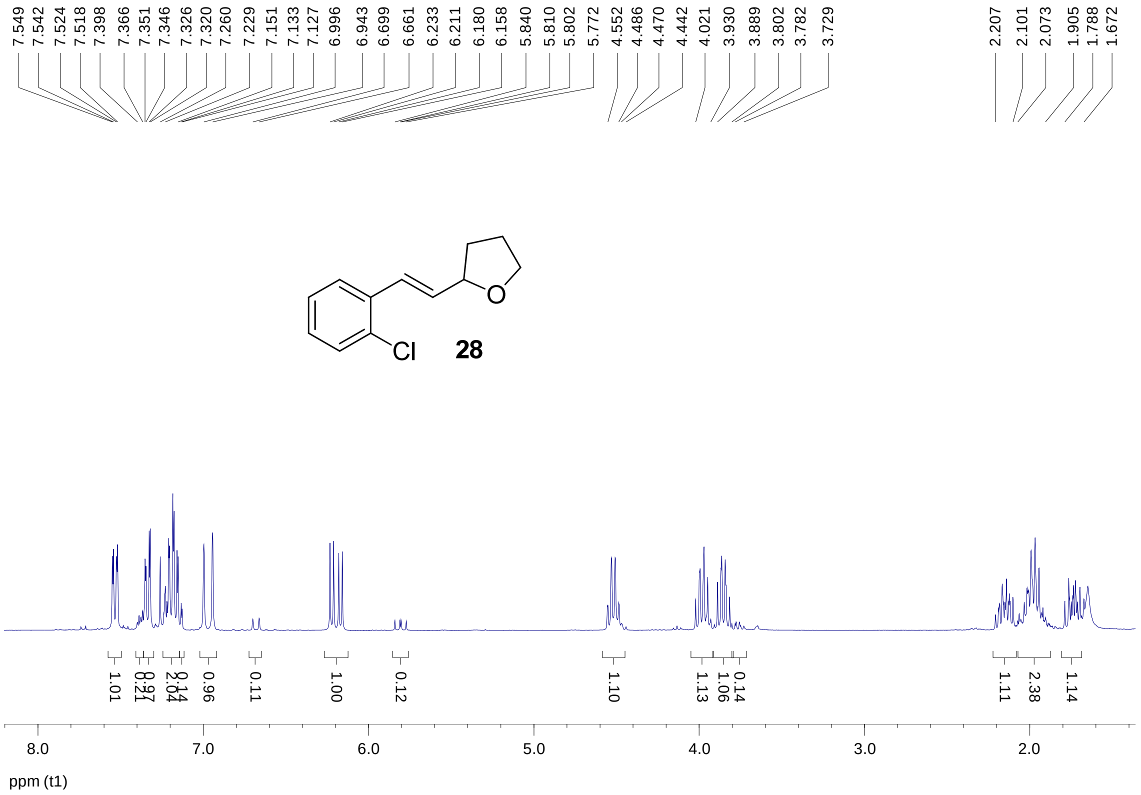
ppm (t1)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7.351
7.346
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7.320
7.260
7.229
7.151
7.133
7.127
6.996
6.943
6.699
6.661
6.233
6.211
6.180
6.158
5.840
5.810
5.802
5.772
4.552
4.486
4.470
4.442
4.021
3.930
3.889
3.802
3.782
3.729
2.207
2.101
2.073
1.905
1.788
1.672
Cl
O
28
1.01
0.21
0.97
2.04
0.14
0.96
0.11
1.00
0.12
1.10
1.13
1.06
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1.14
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3.0
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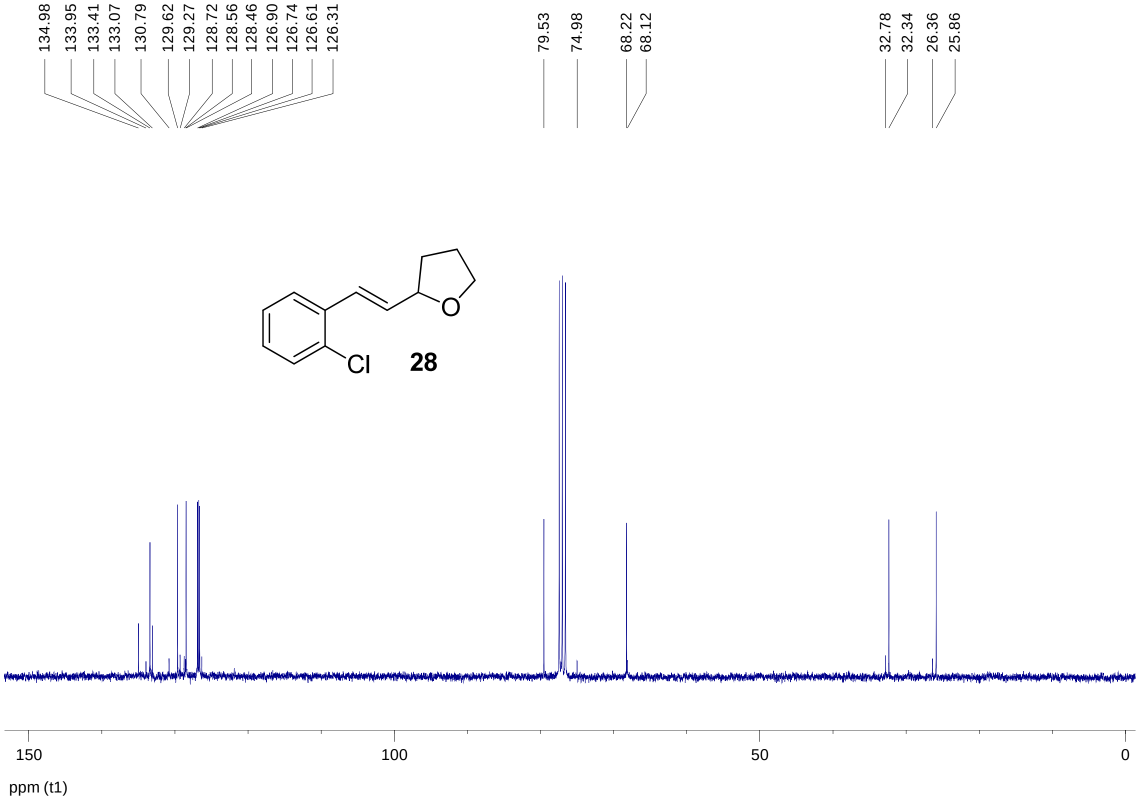
ppm (t1)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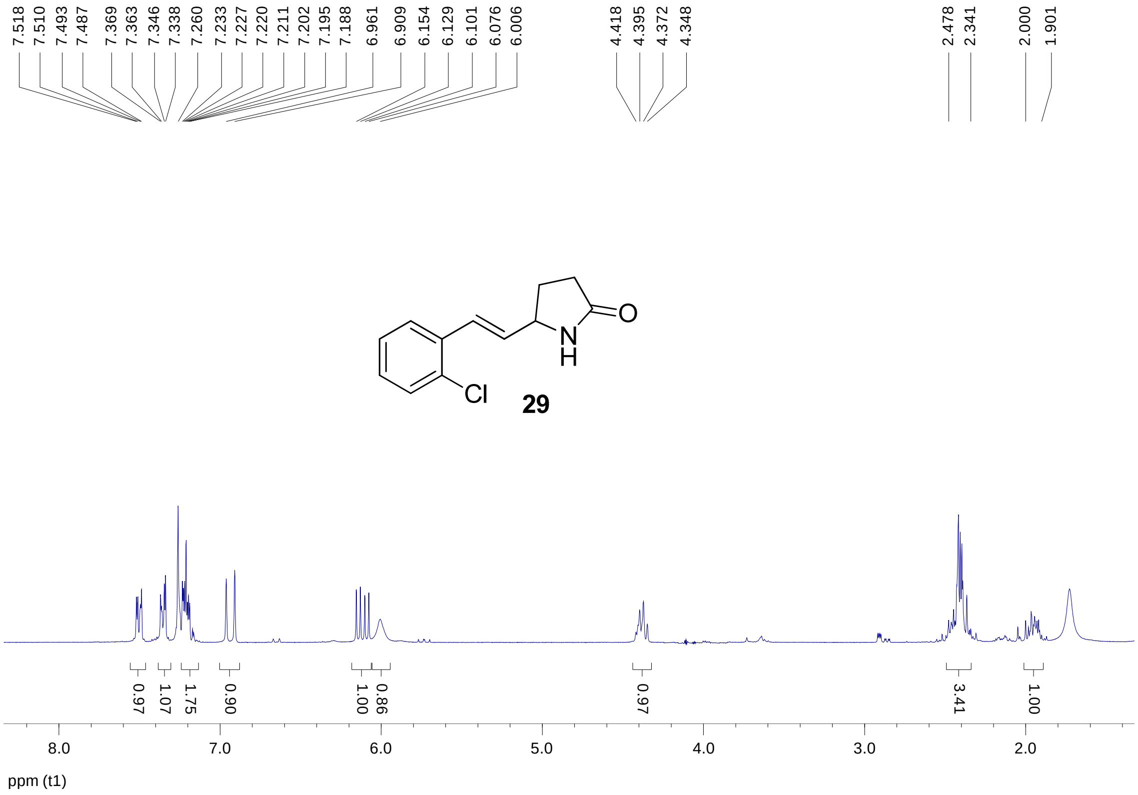
128.46
126.90
126.74
126.61
126.31
79.53
74.98
68.22
68.12
32.78
32.34
26.36
25.86
Cl
O
28
150
100
50
0
ppm (t1)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7.338
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7.233
7.227
7.220
7.211
7.202
7.195
7.188
6.961
6.909
6.154
6.129
6.101
6.076
6.006
4.418
4.395
4.372
4.348
2.478
2.341
2.000
1.901
O
N
H
Cl
29
0.97
1.07
1.75
0.90
1.00
0.86
0.97
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1.00
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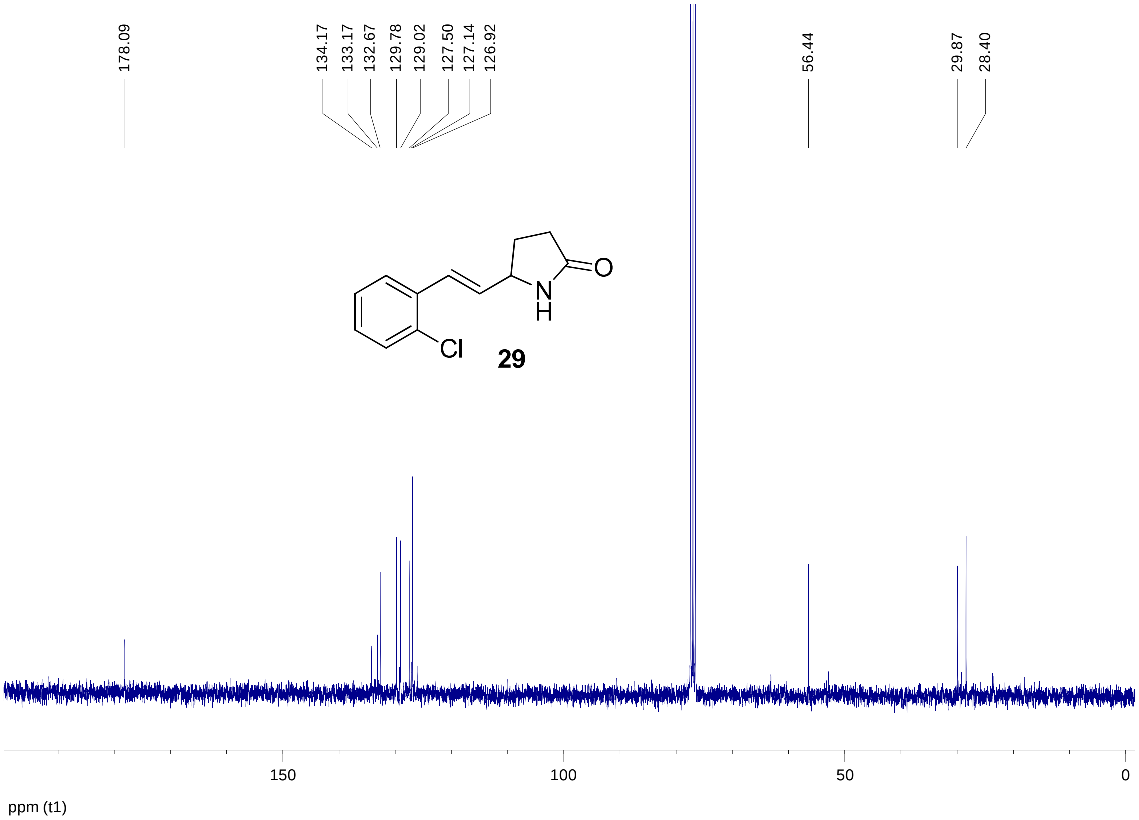
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


178.09
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129.78
129.02
127.50
127.14
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56.44
29.87
28.40
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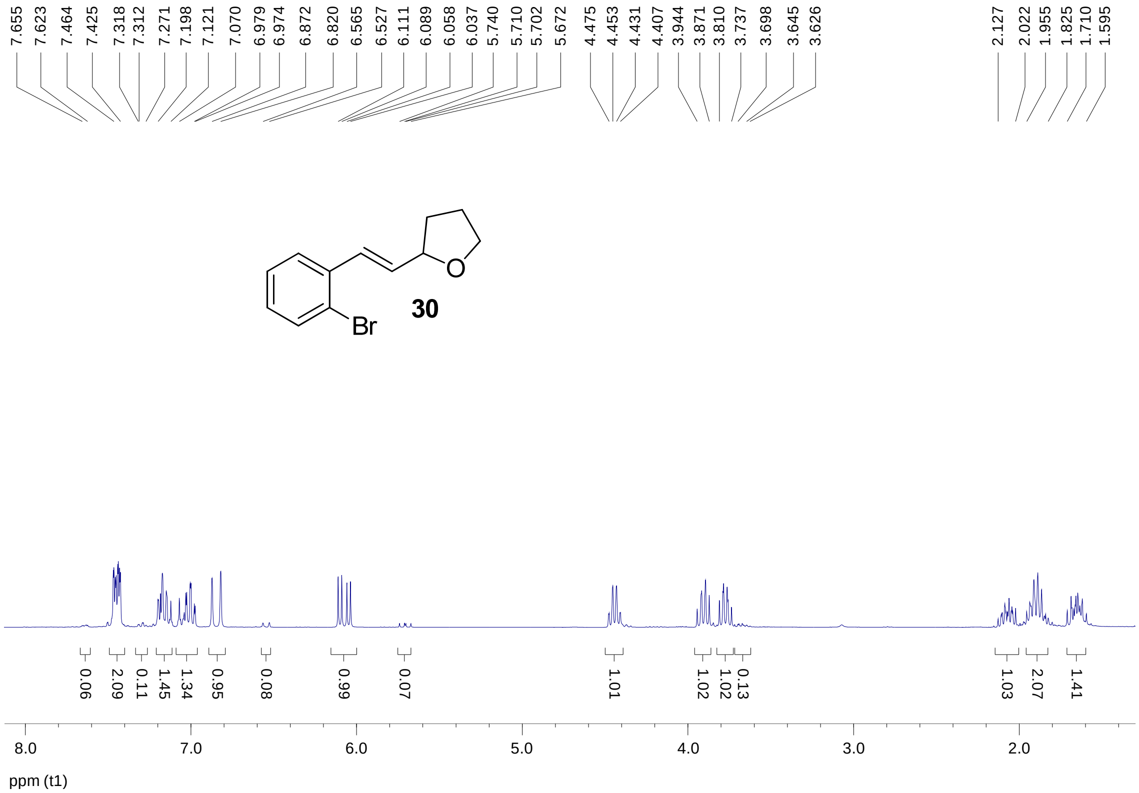
N
H
Cl
29
150
100
50
0
ppm (t1)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7.464
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7.318
7.312
7.271
7.198
7.121
7.070
6.979
6.974
6.872
6.820
6.565
6.527
6.111
6.089
6.058
6.037
5.740
5.710
5.702
5.672
4.475
4.453
4.431
4.407
3.944
3.871
3.810
3.737
3.698
3.645
3.626
2.127
2.022
1.955
1.825
1.710
1.595
Br
O
30
0.06
2.09
0.11
1.45
1.34
0.95
0.08
0.99
0.07
1.01
1.02
1.02
0.13
1.03
2.07
1.41
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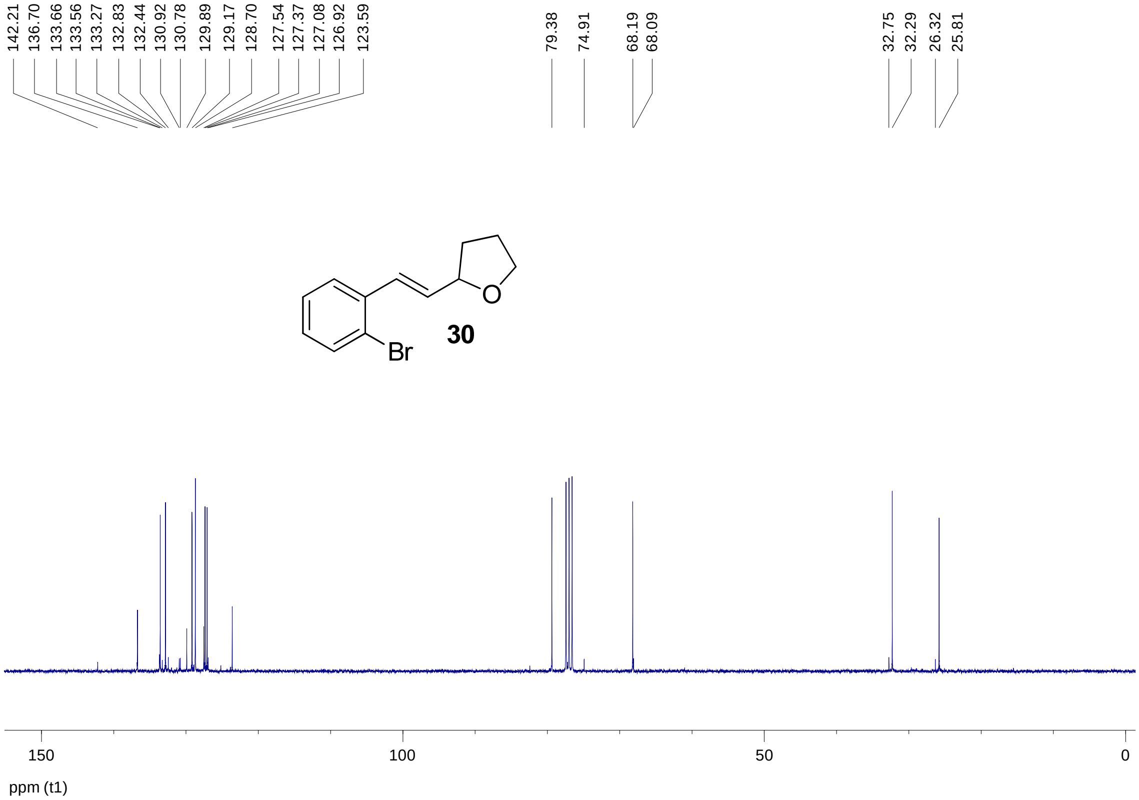
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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133.66
133.56
133.27
132.83
132.44
130.92
130.78
129.89
129.17
128.70
127.54
127.37
127.08
126.92
123.59
79.38
74.91
68.19
68.09
32.75
32.29
26.32
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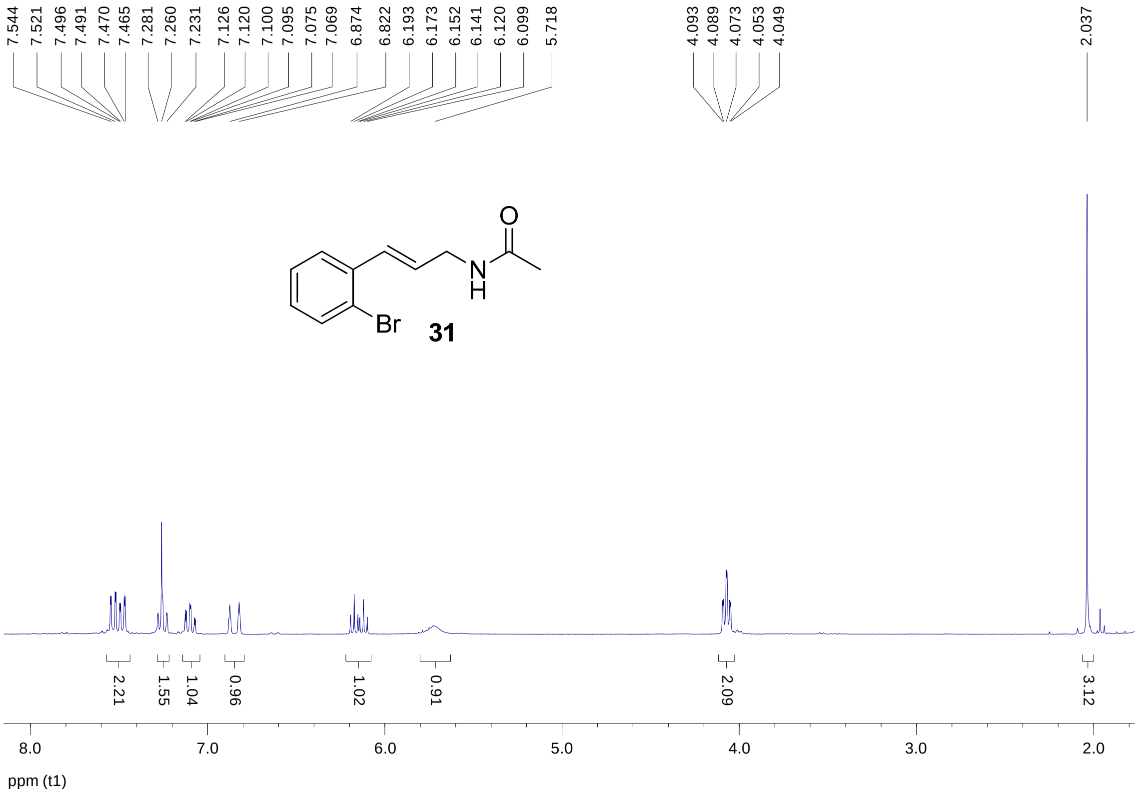
Br
O
30
150
100
50
0
ppm (t1)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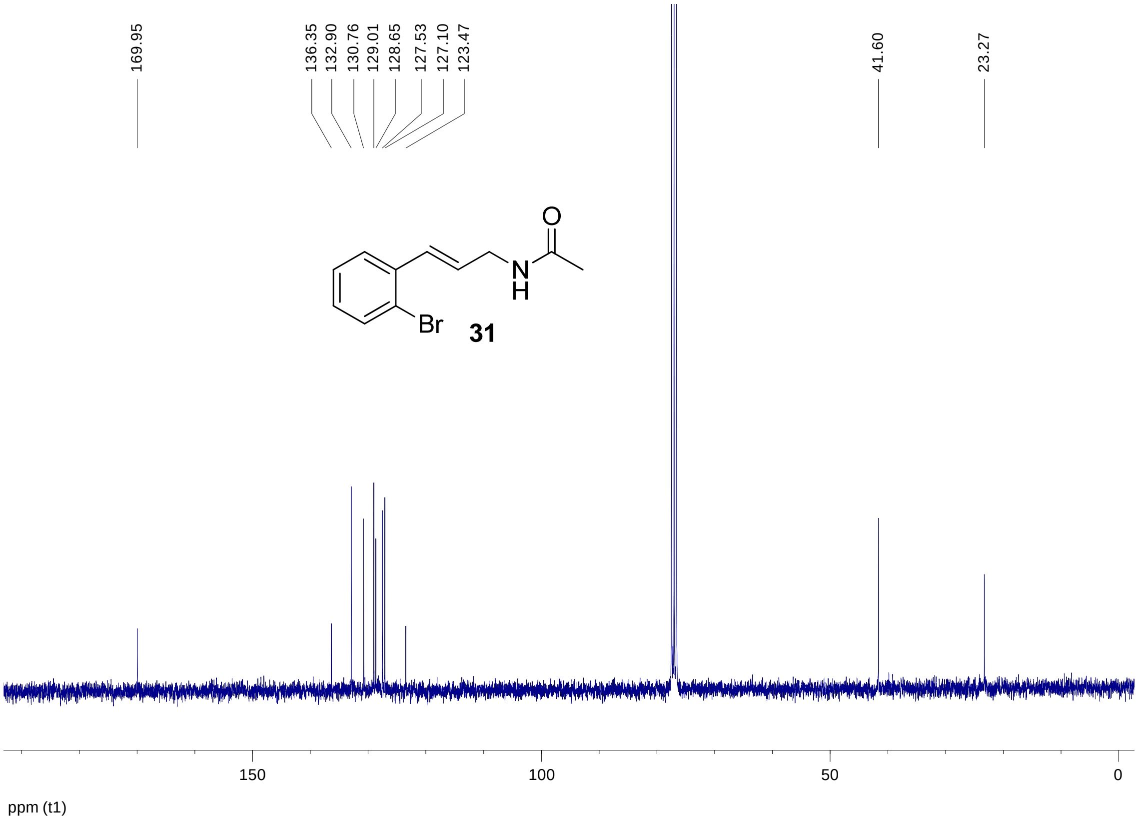
7.470
7.465
7.281
7.260
7.231
7.126
7.120
7.100
7.095
7.075
7.069
6.874
6.822
6.193
6.173
6.152
6.141
6.120
6.099
5.718
4.093
4.089
4.073
4.053
4.049
2.037
O
N
H
Br
31
2.21
1.55
1.04
0.96
1.02
0.91
2.09
3.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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23.27
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N
H
Br
31
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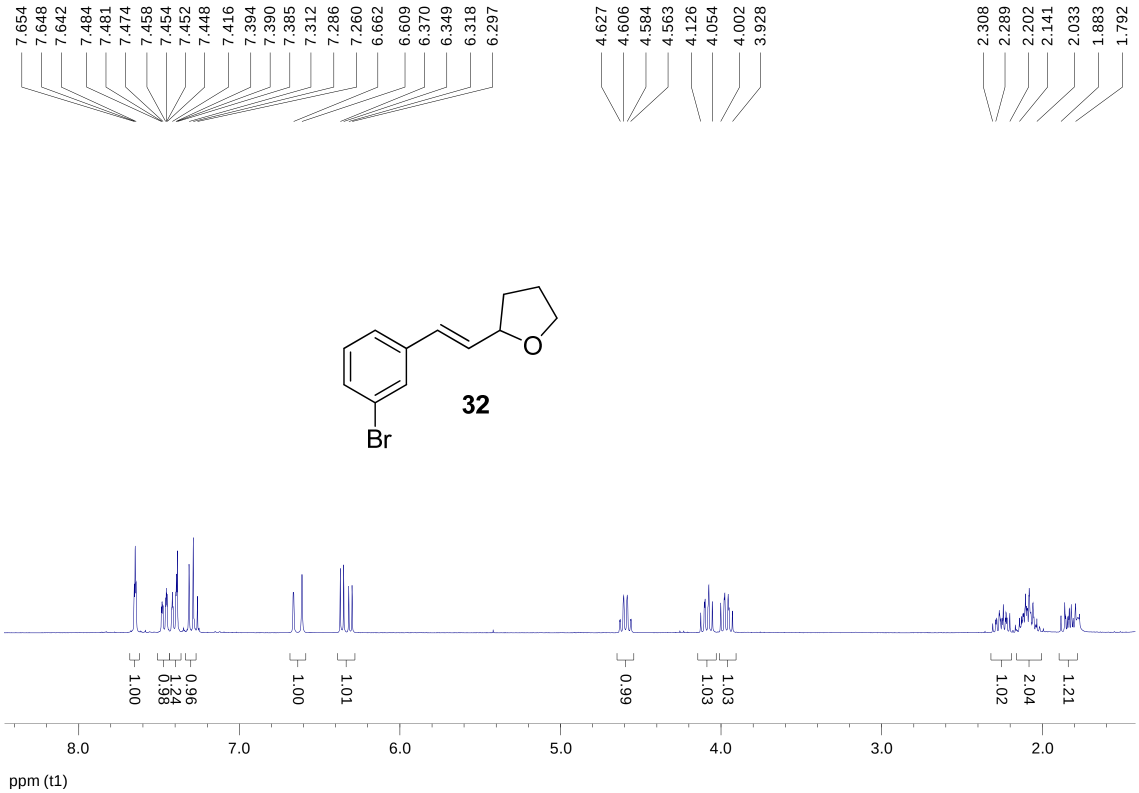
100
50
0
ppm (t1)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7.474
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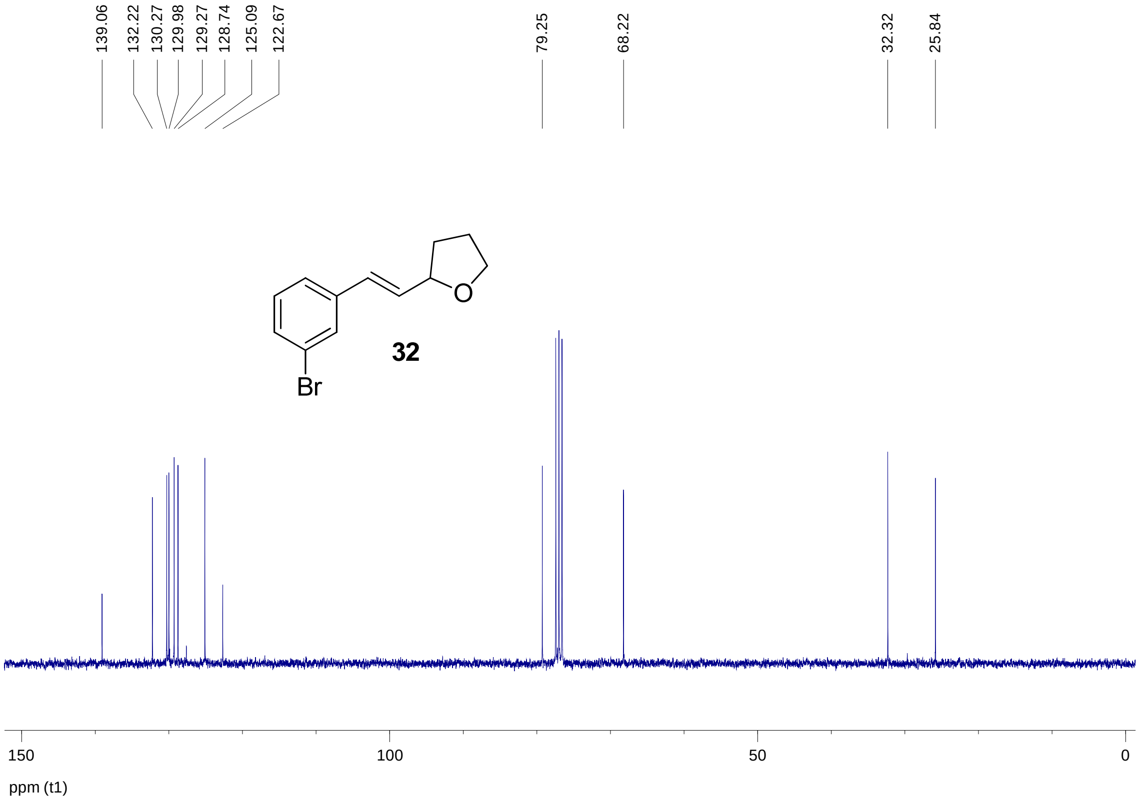
7.452
7.448
7.416
7.394
7.390
7.385
7.312
7.286
7.260
6.662
6.609
6.370
6.349
6.318
6.297
4.627
4.606
4.584
4.563
4.126
4.054
4.002
3.928
2.308
2.289
2.202
2.141
2.033
1.883
1.792
O
Br
1.00
0.98
1.24
0.96
1.00
1.01
0.99
1.03
1.03
1.02
2.04
1.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

32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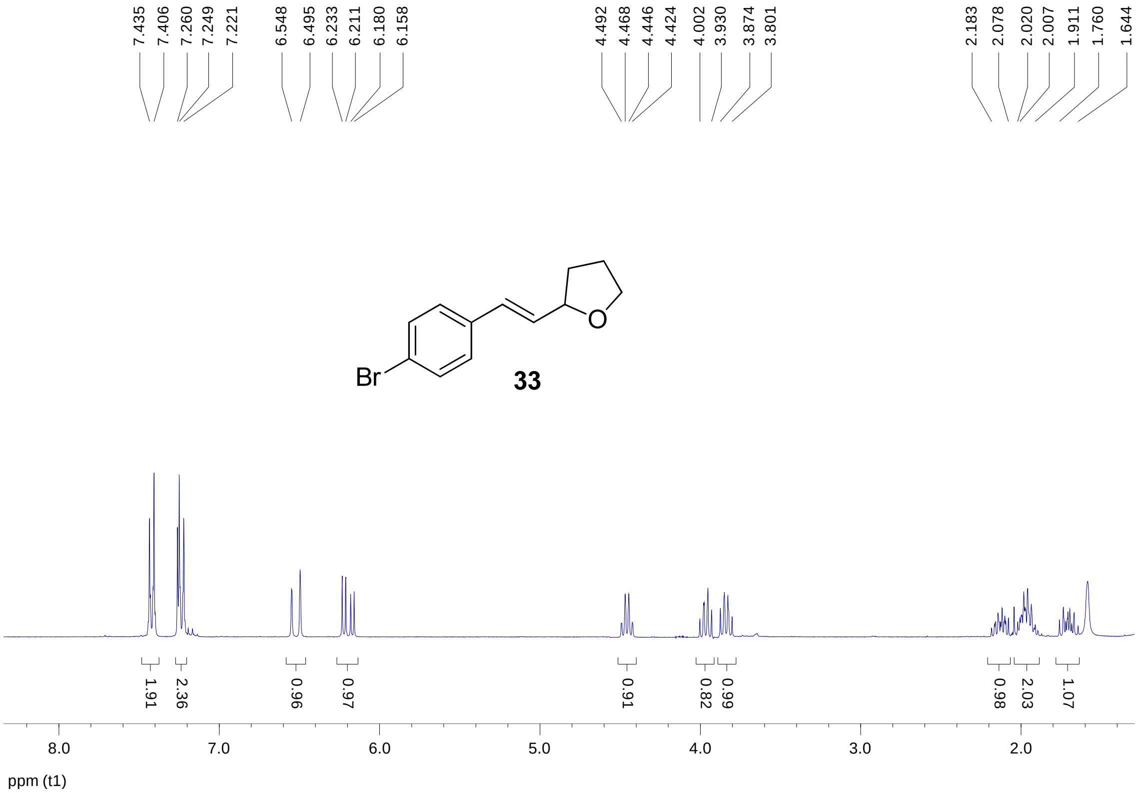
Br
150
100
50
0
ppm (t1)

32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7.260
7.249
7.221
6.548
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6.233
6.211
6.180
6.158
4.492
4.468
4.446
4.424
4.002
3.930
3.874
3.801
2.183
2.078
2.020
2.007
1.911
1.760
1.644
Br
O
33
1.91
2.36
0.96
0.97
0.91
0.82
0.99
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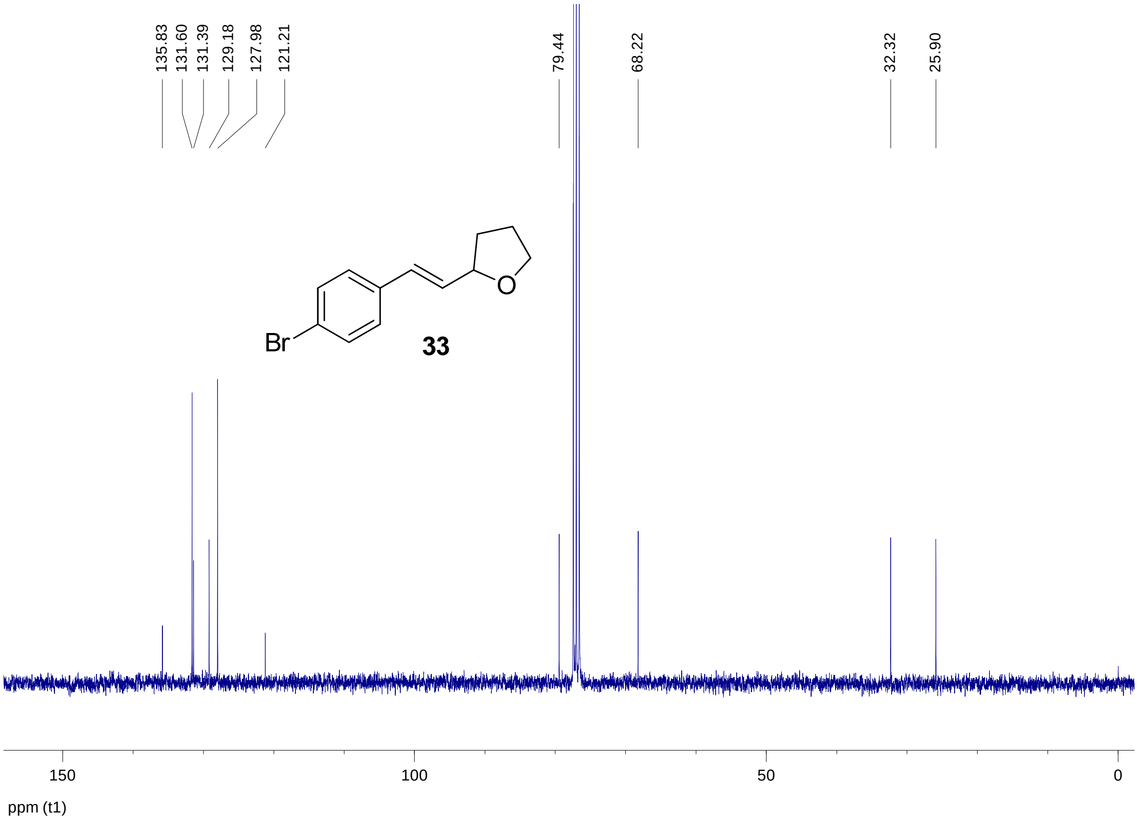
1.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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Br
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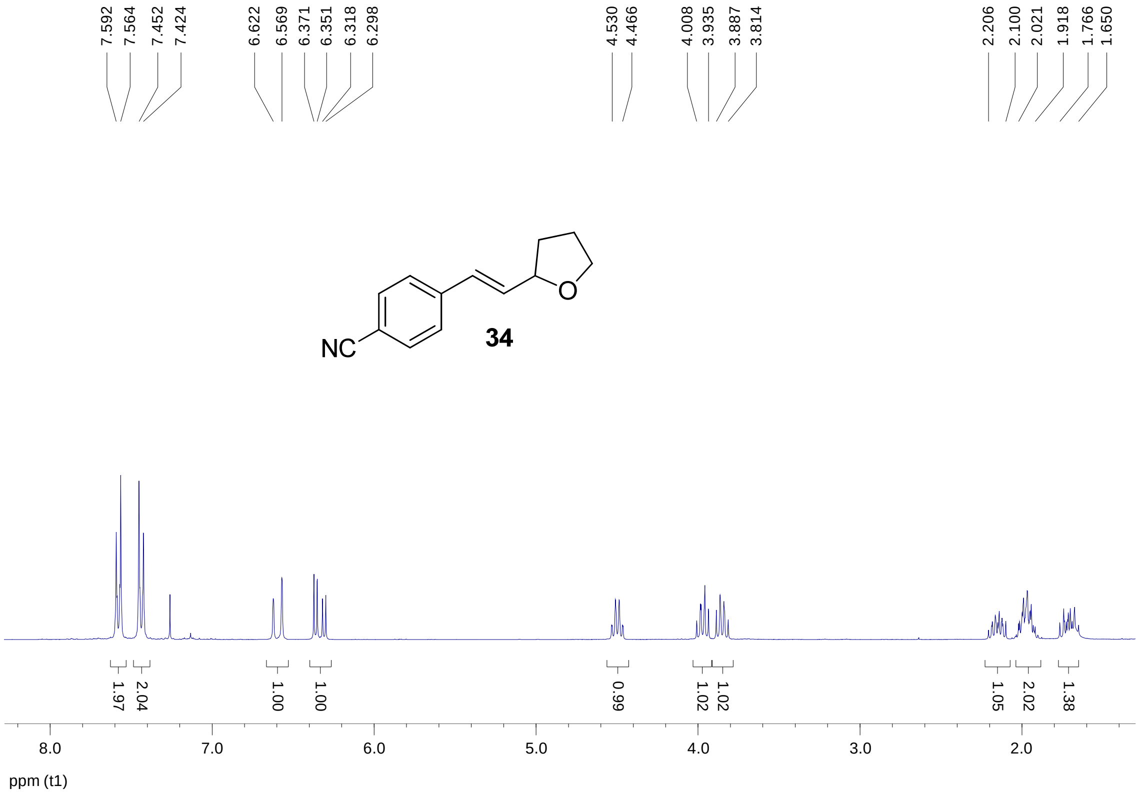
150
100
50
0
ppm (t1)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6.351
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6.298
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4.466
4.008
3.935
3.887
3.814
2.206
2.100
2.021
1.918
1.766
1.650
NC
O
34
1.97
2.04
1.00
1.00
0.99
1.02
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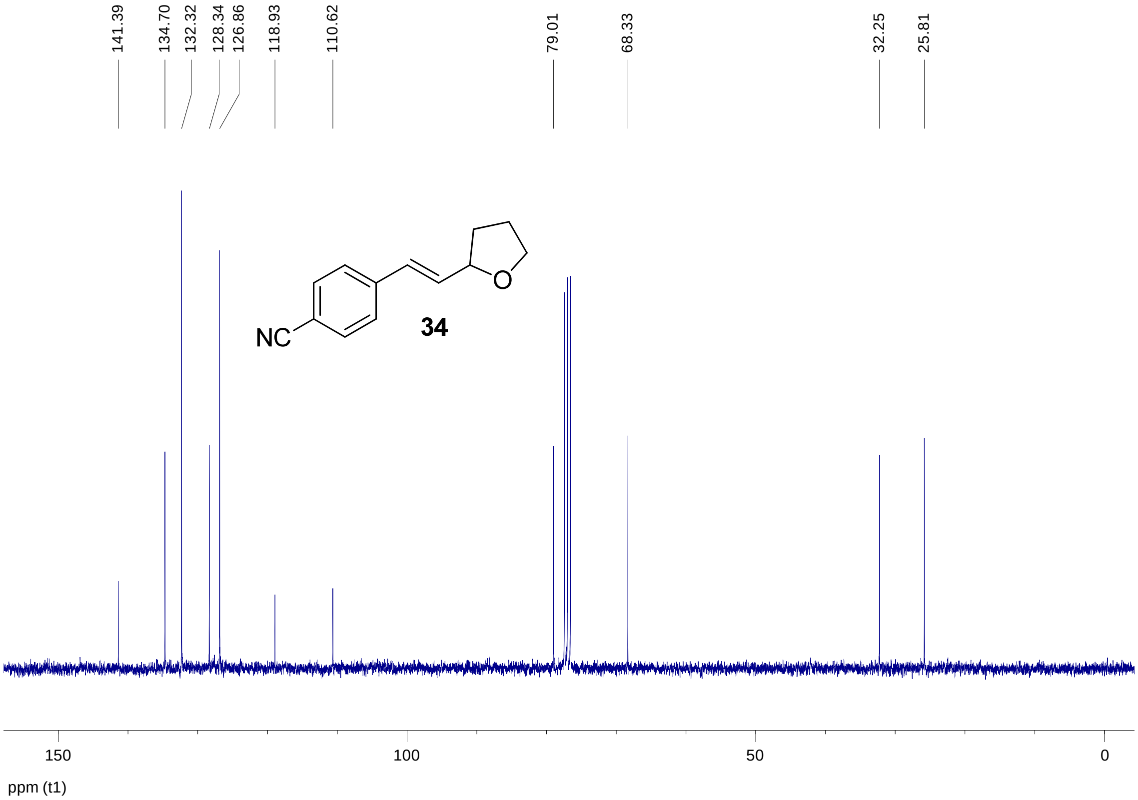
2.02
1.38
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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132.32
128.34
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68.33
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25.81
NC
O
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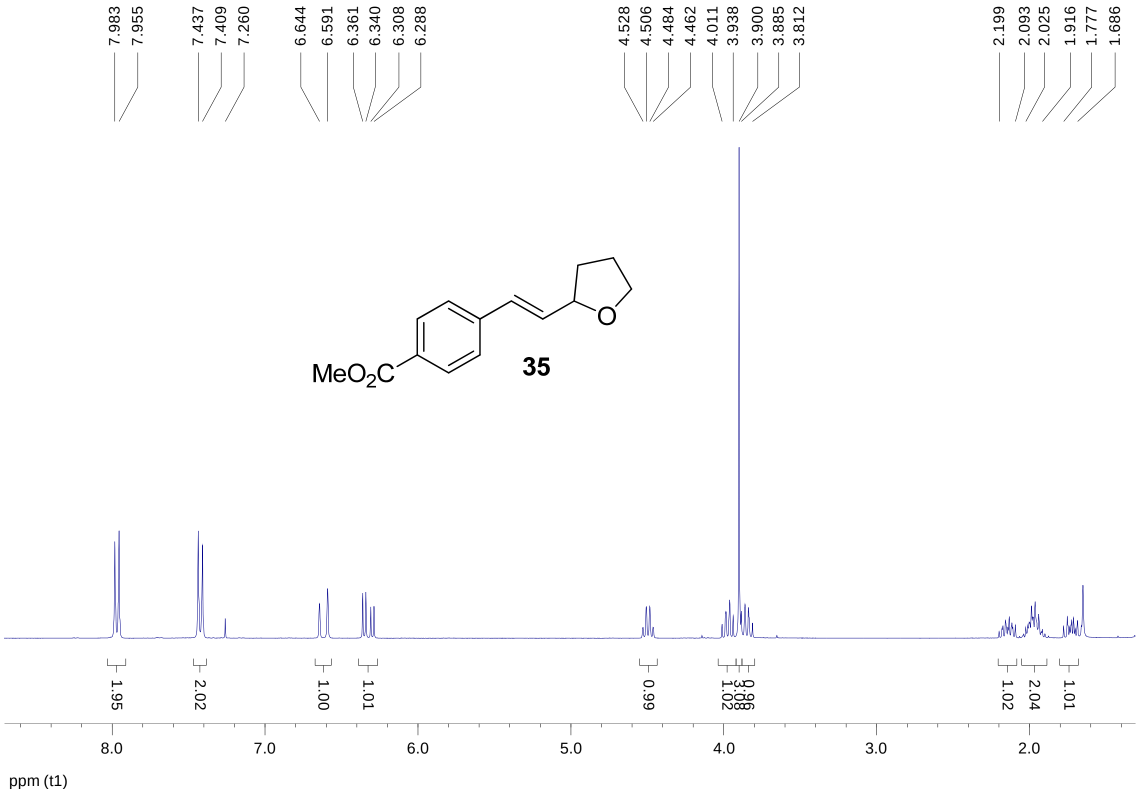
150
100
50
0
ppm (t1)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7.409
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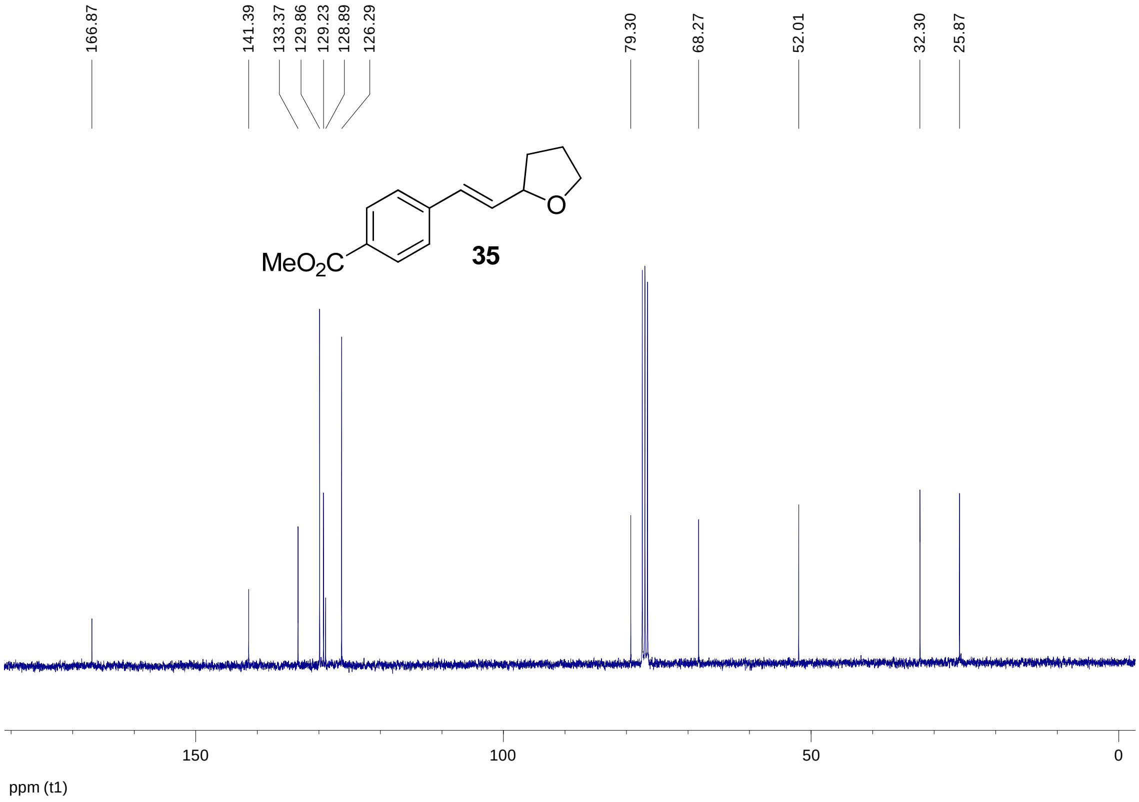
6.644
6.591
6.361
6.340
6.308
6.288
4.528
4.506
4.484
4.462
4.011
3.938
3.900
3.885
3.812
2.199
2.093
2.025
1.916
1.777
1.686
MeO$_2$C
35
1.95
2.02
1.00
1.01
0.99
1.02
3.08
0.96
1.02
2.04
1.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)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129.23
128.89
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79.30
68.27
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MeO$_2$C
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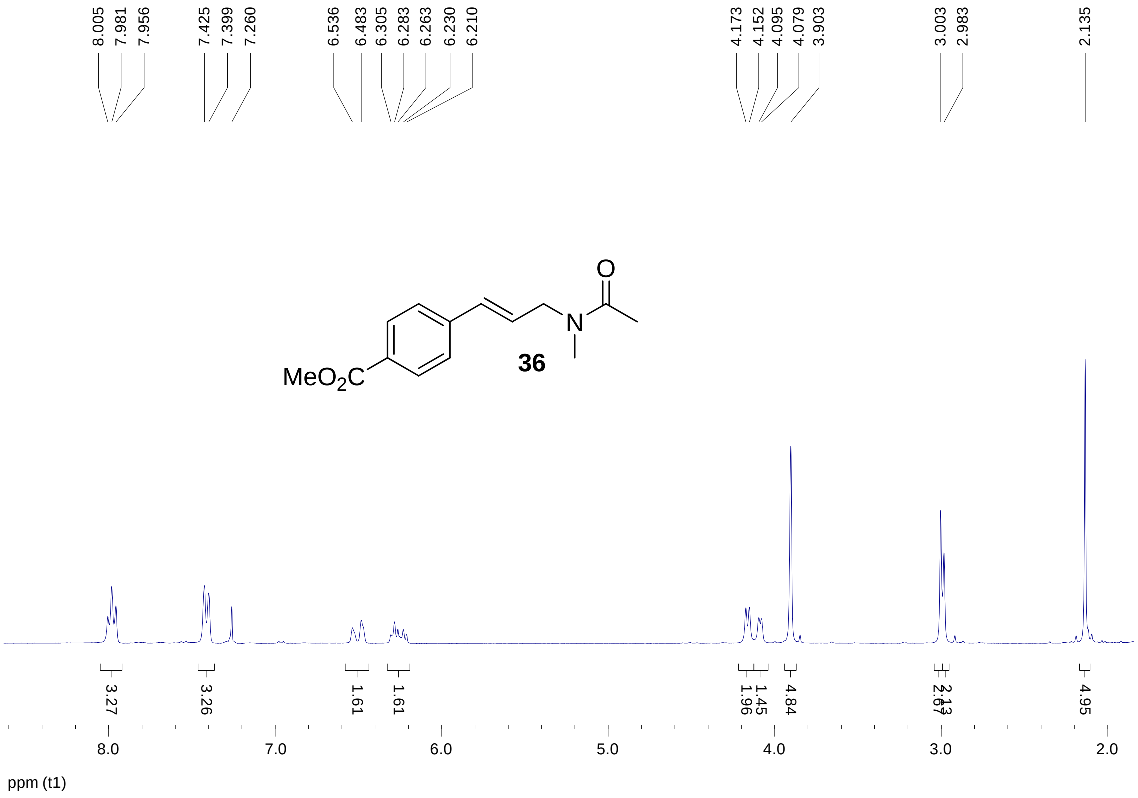
150
100
50
0
ppm (t1)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7.260
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6.483
6.305
6.283
6.263
6.230
6.210
4.173
4.152
4.095
4.079
3.903
3.003
2.983
2.135
MeO$_2$C
N
O
36
3.27
3.26
1.61
1.61
1.96
1.45
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2.67
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4.95
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7.0
6.0
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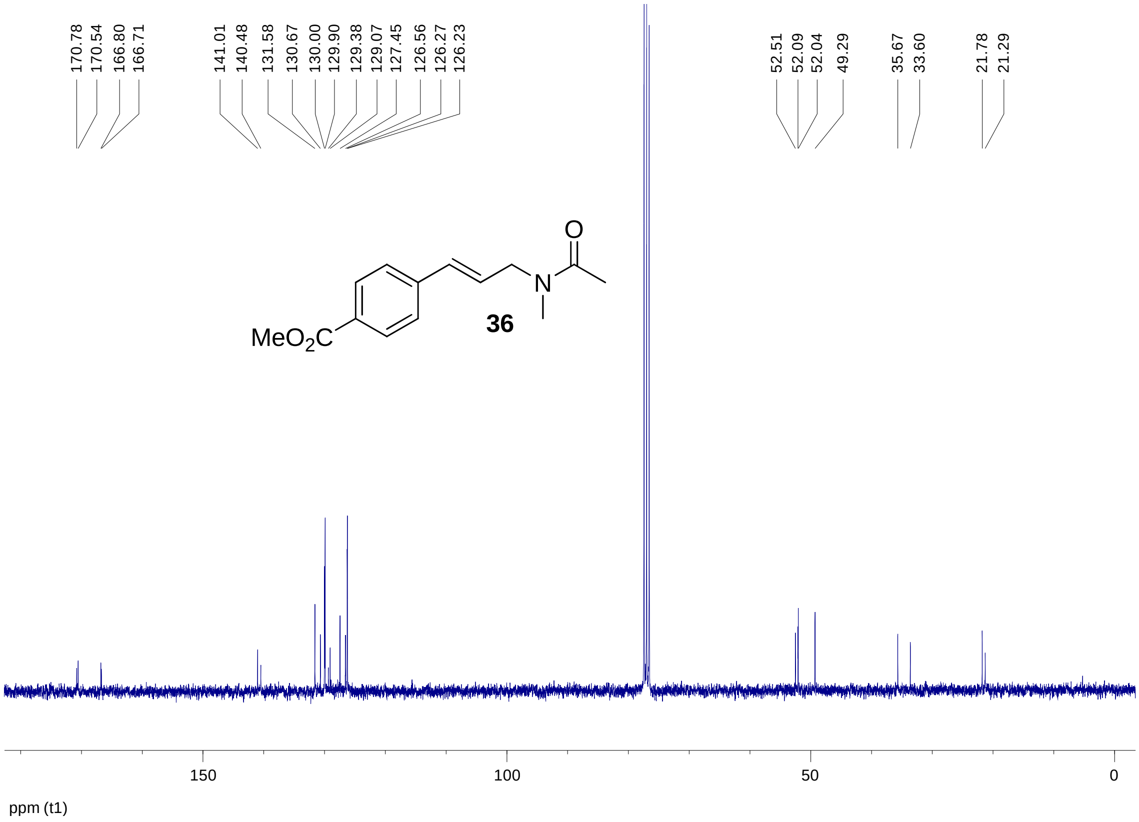
4.0
3.0
2.0
ppm (t1)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127.45
126.56
126.27
126.23
52.51
52.09
52.04
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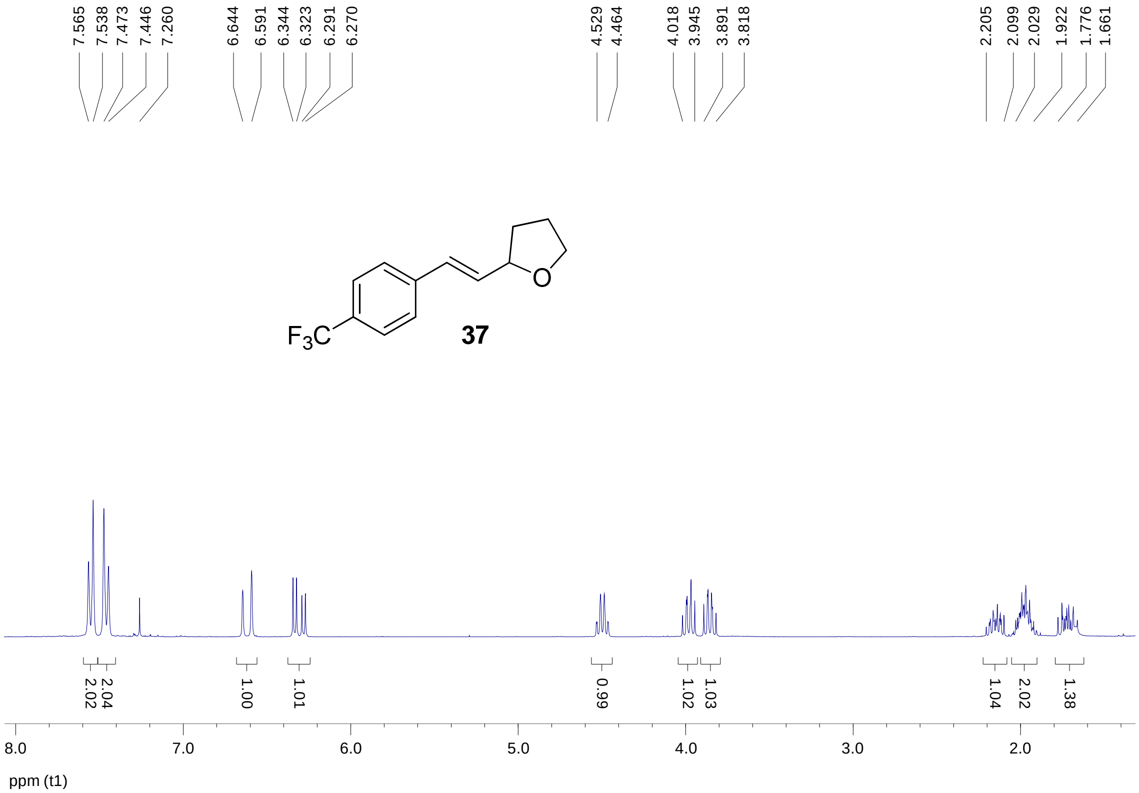
21.78
21.29
MeO$_2$C
N
O
36
150
100
50
0
ppm (t1)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6.344
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4.464
4.018
3.945
3.891
3.818
2.205
2.099
2.029
1.922
1.776
1.661
F3C
O
37
2.02
2.04
1.00
1.01
0.99
1.02
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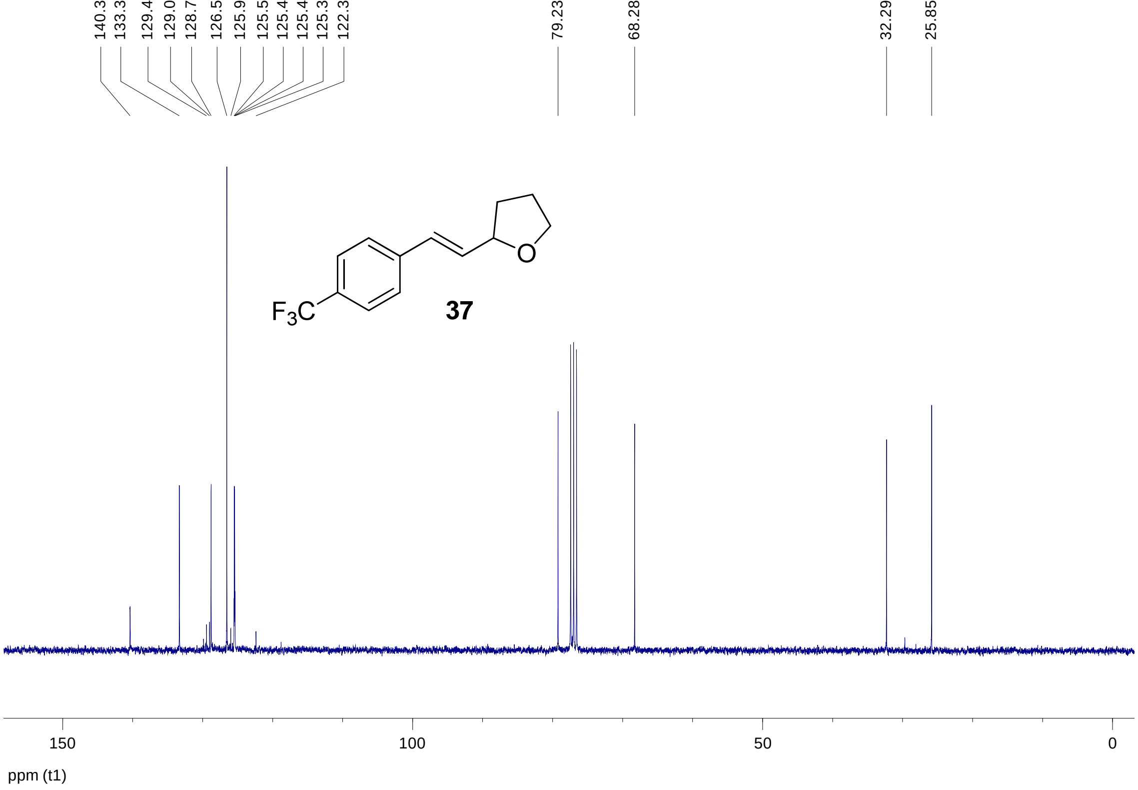
ppm (t1)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125.41
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68.28
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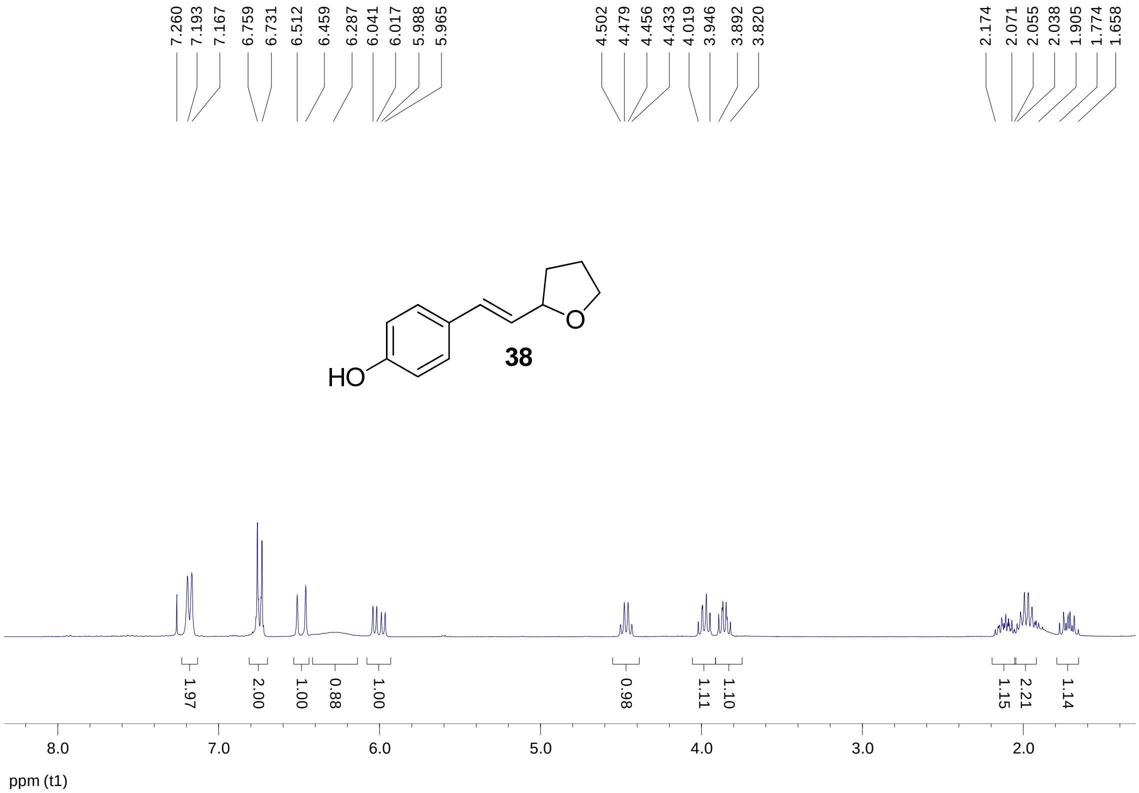
F3C
O
37
150
100
50
0
ppm (t1)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6.287
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6.017
5.988
5.965
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4.479
4.456
4.433
4.019
3.946
3.892
3.820
2.174
2.071
2.055
2.038
1.905
1.774
1.658
HO
O
38
1.97
2.00
1.00
0.88
1.00
0.98
1.11
1.10
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1.14
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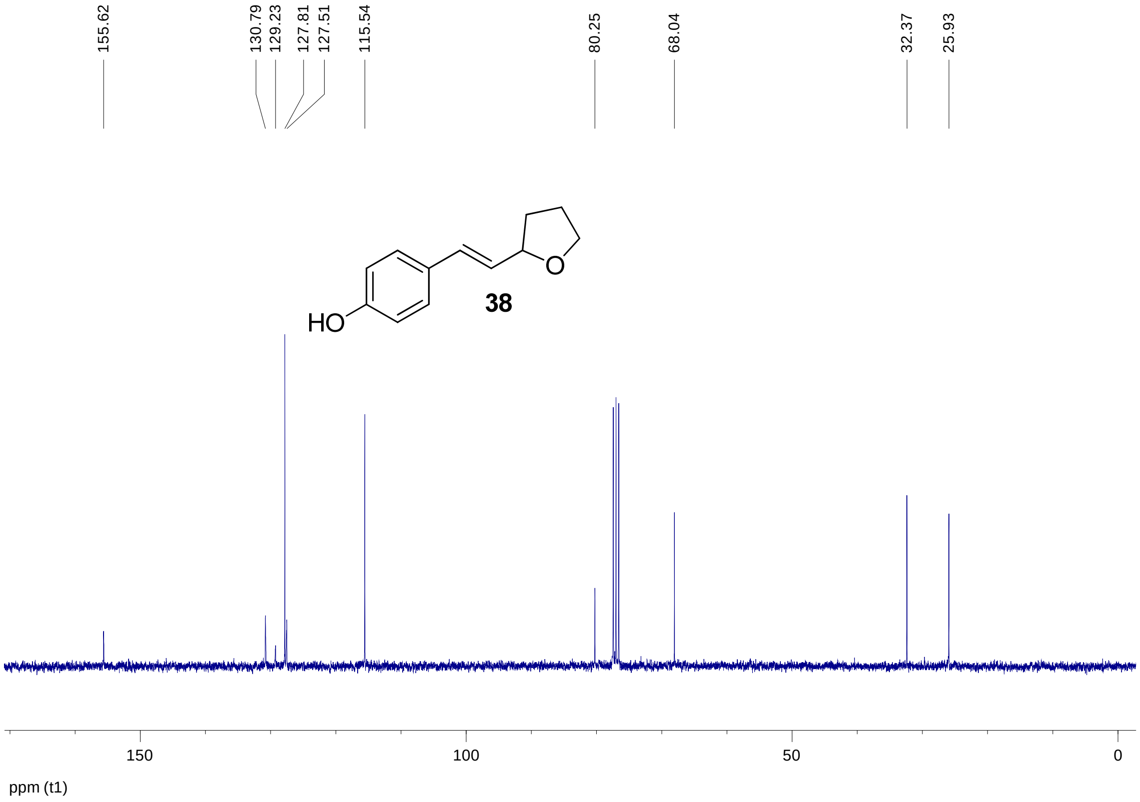
6.0
5.0
4.0
3.0
2.0
ppm (t1)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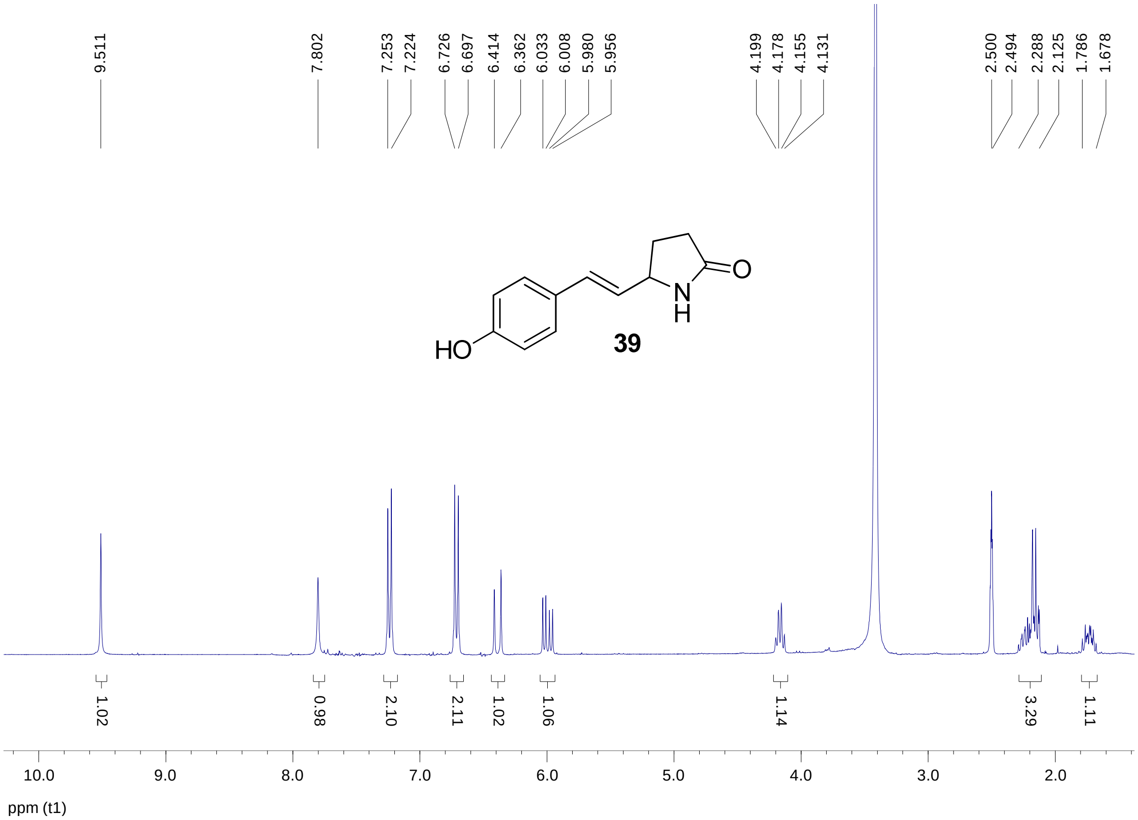
100
50
0
ppm (t1)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6.362
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6.008
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5.956
4.199
4.178
4.155
4.131
2.500
2.494
2.288
2.125
1.786
1.678
HO
N
H
O
39
1.02
0.98
2.10
2.11
1.02
1.06
1.14
3.29
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6.0
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3.0
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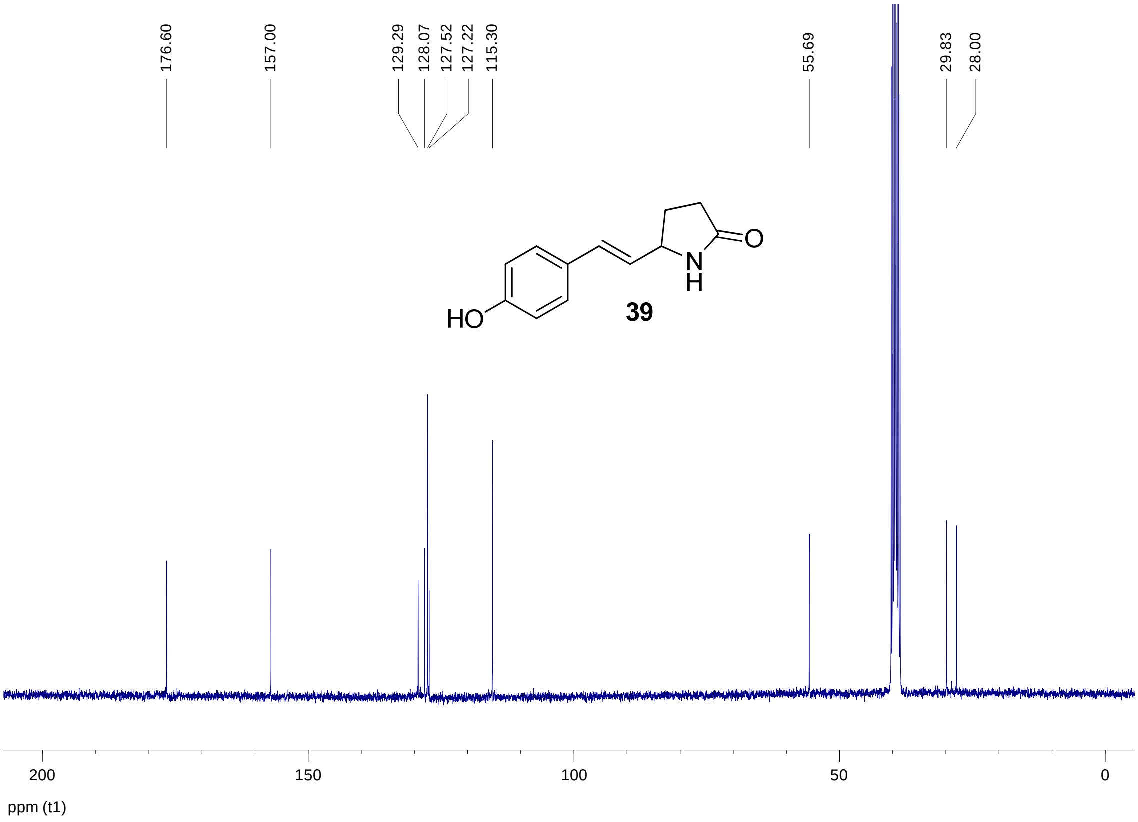
ppm (t1)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HO
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H
O
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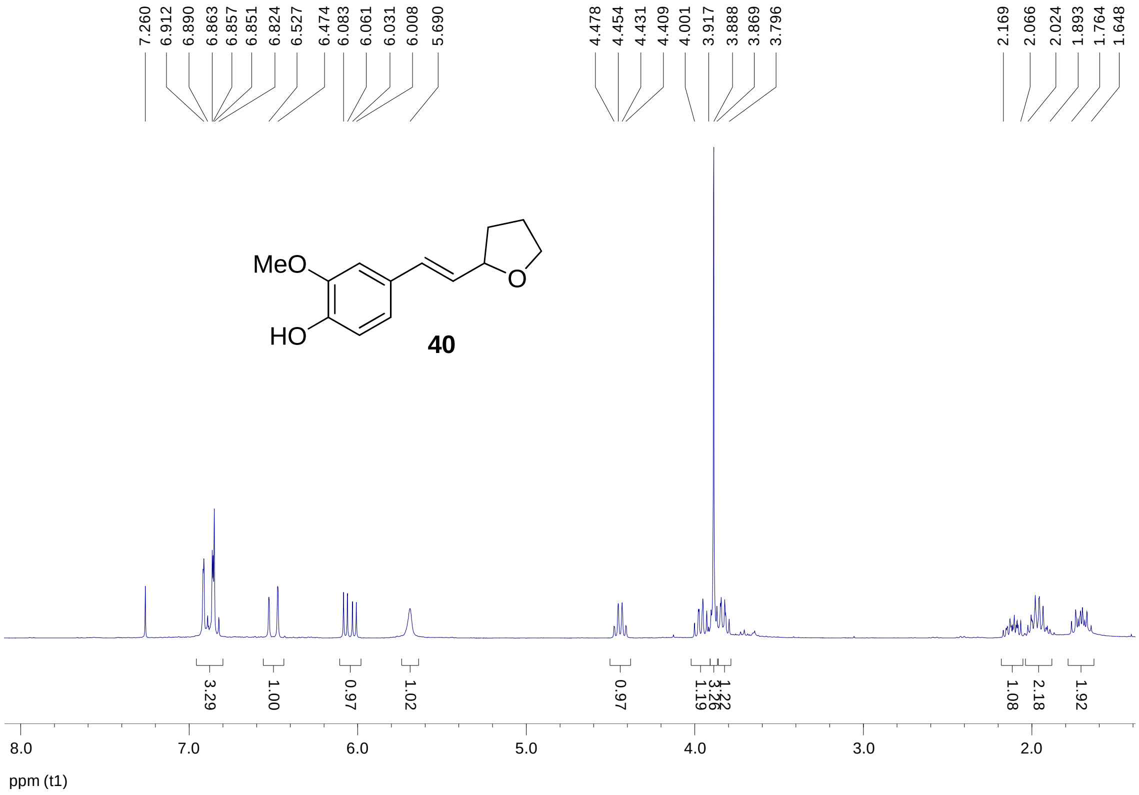
200
150
100
50
0
ppm (t1)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6.031
6.008
5.690
4.478
4.454
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4.409
4.001
3.917
3.888
3.869
3.796
2.169
2.066
2.024
1.893
1.764
1.648
MeO
HO
O
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3.29
1.00
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1.02
0.97
1.19
3.26
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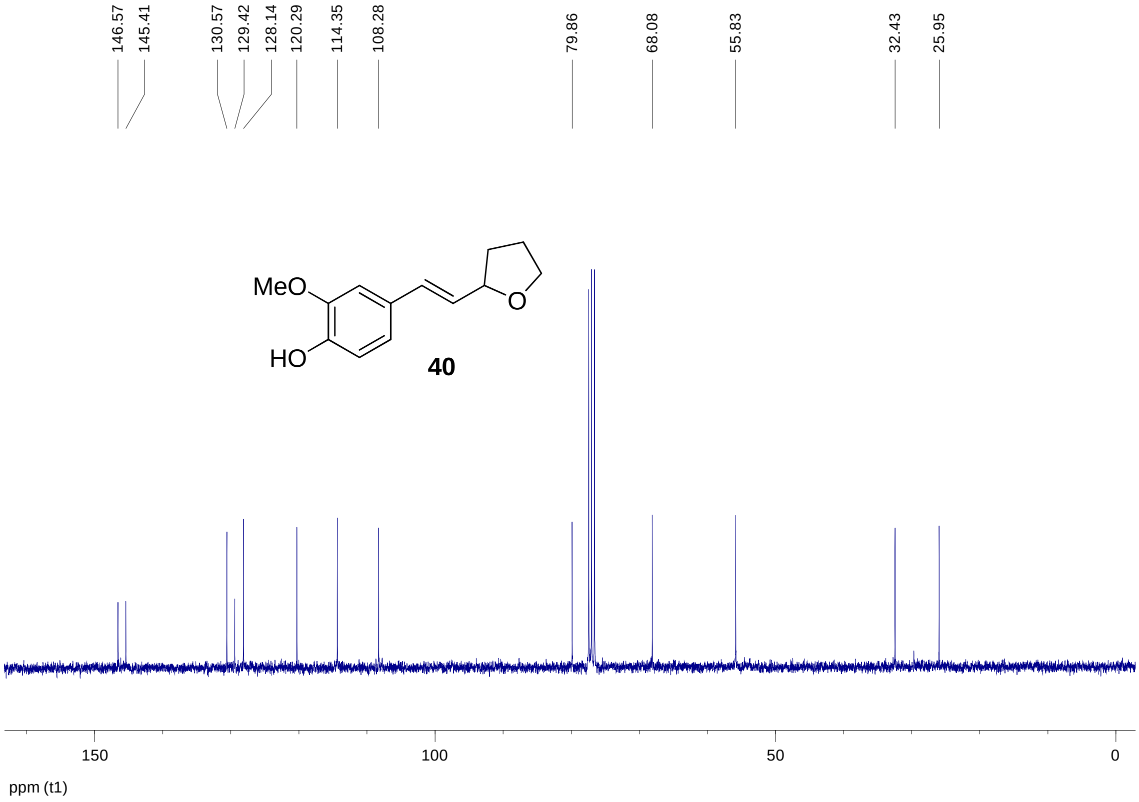
ppm (t1)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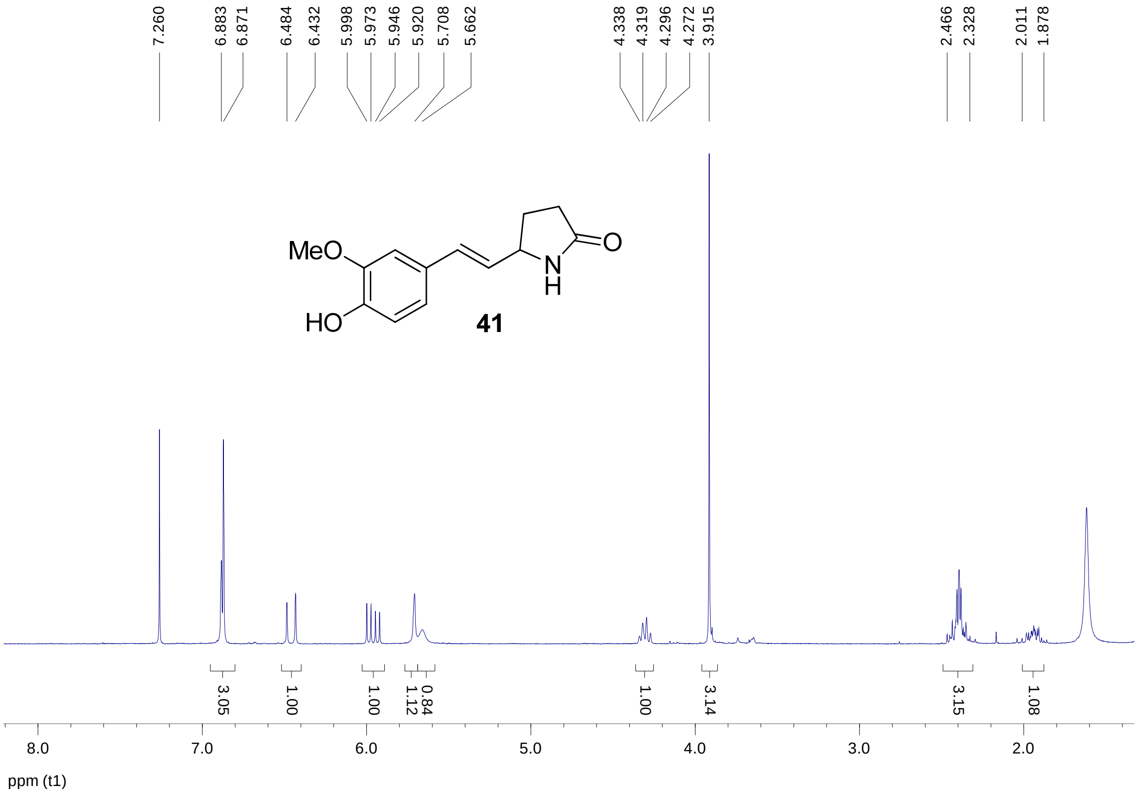
145.41
130.57
129.42
128.14
120.29
114.35
108.28
79.86
68.08
55.83
32.43
25.95
MeO
HO
O
40
150
100
50
0
ppm (t1)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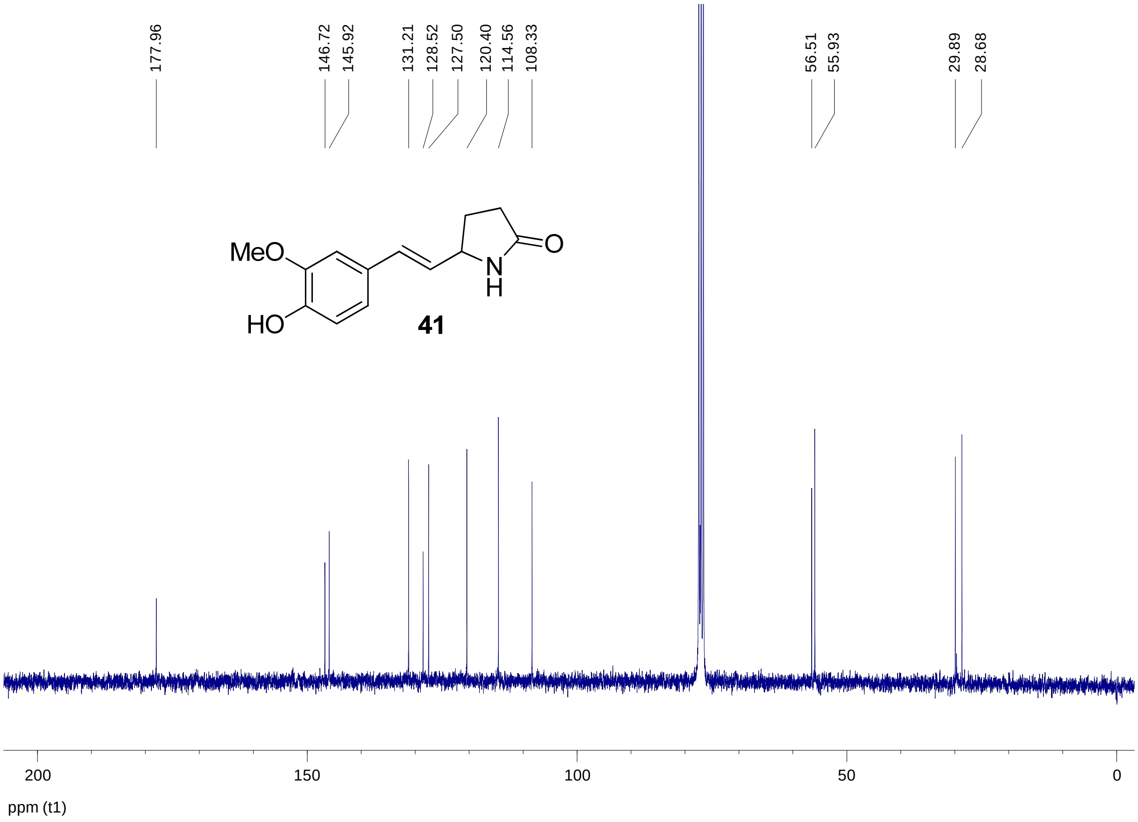
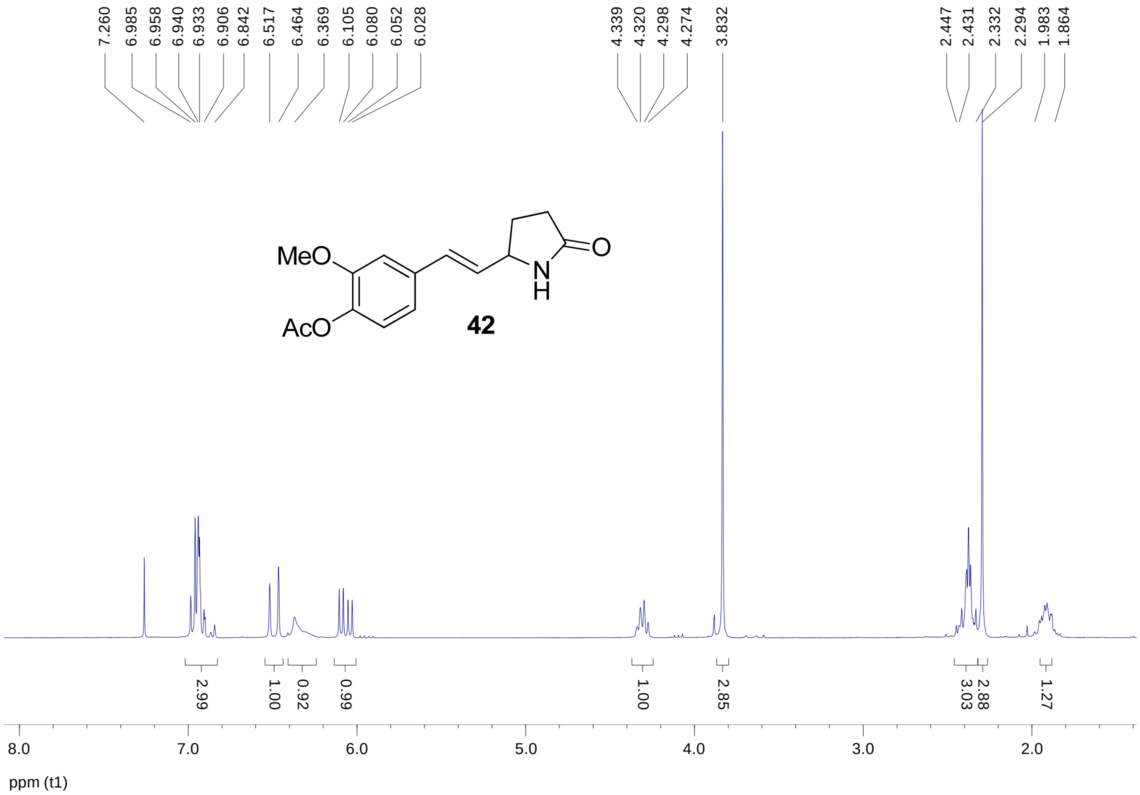
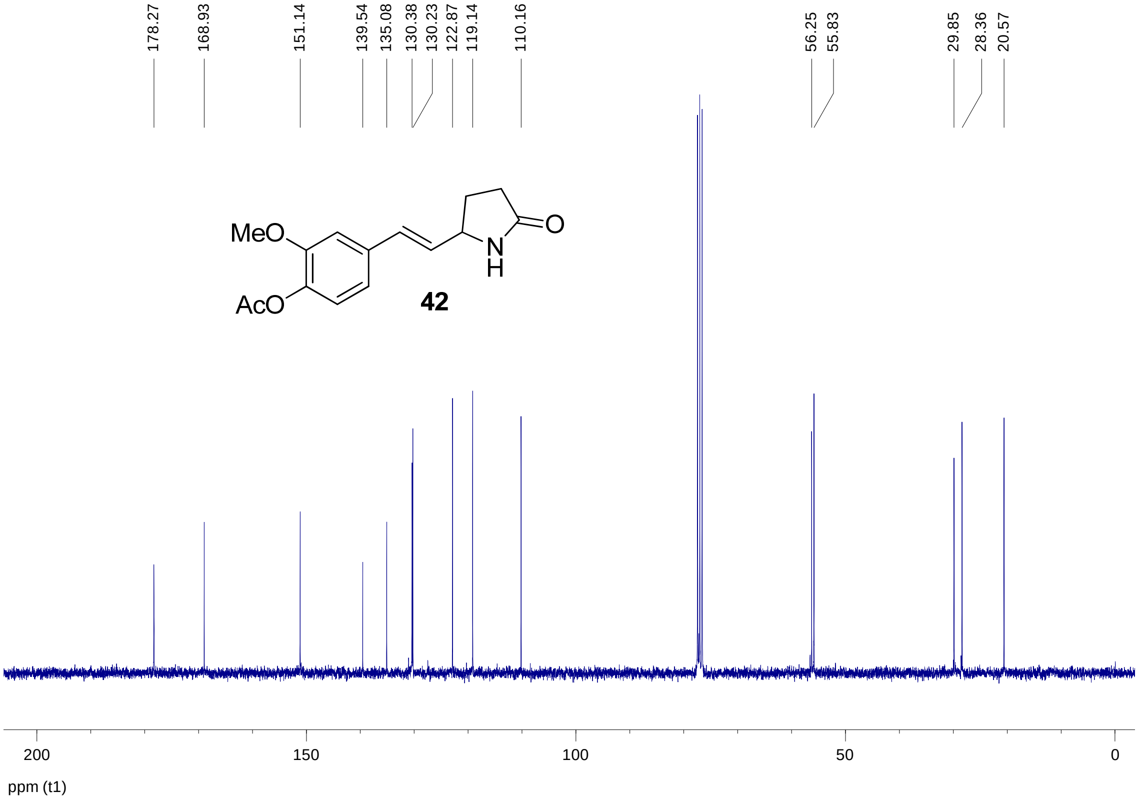
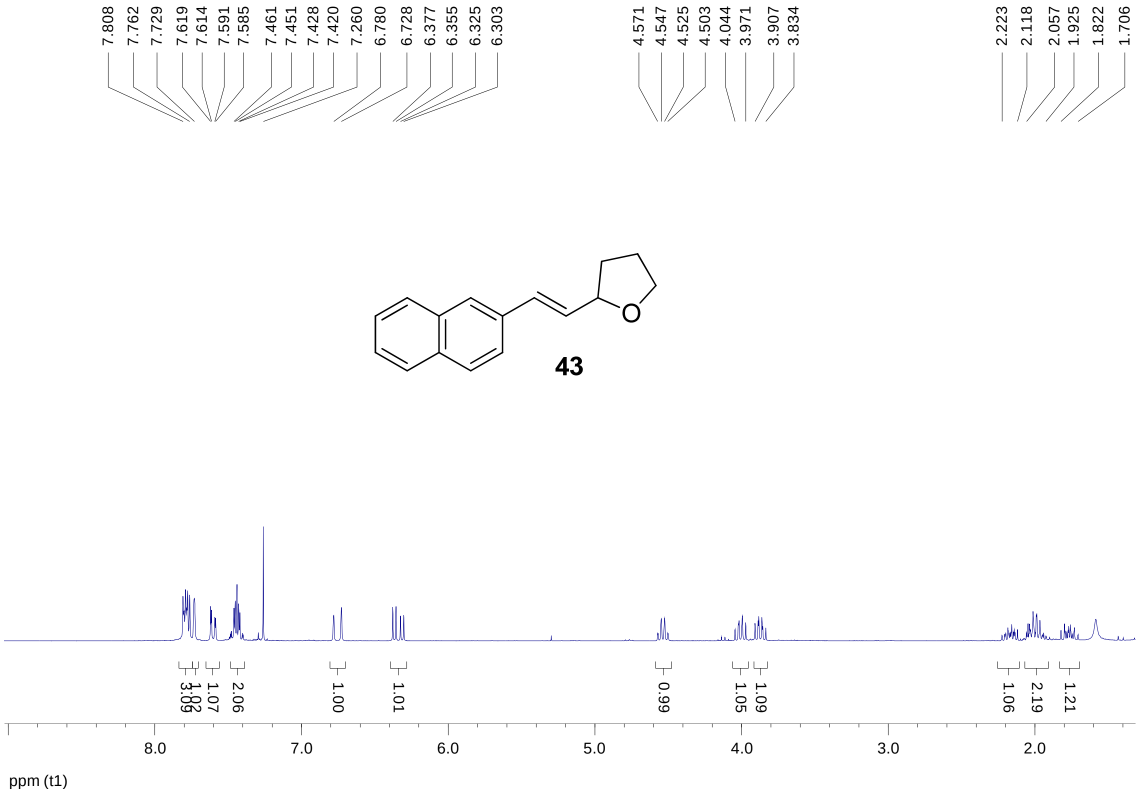
6.883
6.871
6.484
6.432
5.998
5.973
5.946
5.920
5.708
5.662
4.338
4.319
4.296
4.272
3.915
2.466
2.328
2.011
1.878
MeO
HO
N
H
O
41
3.05
1.00
1.00
1.12
0.84
1.00
3.14
3.15
1.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


177.96
146.72
145.92
131.21
128.52
127.50
120.40
114.56
108.33
56.51
55.93
29.89
28.68
MeO
HO
N
H
O
41
200
150
100
50
0
ppm (t1)


7.260
6.985
6.958
6.940
6.933
6.906
6.842
6.517
6.464
6.369
6.105
6.080
6.052
6.028
4.339
4.320
4.298
4.274
3.832
2.447
2.431
2.332
2.294
1.983
1.864
MeO
AcO
NH
O
42
2.99
1.00
0.92
0.99
1.00
2.85
3.03
2.88
1.27
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


178.27
168.93
151.14
139.54
135.08
130.38
130.23
122.87
119.14
110.16
56.25
55.83
29.85
28.36
20.57
MeO
AcO
NH
O
42
200
150
100
50
0
ppm (t1)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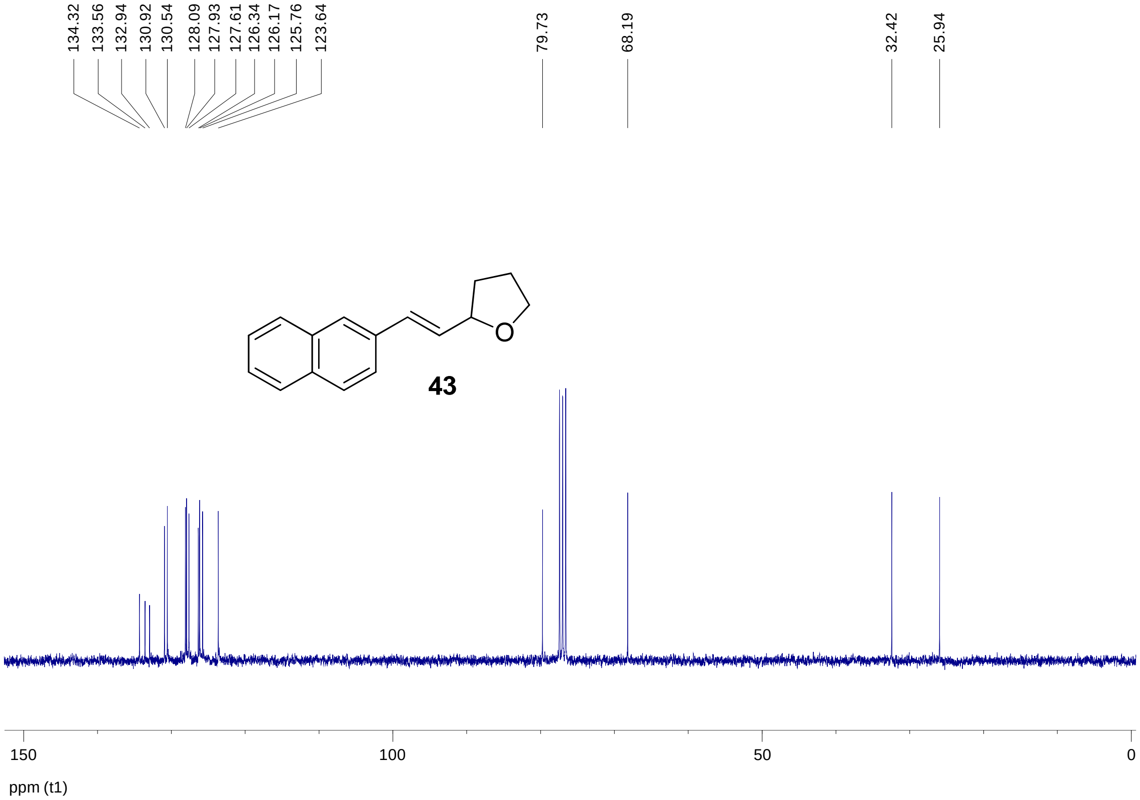
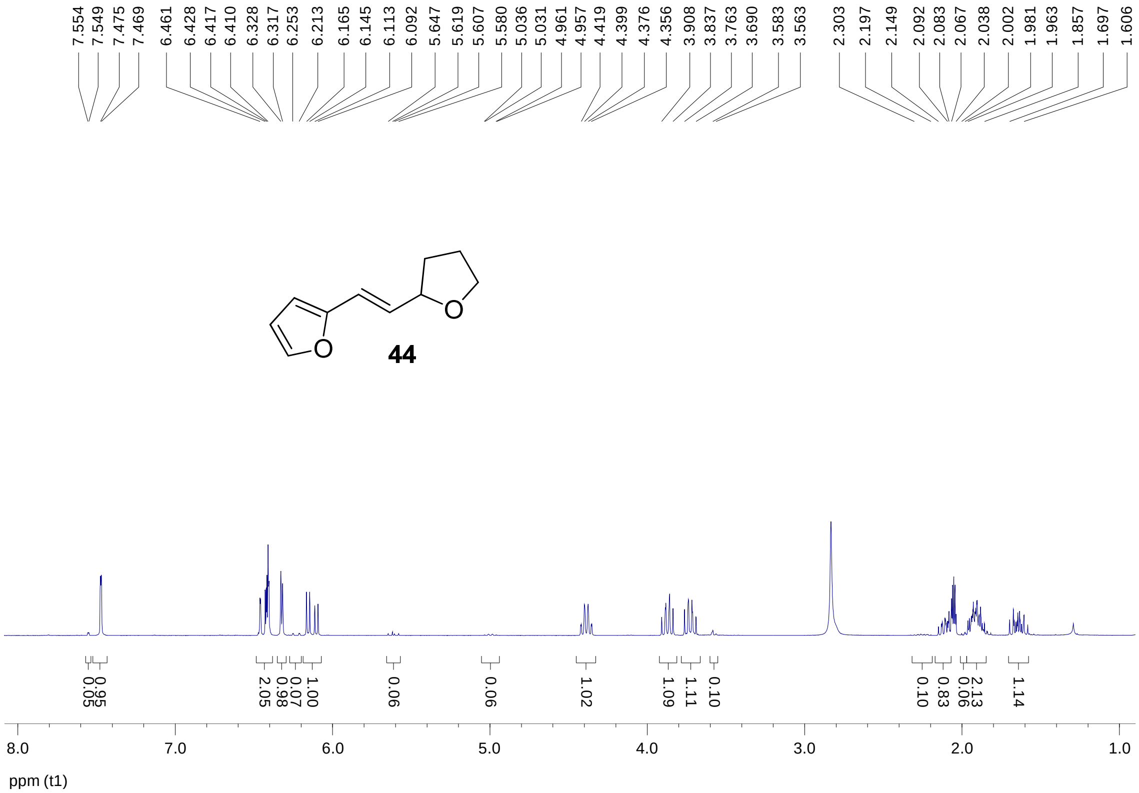
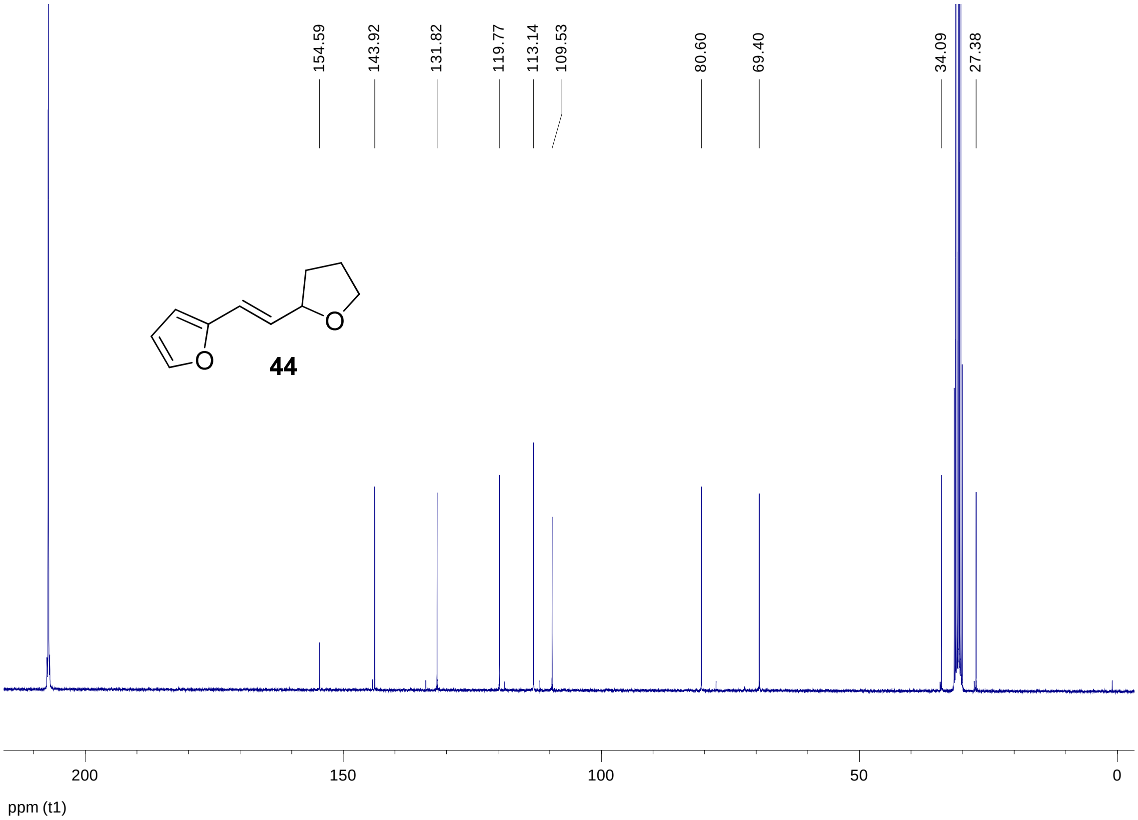
7.762
7.729
7.619
7.614
7.591
7.585
7.461
7.451
7.428
7.420
7.260
6.780
6.728
6.377
6.355
6.325
6.303
4.571
4.547
4.525
4.503
4.044
3.971
3.907
3.834
2.223
2.118
2.057
1.925
1.822
1.706
O
43
3.09
1.02
1.07
2.06
1.00
1.01
0.99
1.05
1.09
1.06
2.19
1.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

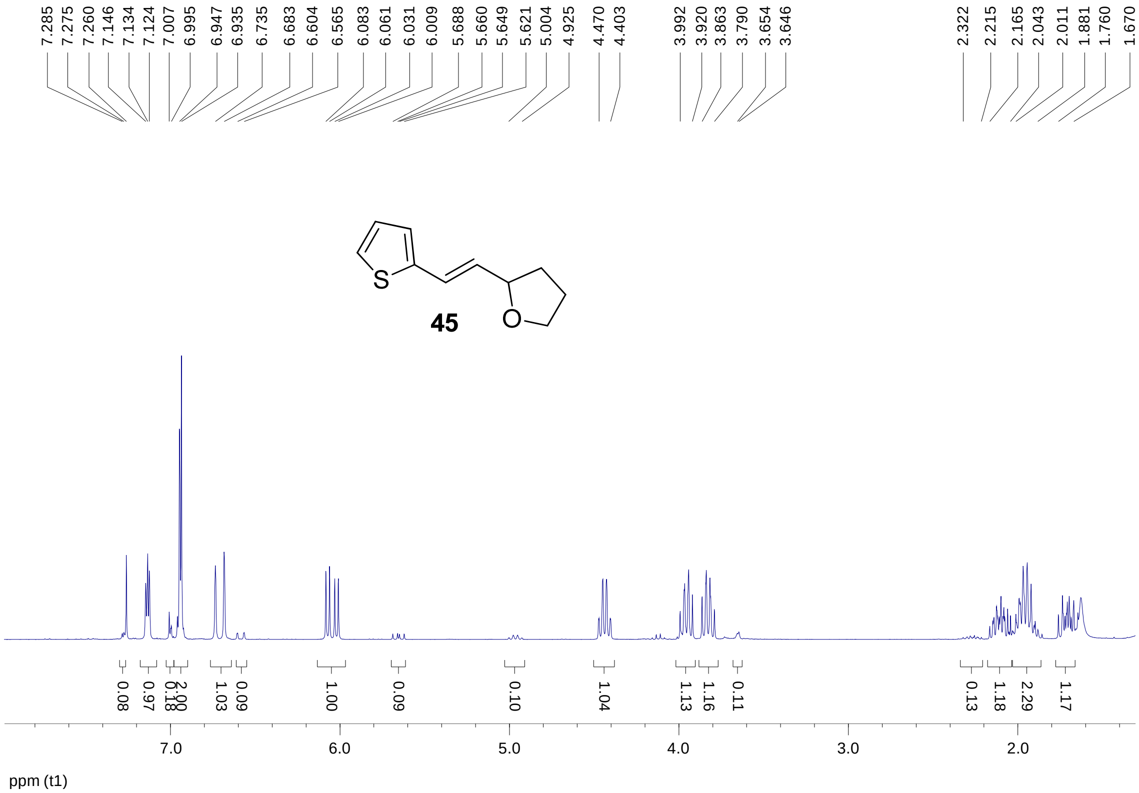

134.32
133.56
132.94
130.92
130.54
128.09
127.93
127.61
126.34
126.17
125.76
123.64
79.73
68.19
32.42
25.94
O
43
150
100
50
0
ppm (t1)

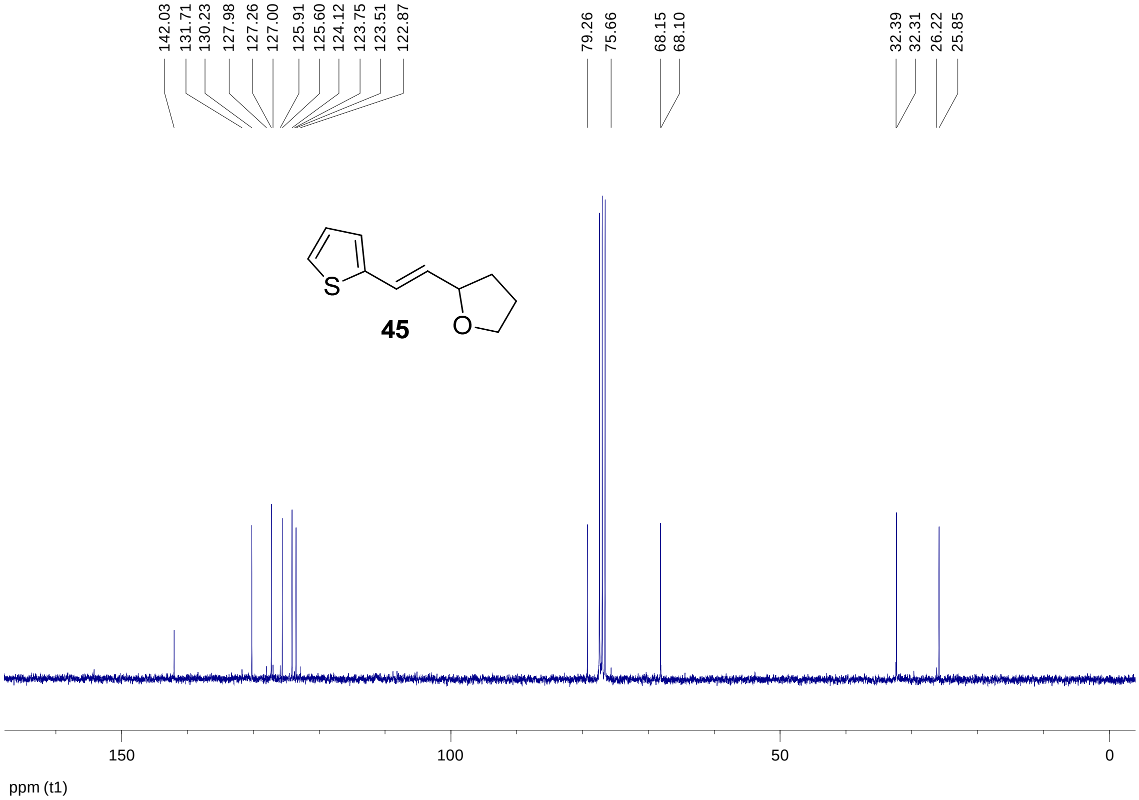

7.554
7.549
7.475
7.469
6.461
6.428
6.417
6.410
6.328
6.317
6.253
6.213
6.165
6.145
6.113
6.092
5.647
5.619
5.607
5.580
5.036
5.031
4.961
4.957
4.419
4.399
4.376
4.356
3.908
3.837
3.763
3.690
3.583
3.563
2.303
2.197
2.149
2.092
2.083
2.067
2.038
2.002
1.981
1.963
1.857
1.697
1.606
O
O
0.05
0.95
2.05
0.98
0.07
1.00
0.06
0.06
1.02
1.09
1.11
0.10
0.10
0.83
0.06
2.13
1.14
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

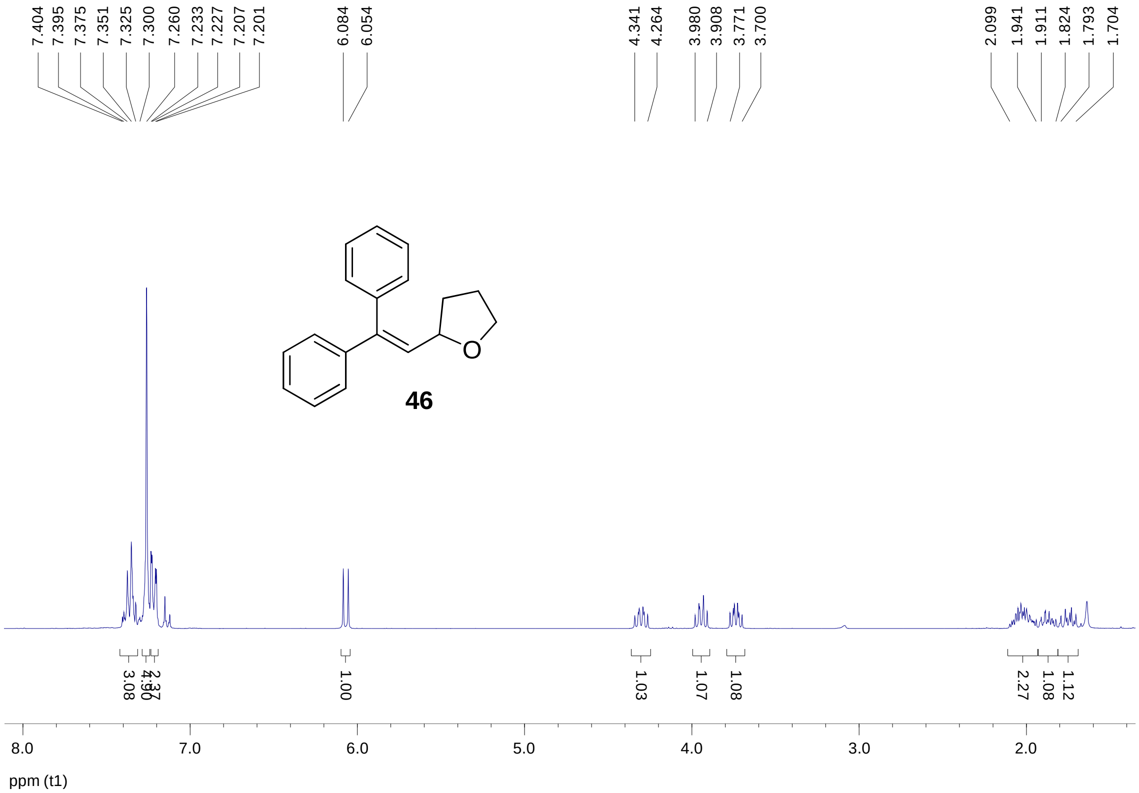
44


154.59
143.92
131.82
119.77
113.14
109.53
80.60
69.40
34.09
27.38
O
O
200
150
100
50
0
ppm (t1)

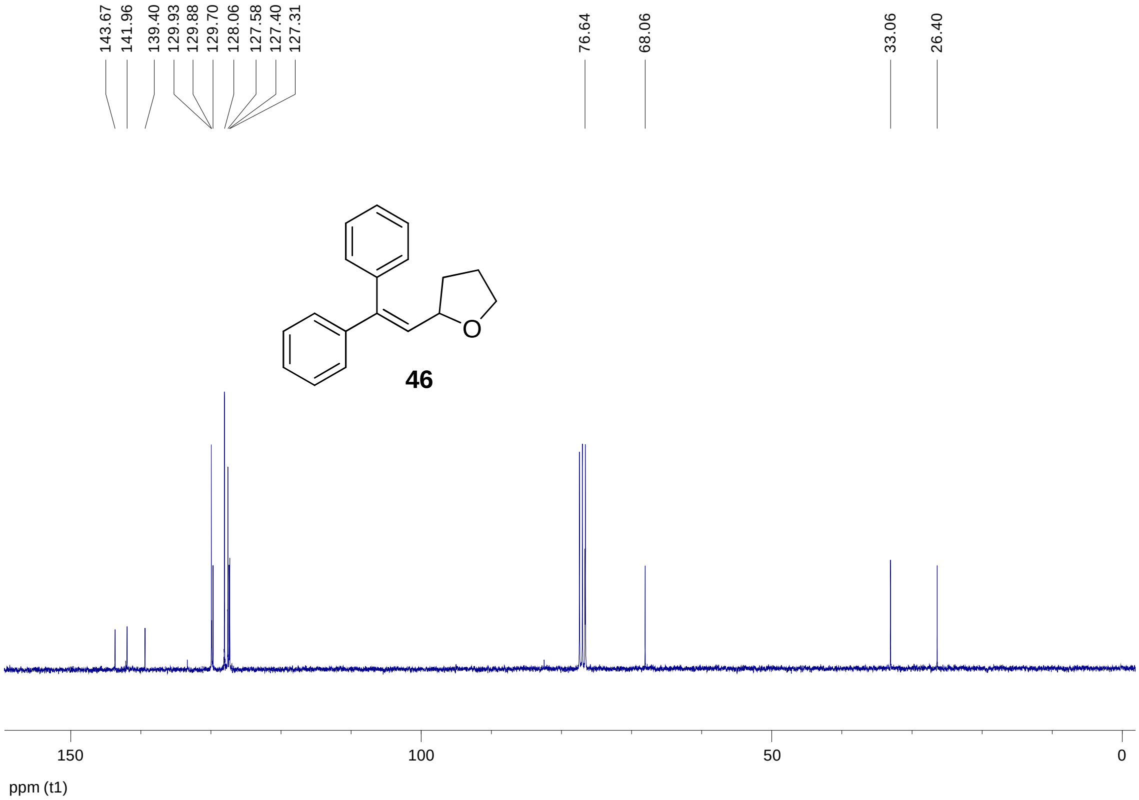
44


45
7.285
7.275
7.260
7.146
7.134
7.124
7.007
6.995
6.947
6.935
6.735
6.683
6.604
6.565
6.083
6.061
6.031
6.009
5.688
5.660
5.649
5.621
5.004
4.925
4.470
4.403
3.992
3.920
3.863
3.790
3.654
3.646
2.322
2.215
2.165
2.043
2.011
1.881
1.760
1.670
S
O
0.08
0.97
0.18
2.00
1.03
0.09
1.00
0.09
0.10
1.04
1.13
1.16
0.11
0.13
1.18
2.29
1.17
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

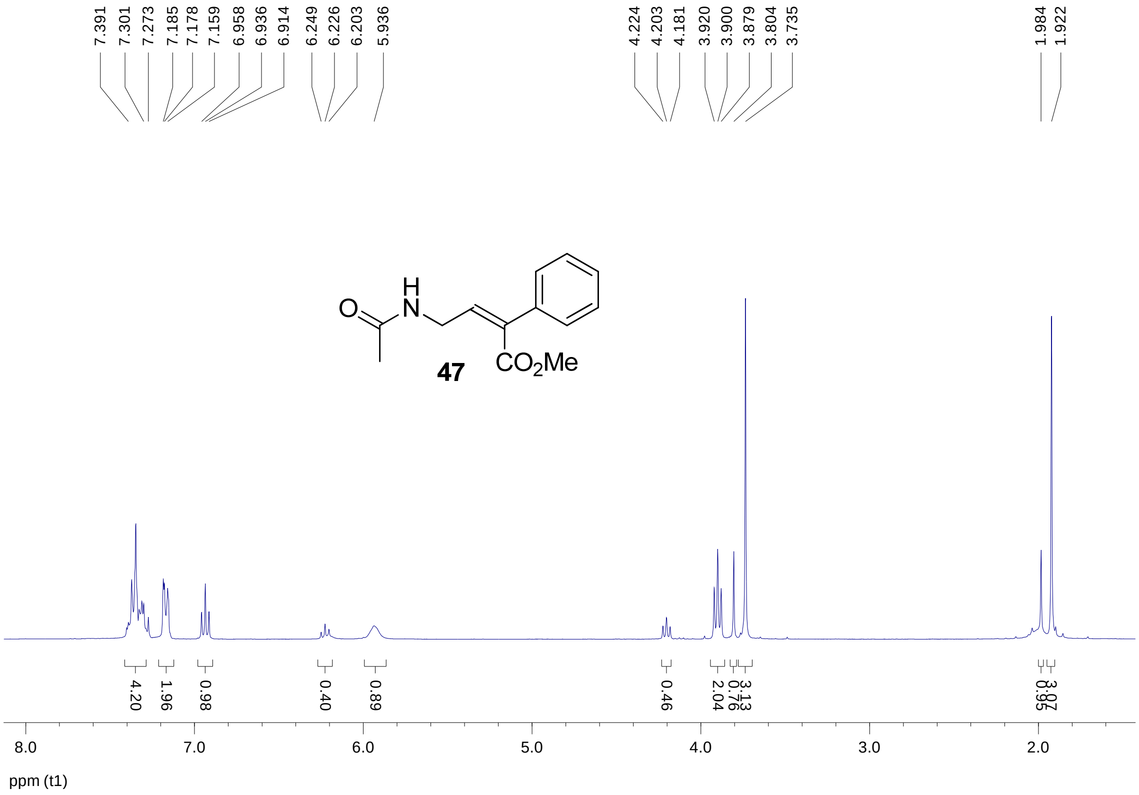

45
142.03
131.71
130.23
127.98
127.26
127.00
125.91
125.60
124.12
123.75
123.51
122.87
79.26
75.66
68.15
68.10
32.39
32.31
26.22
25.85
S
O
150
100
50
0
ppm (t1)

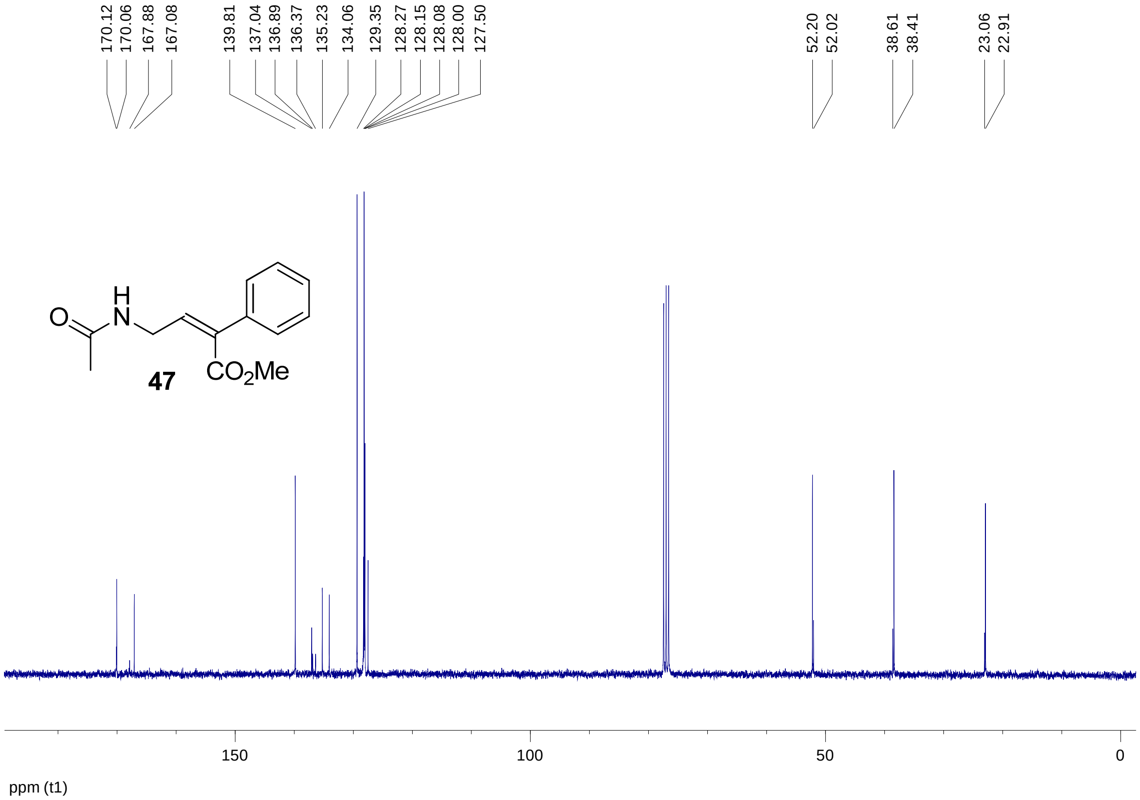

7.404
7.395
7.375
7.351
7.325
7.300
7.260
7.233
7.227
7.207
7.201
6.084
6.054
4.341
4.264
3.980
3.908
3.771
3.700
2.099
1.941
1.911
1.824
1.793
1.704
O
3.08
4.90
2.37
1.00
1.03
1.07
1.08
2.27
1.08
1.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

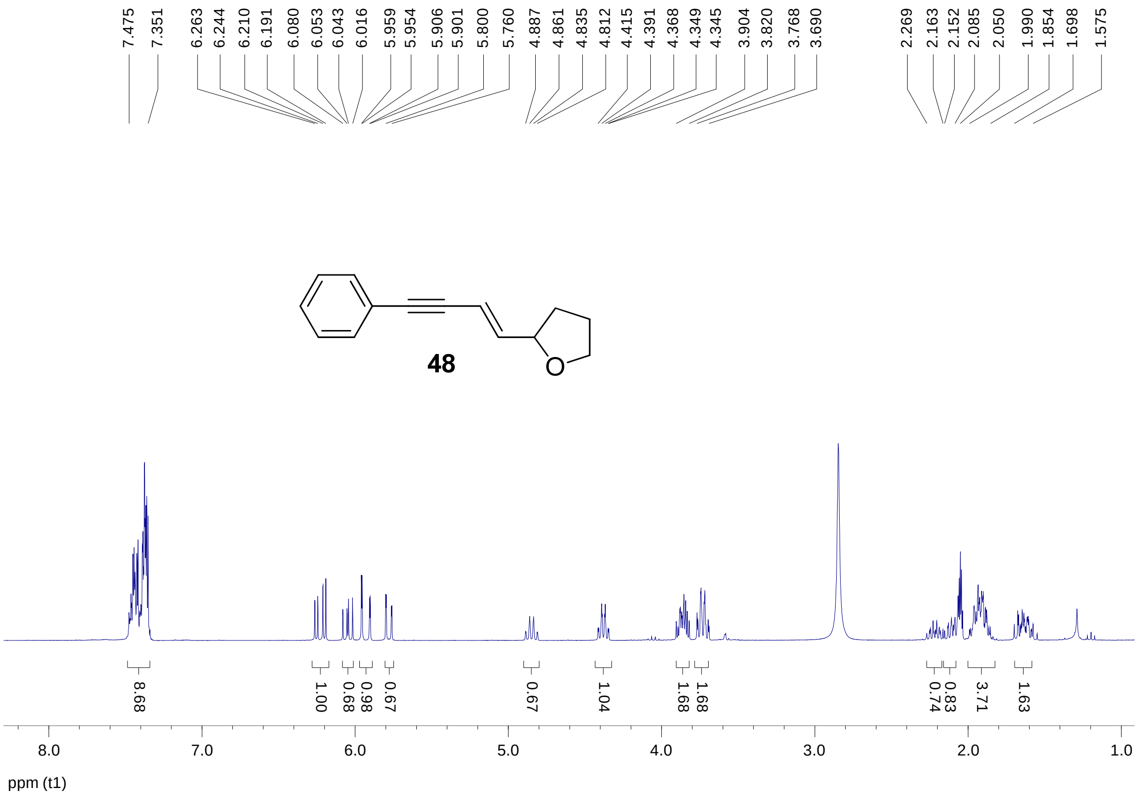
46

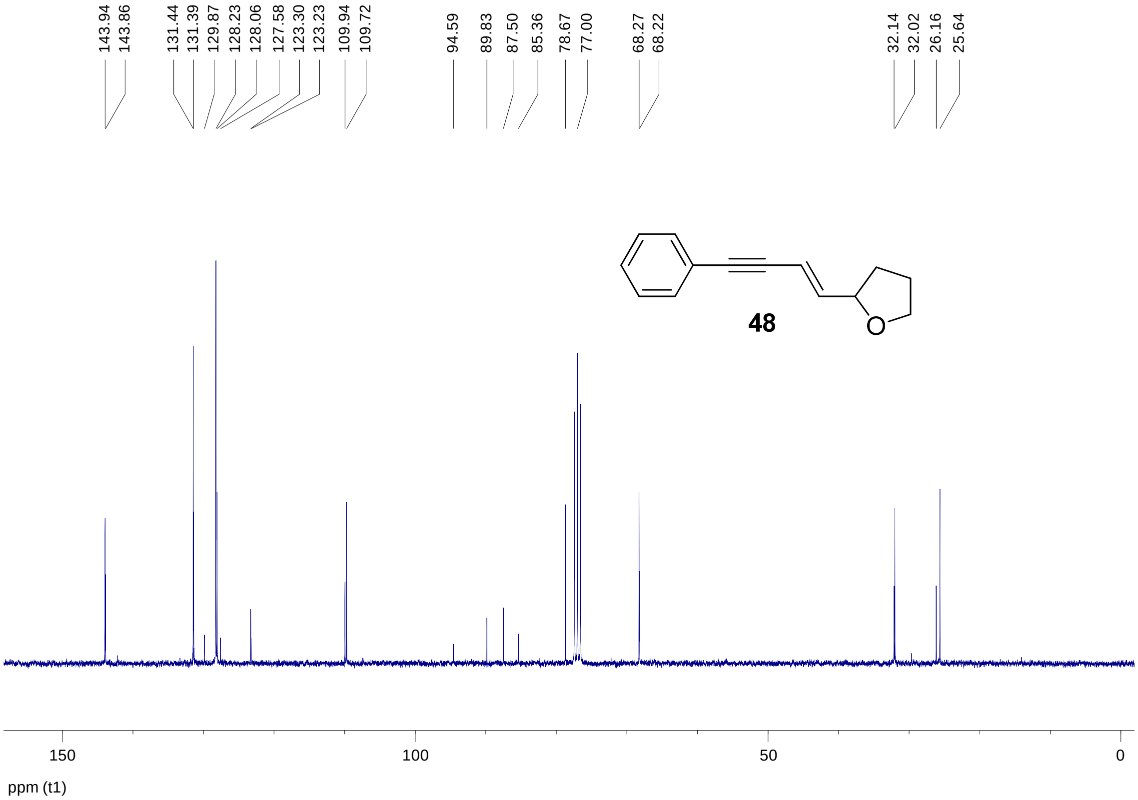

143.67
141.96
139.40
129.93
129.88
129.70
128.06
127.58
127.40
127.31
76.64
68.06
33.06
26.40
O
150
100
50
0
ppm (t1)

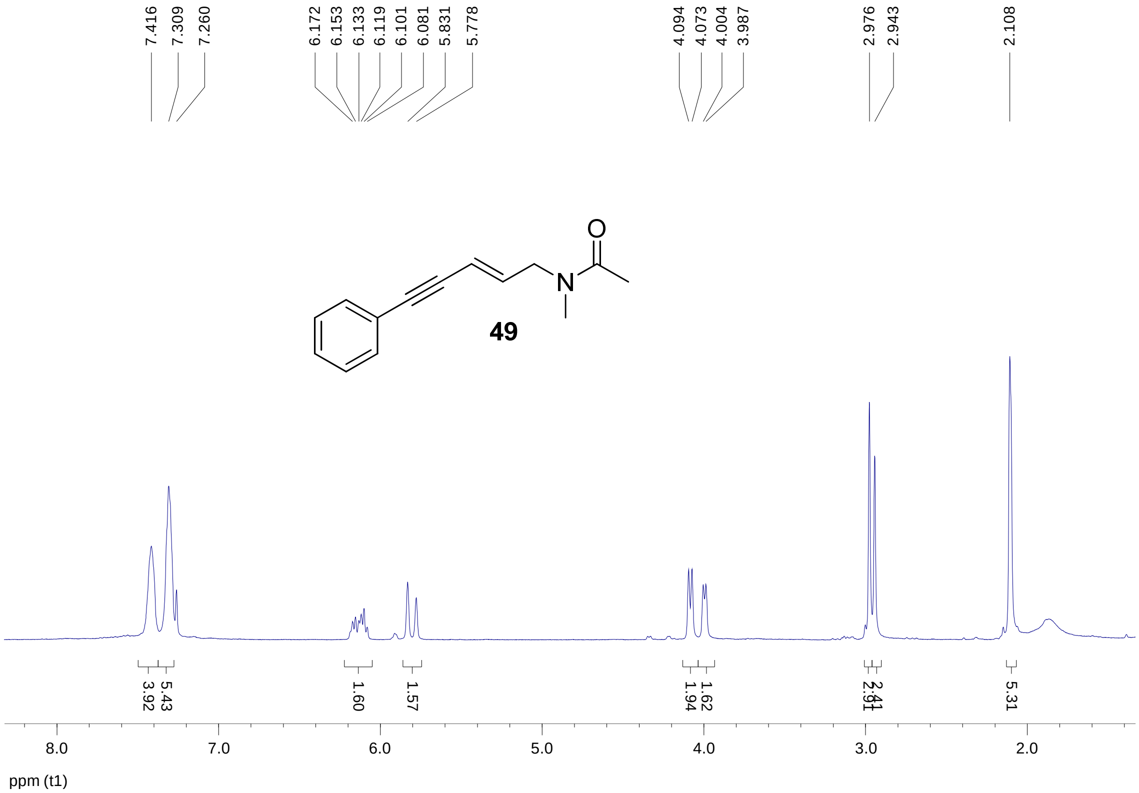
46

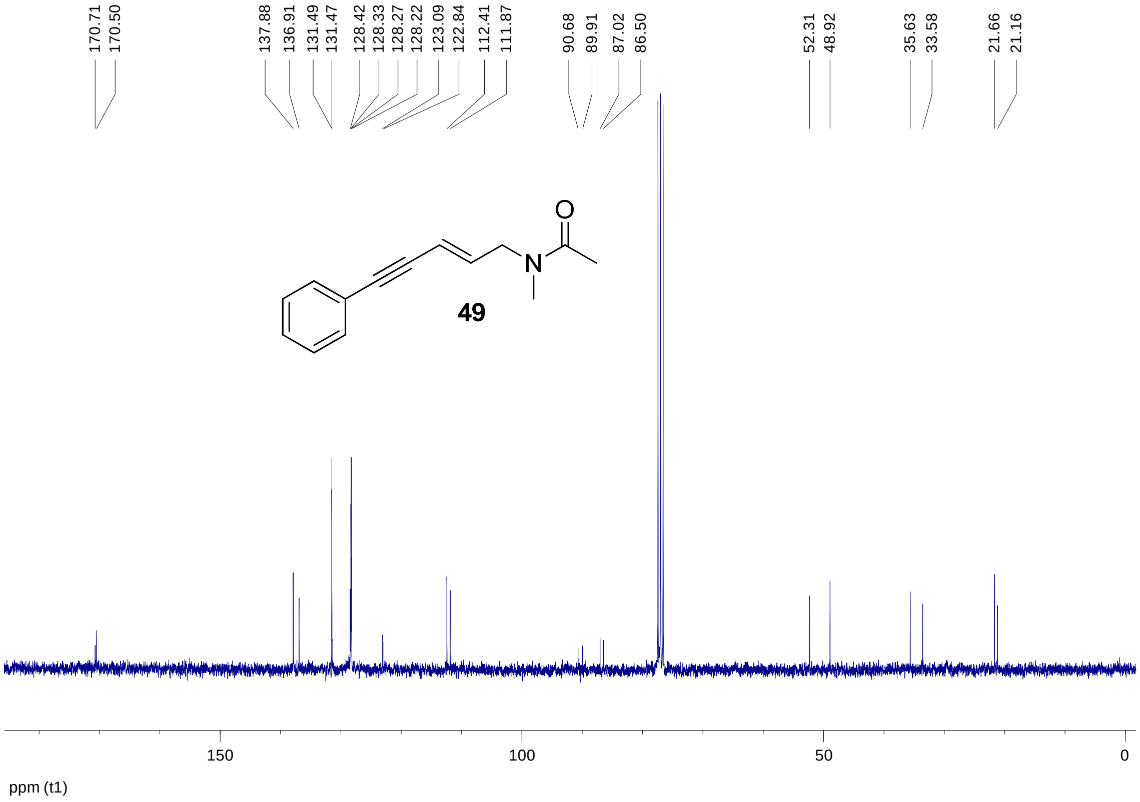

7.391
7.301
7.273
7.185
7.178
7.159
6.958
6.936
6.914
6.249
6.226
6.203
5.936
4.224
4.203
4.181
3.920
3.900
3.879
3.804
3.735
1.984
1.922
O
H
N
CO$_2$Me
47
4.20
1.96
0.98
0.40
0.89
0.46
2.04
0.76
3.13
0.95
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

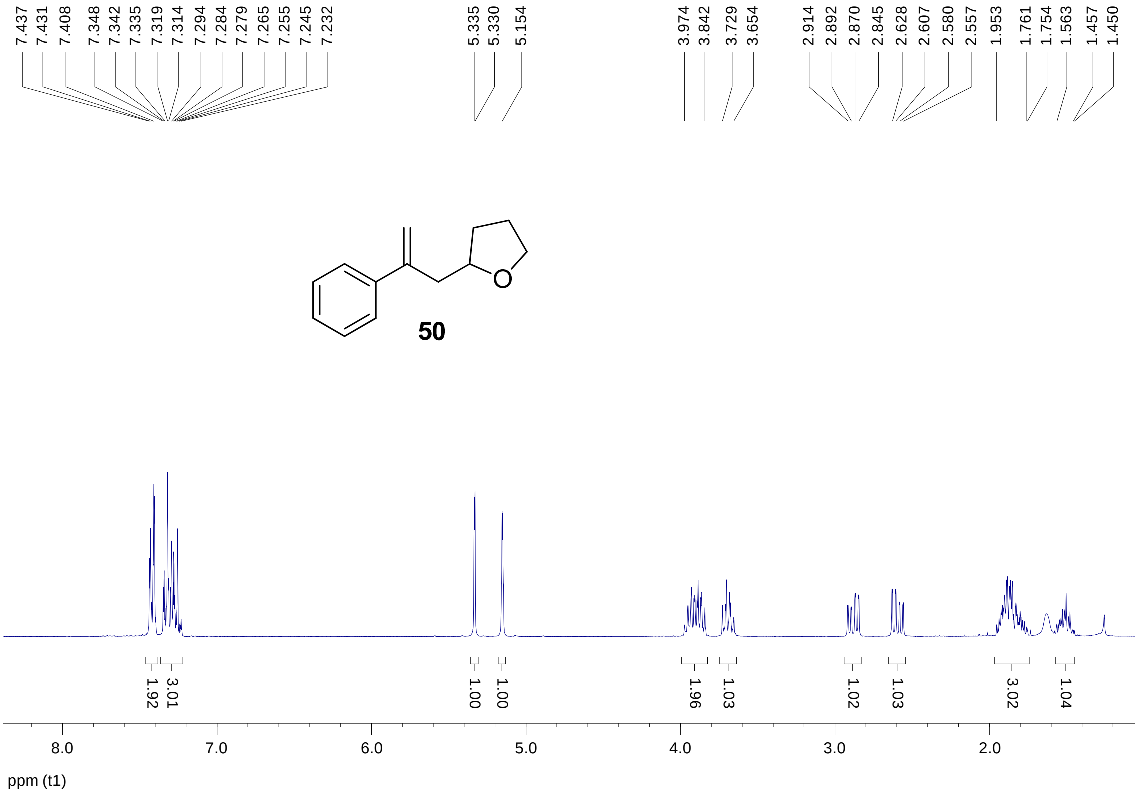

170.12
170.06
167.88
167.08
139.81
137.04
136.89
136.37
135.23
134.06
129.35
128.27
128.15
128.08
128.00
127.50
52.20
52.02
38.61
38.41
23.06
22.91
O
H
N
CO$_2$Me
47
150
100
50
0
ppm (t1)


7.475
7.351
6.263
6.244
6.210
6.191
6.080
6.053
6.043
6.016
5.959
5.954
5.906
5.901
5.800
5.760
4.887
4.861
4.835
4.812
4.415
4.391
4.368
4.349
4.345
3.904
3.820
3.768
3.690
2.269
2.163
2.152
2.085
2.050
1.990
1.854
1.698
1.575
48
O
8.68
1.00
0.68
0.98
0.67
0.67
1.04
1.68
1.68
0.74
0.83
3.71
1.63
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


143.94
143.86
131.44
131.39
129.87
128.23
128.06
127.58
123.30
123.23
109.94
109.72
94.59
89.83
87.50
85.36
78.67
77.00
68.27
68.22
32.14
32.02
26.16
25.64
48
O
150
100
50
0
ppm (t1)


7.416
7.309
7.260
6.172
6.153
6.133
6.119
6.101
6.081
5.831
5.778
4.094
4.073
4.004
3.987
2.976
2.943
2.108
O
N
49
3.92
5.43
1.60
1.57
1.94
1.62
2.91
2.41
5.31
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


170.71
170.50
137.88
136.91
131.49
131.47
128.42
128.33
128.27
128.22
123.09
122.84
112.41
111.87
90.68
89.91
87.02
86.50
52.31
48.92
35.63
33.58
21.66
21.16
O
N
49
150
100
50
0
ppm (t1)


7.437
7.431
7.408
7.348
7.342
7.335
7.319
7.314
7.294
7.284
7.279
7.265
7.255
7.245
7.232
5.335
5.330
5.154
3.974
3.842
3.729
3.654
2.914
2.892
2.870
2.845
2.628
2.607
2.580
2.557
1.953
1.761
1.754
1.563
1.457
1.450
50
1.92
3.01
1.00
1.00
1.96
1.03
1.02
1.03
3.02
1.04
8.0
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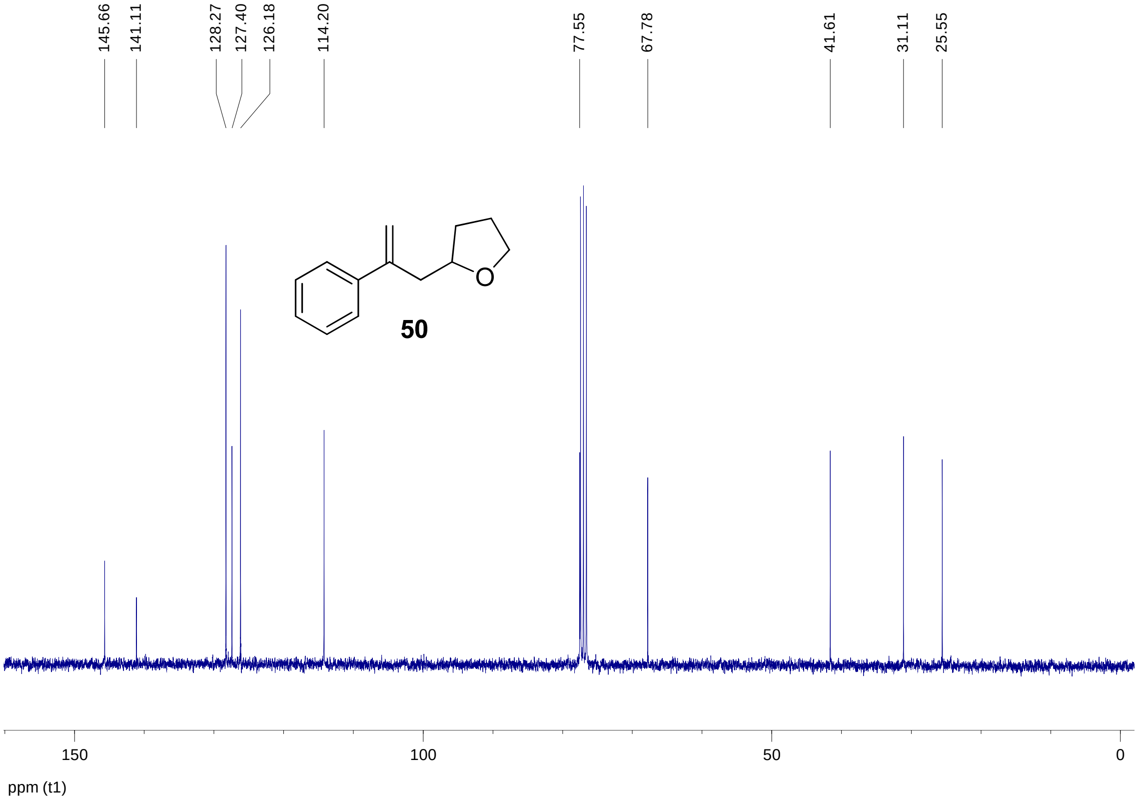
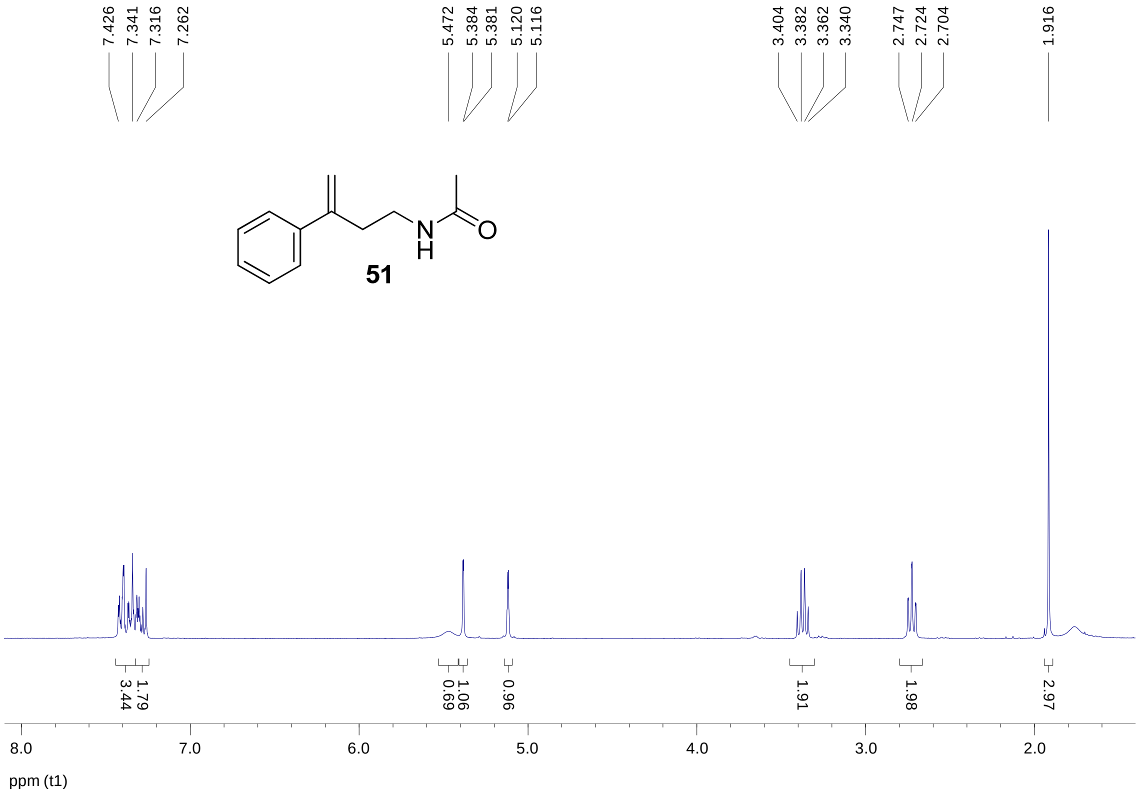
3.0
2.0
ppm (t1)


145.66
141.11
128.27
127.40
126.18
114.20
77.55
67.78
41.61
31.11
25.55
50
150
100
50
0
ppm (t1)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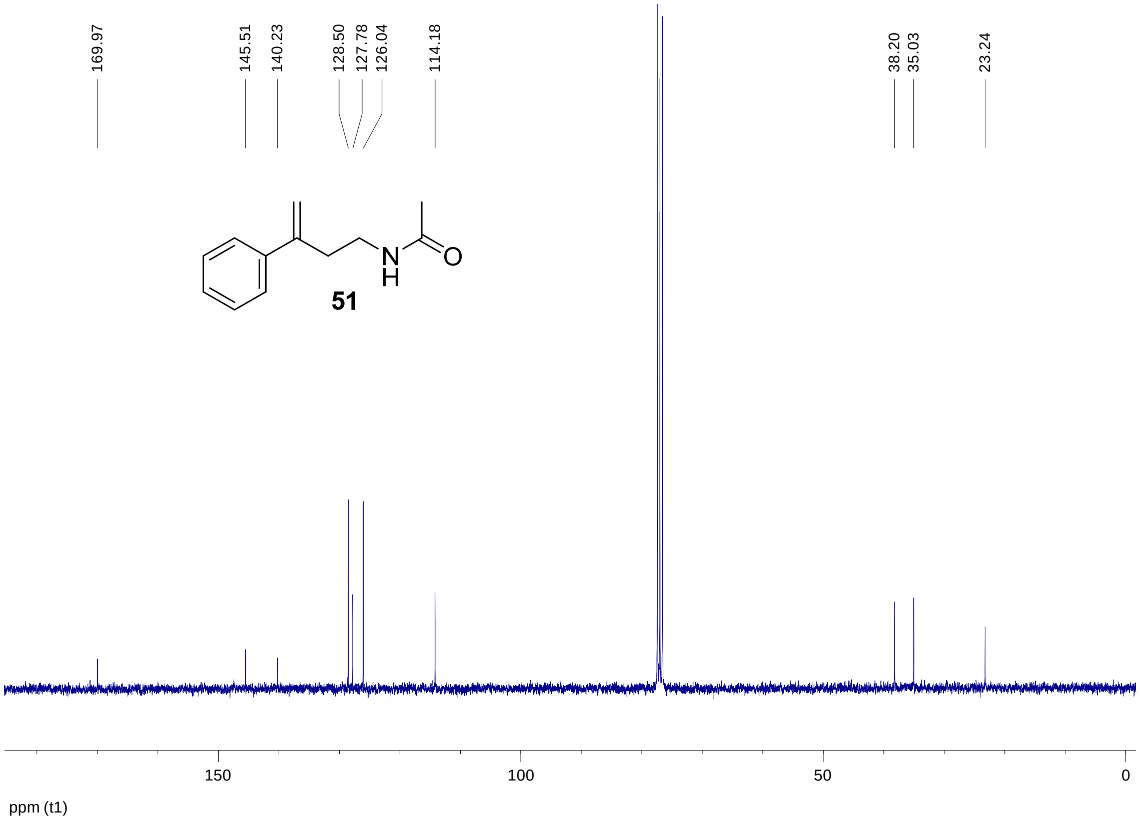
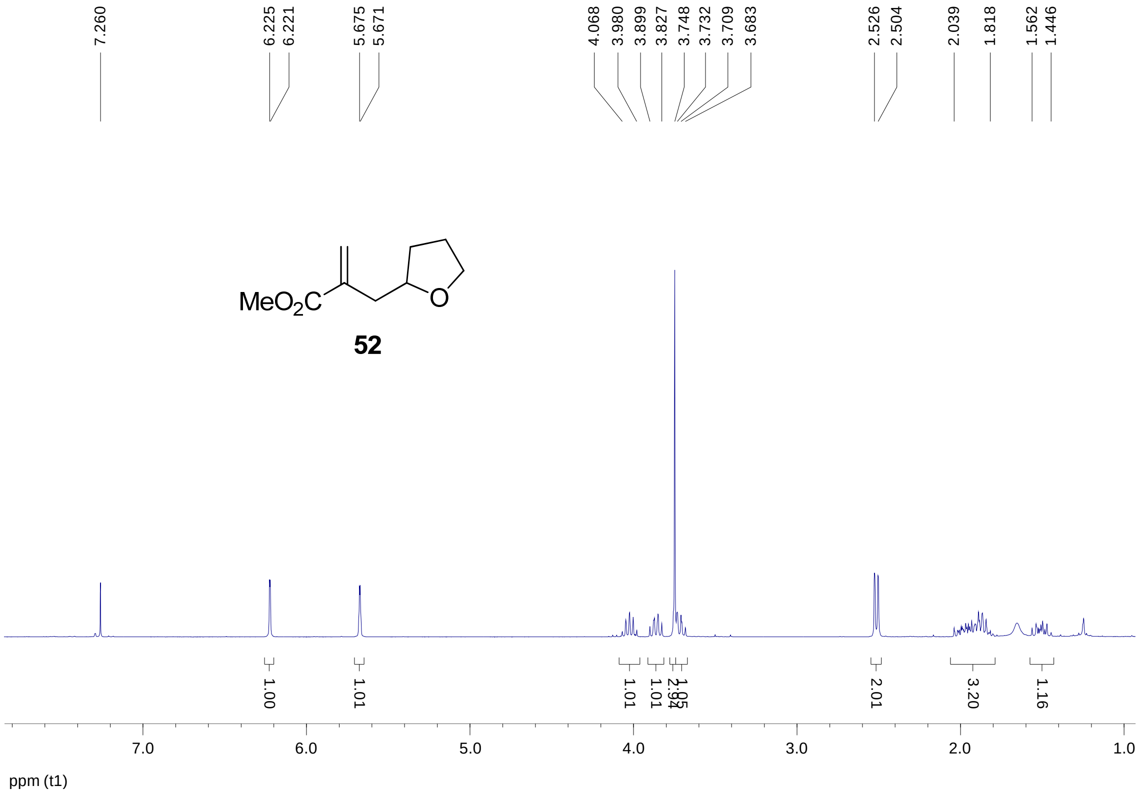
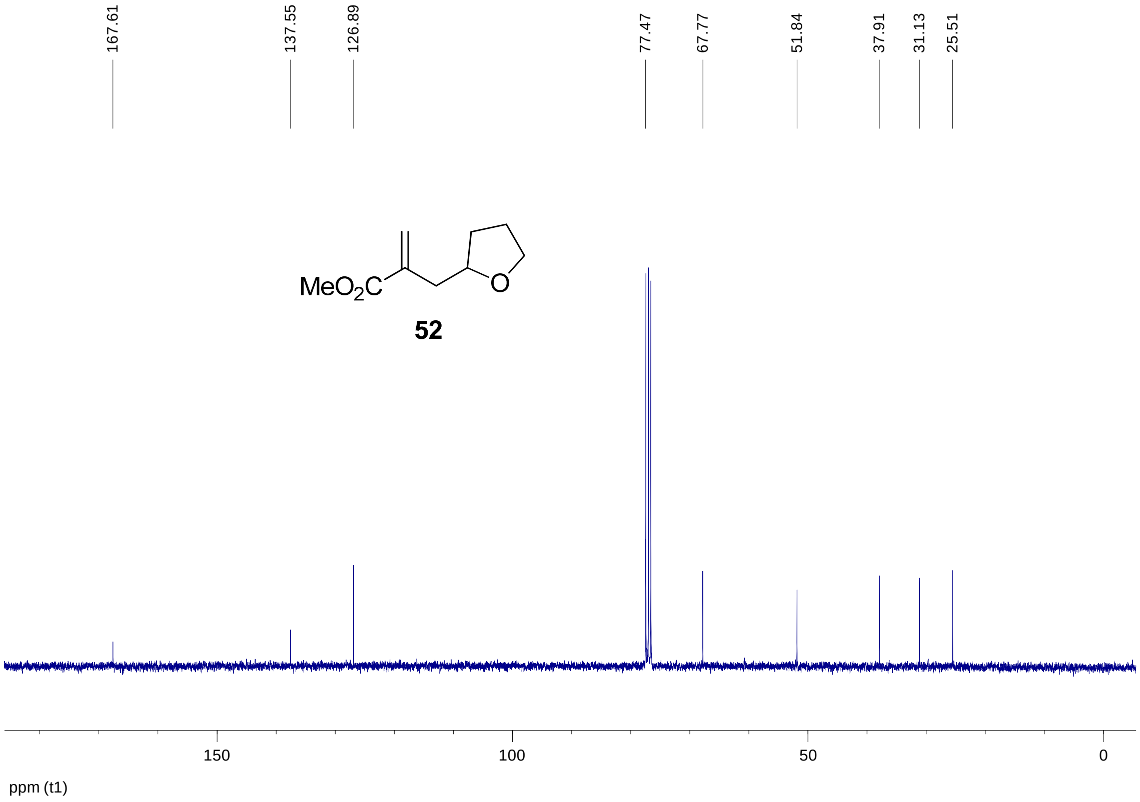
7.341
7.316
7.262
5.472
5.384
5.381
5.120
5.116
3.404
3.382
3.362
3.340
2.747
2.724
2.704
1.916
H
N
O
51
3.44
1.79
0.69
1.06
0.96
1.91
1.98
2.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

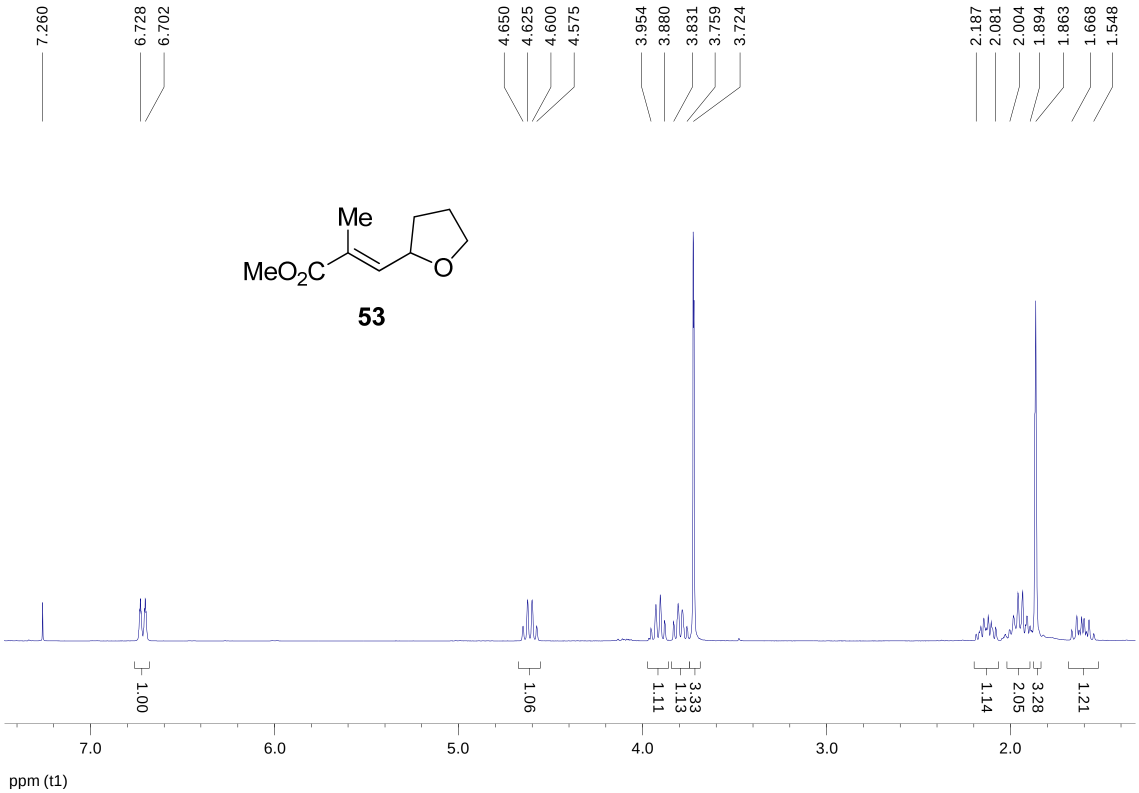

169.97
145.51
140.23
128.50
127.78
126.04
114.18
38.20
35.03
23.24
H
N
O
51
150
100
50
0
ppm (t1)

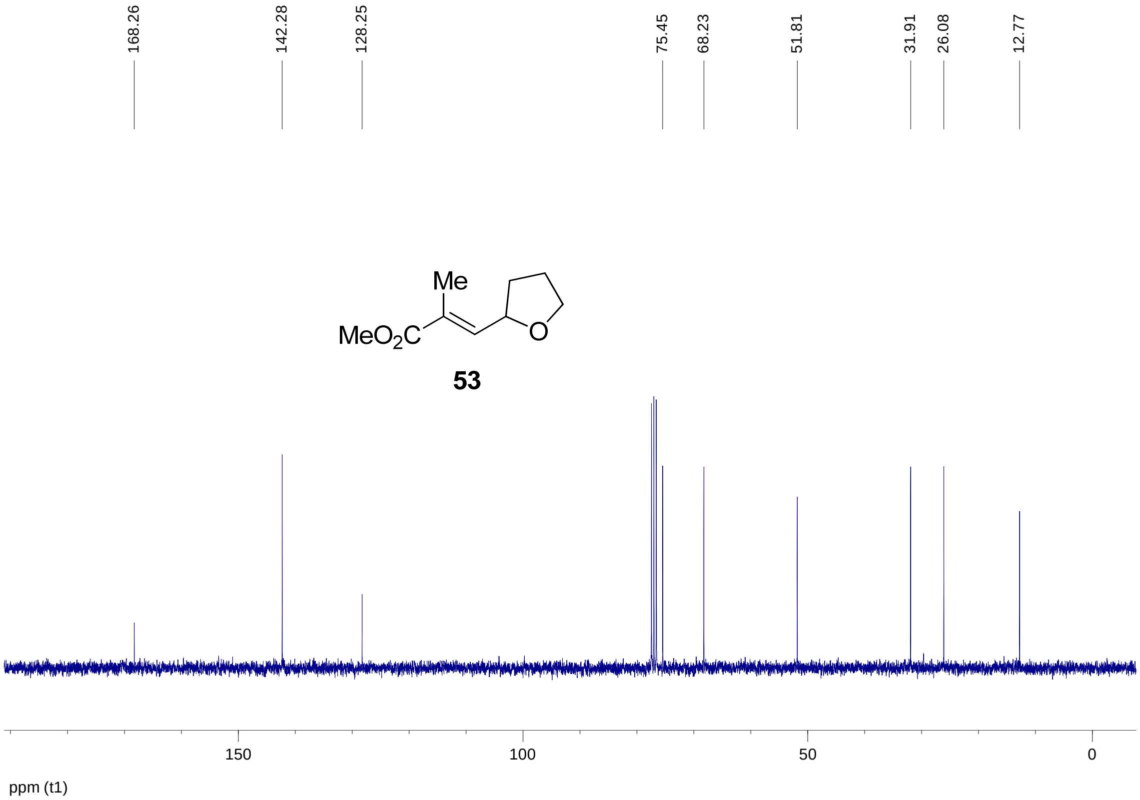

7.260
6.225
6.221
5.675
5.671
4.068
3.980
3.899
3.827
3.748
3.732
3.709
3.683
2.526
2.504
2.039
1.818
1.562
1.446
MeO$_2$C
O
1.00
1.01
1.01
1.01
1.05
2.01
3.20
1.16
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

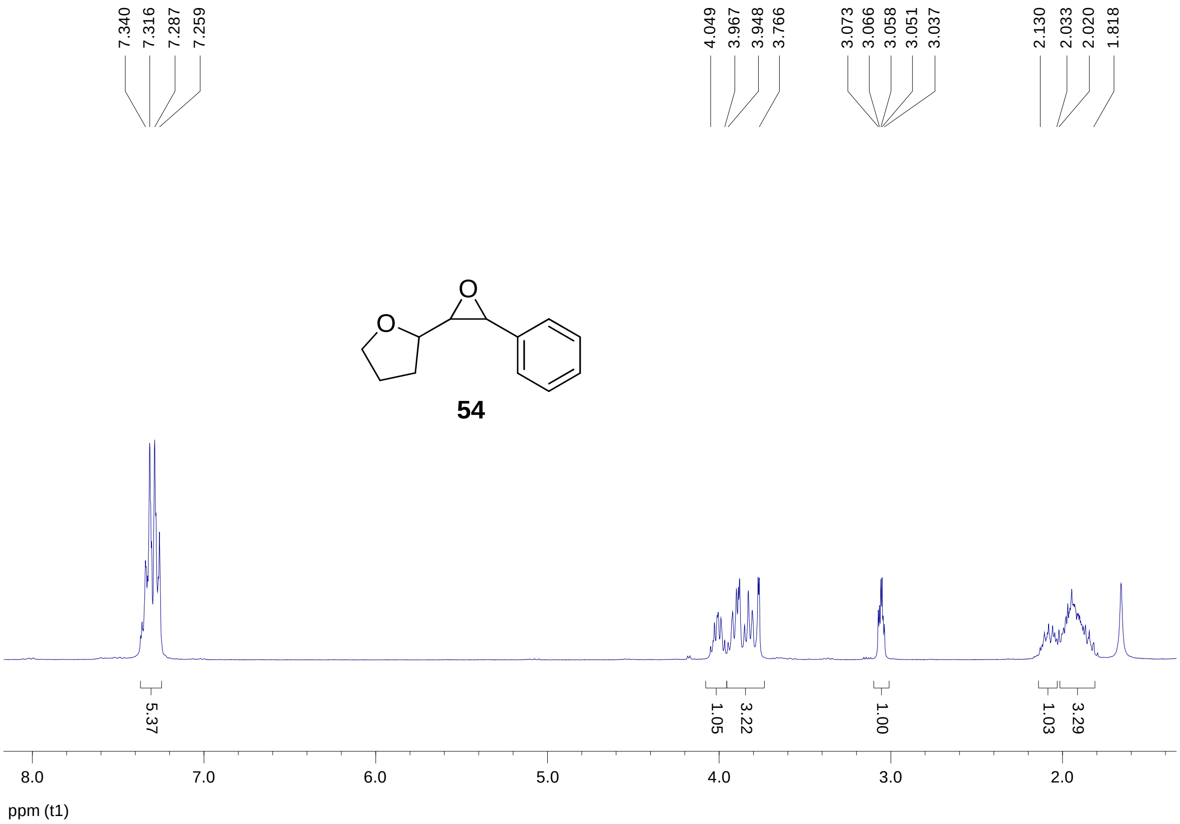
52


167.61
137.55
126.89
77.47
67.77
51.84
37.91
31.13
25.51
MeO$_2$C
O
150
100
50
0
ppm (t1)

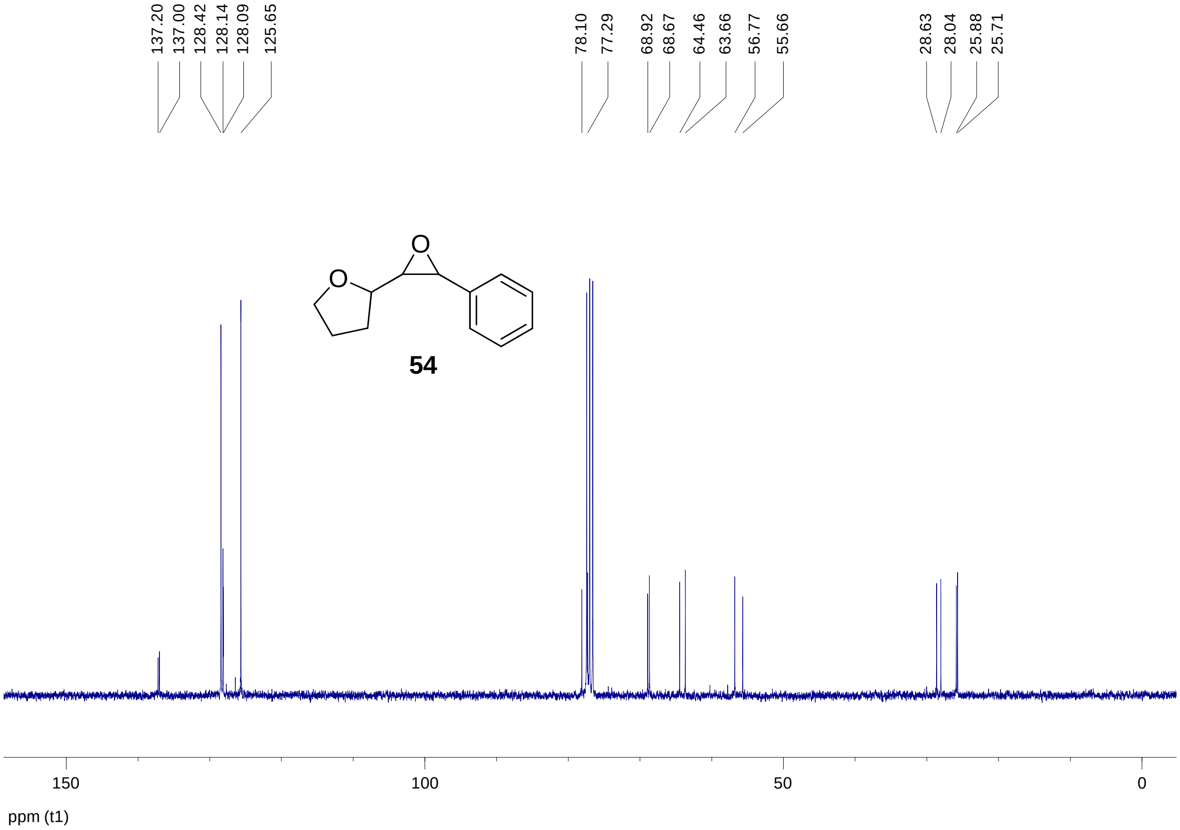
52


7.260
6.728
6.702
4.650
4.625
4.600
4.575
3.954
3.880
3.831
3.759
3.724
2.187
2.081
2.004
1.894
1.863
1.668
1.548
Me
MeO2C
O
53
1.00
1.06
1.11
1.13
3.33
1.14
2.05
3.28
1.21
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

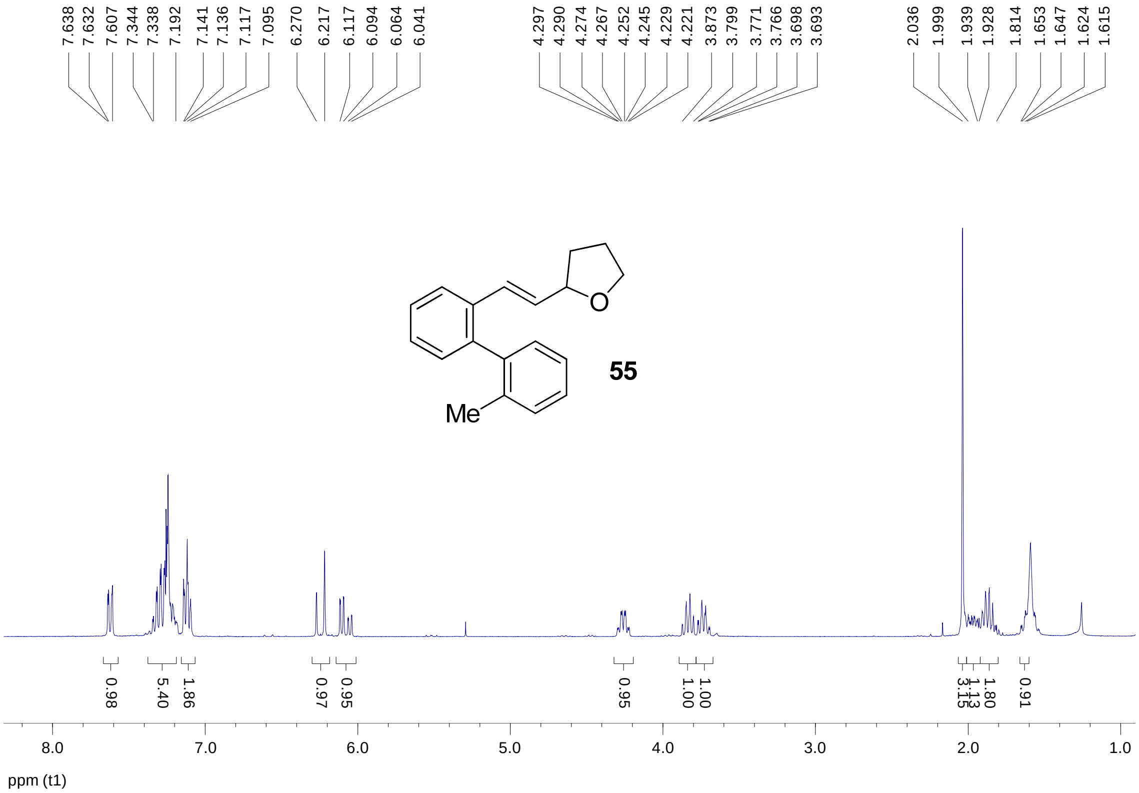

168.26
142.28
128.25
75.45
68.23
51.81
31.91
26.08
12.77
Me
MeO2C
O
53
150
100
50
0
ppm (t1)

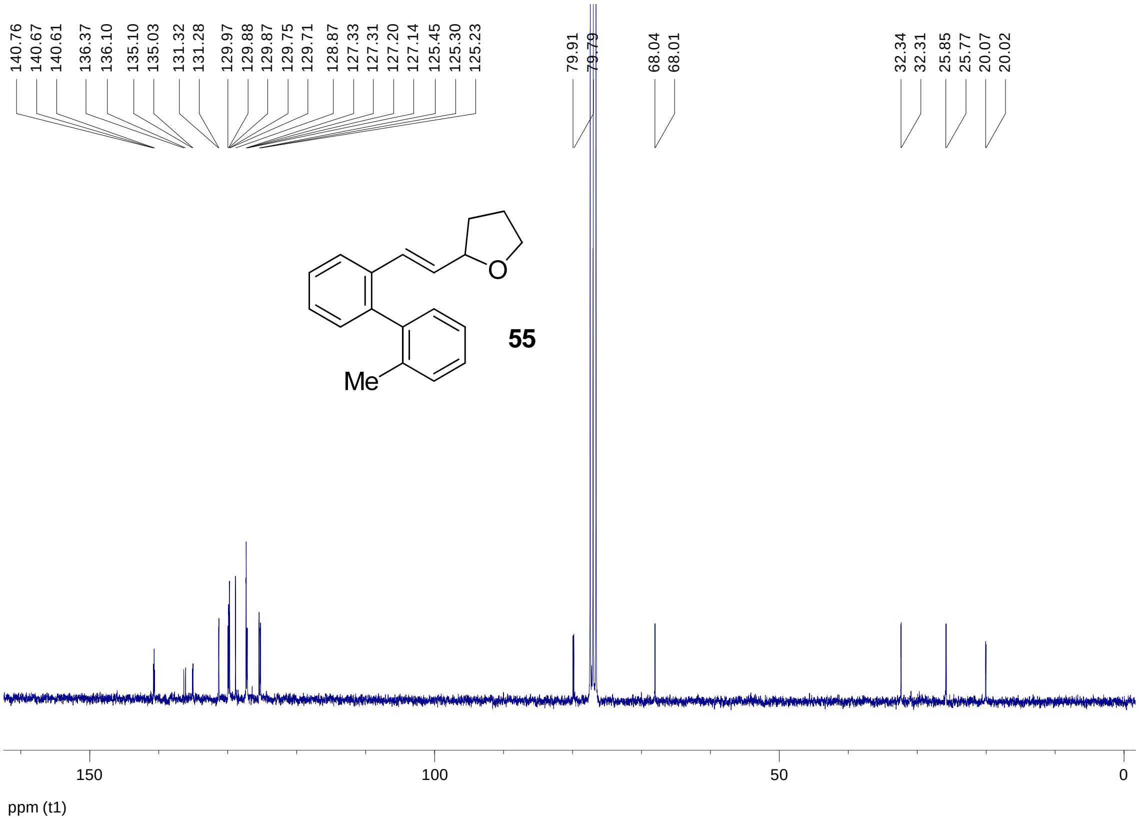

7.340
7.316
7.287
7.259
4.049
3.967
3.948
3.766
3.073
3.066
3.058
3.051
3.037
2.130
2.033
2.020
1.818
5.37
1.05
3.22
1.00
1.03
3.29
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

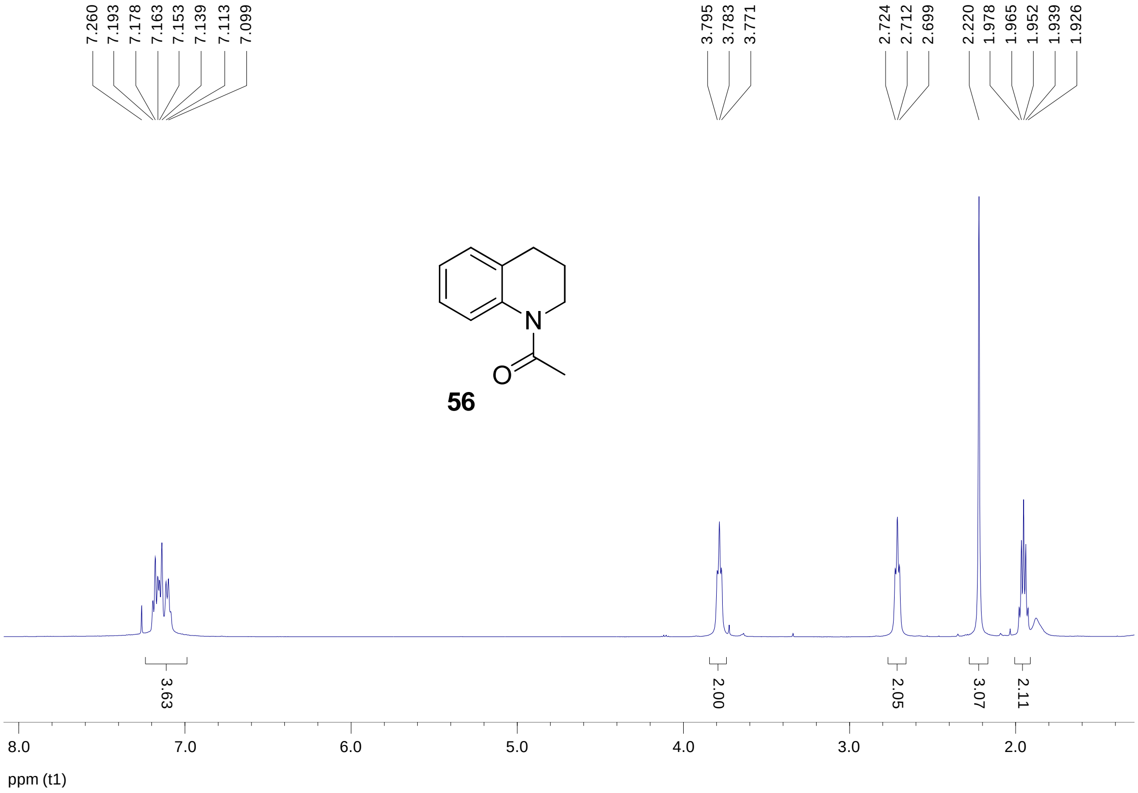
54

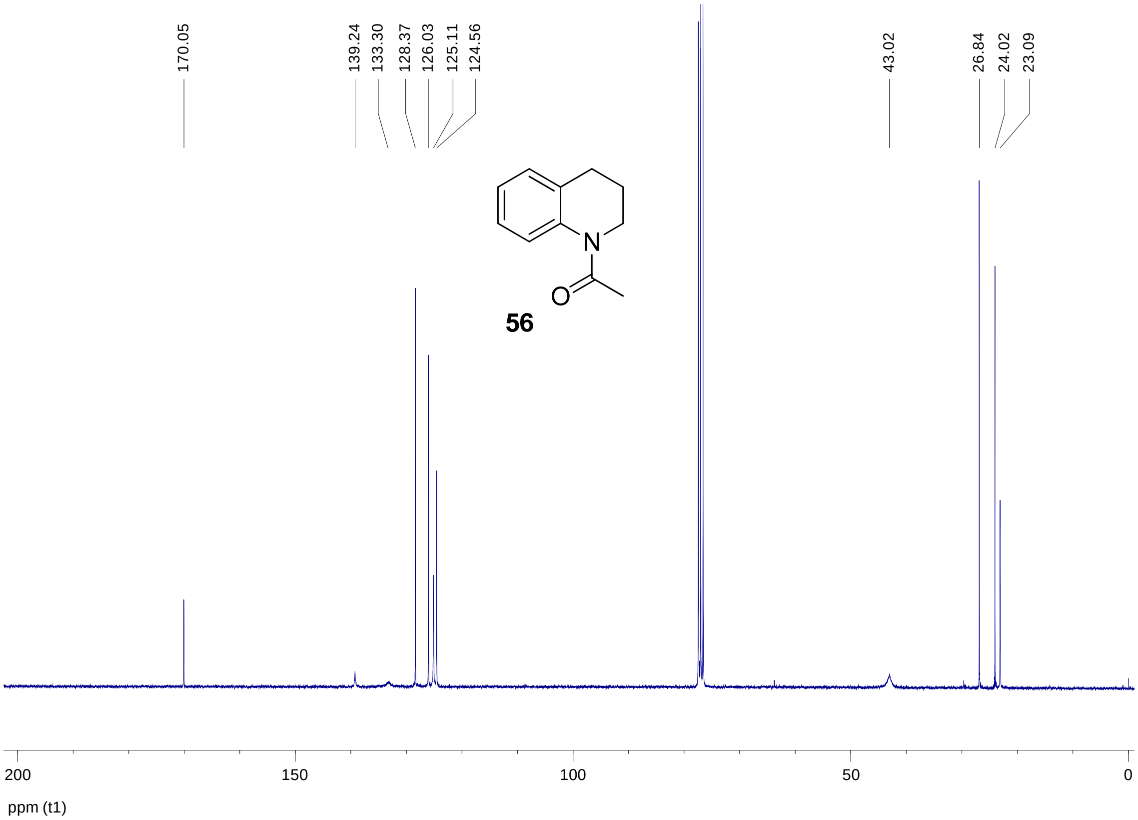

137.20
137.00
128.42
128.14
128.09
125.65
78.10
77.29
68.92
68.67
64.46
63.66
56.77
55.66
28.63
28.04
25.88
25.71
150
100
50
0
ppm (t1)

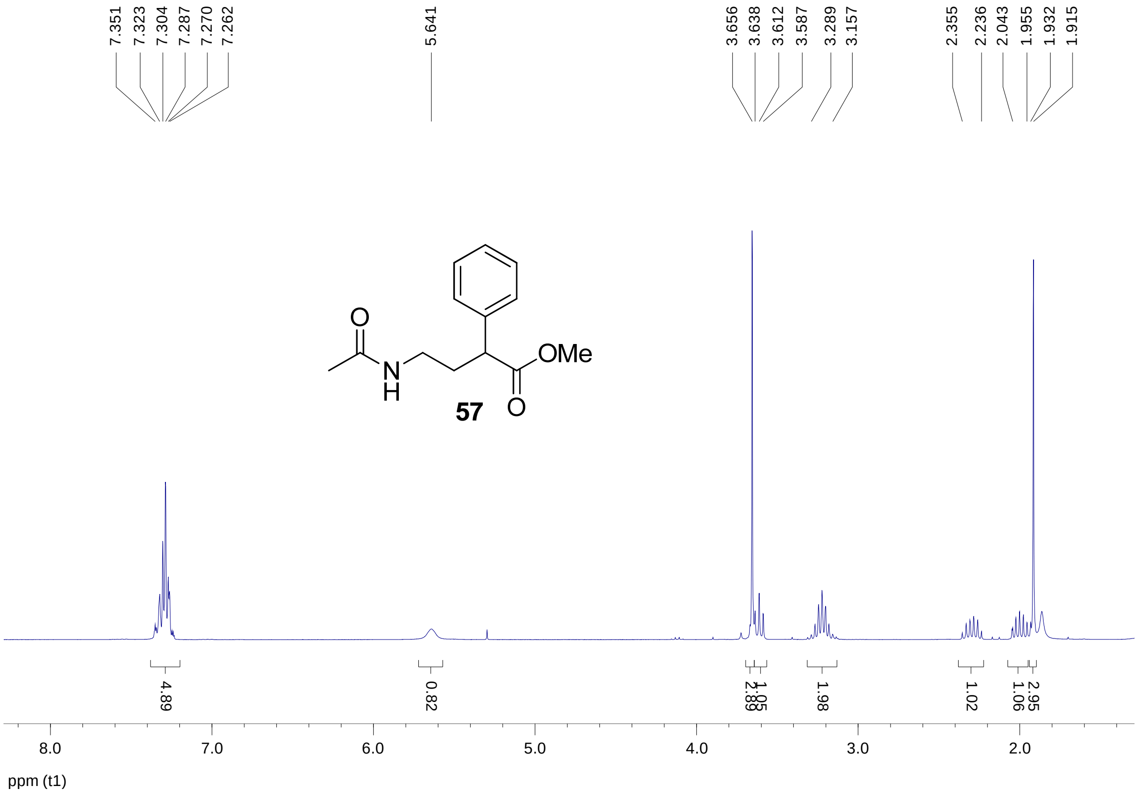
54

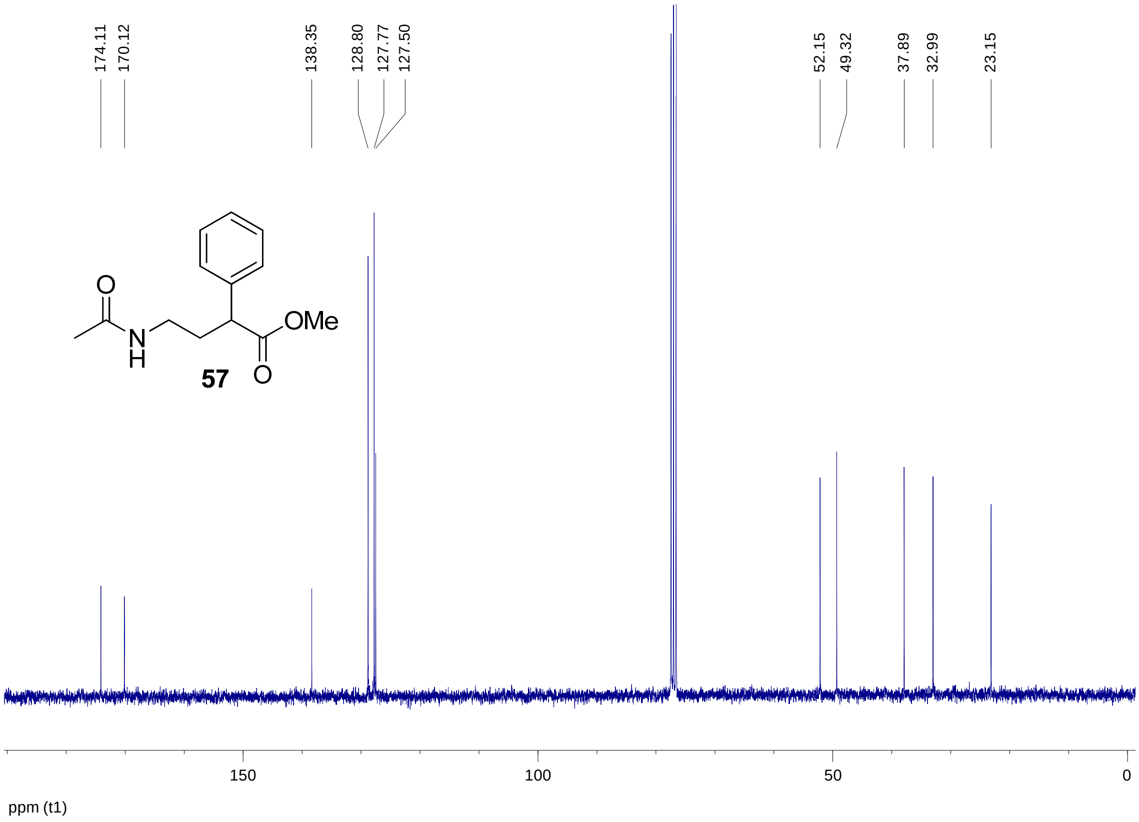

7.638
7.632
7.607
7.344
7.338
7.192
7.141
7.136
7.117
7.095
6.270
6.217
6.117
6.094
6.064
6.041
4.297
4.290
4.274
4.267
4.252
4.245
4.229
4.221
3.873
3.799
3.771
3.766
3.698
3.693
2.036
1.999
1.939
1.928
1.814
1.653
1.647
1.624
1.615
O
Me
55
0.98
5.40
1.86
0.97
0.95
0.95
1.00
1.00
3.15
1.13
1.80
0.91
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


140.76
140.67
140.61
136.37
136.10
135.10
135.03
131.32
131.28
129.97
129.88
129.87
129.75
129.71
128.87
127.33
127.31
127.20
127.14
125.45
125.30
125.23
79.91
79.79
68.04
68.01
32.34
32.31
25.85
25.77
20.07
20.02
O
Me
55
150
100
50
0
ppm (t1)

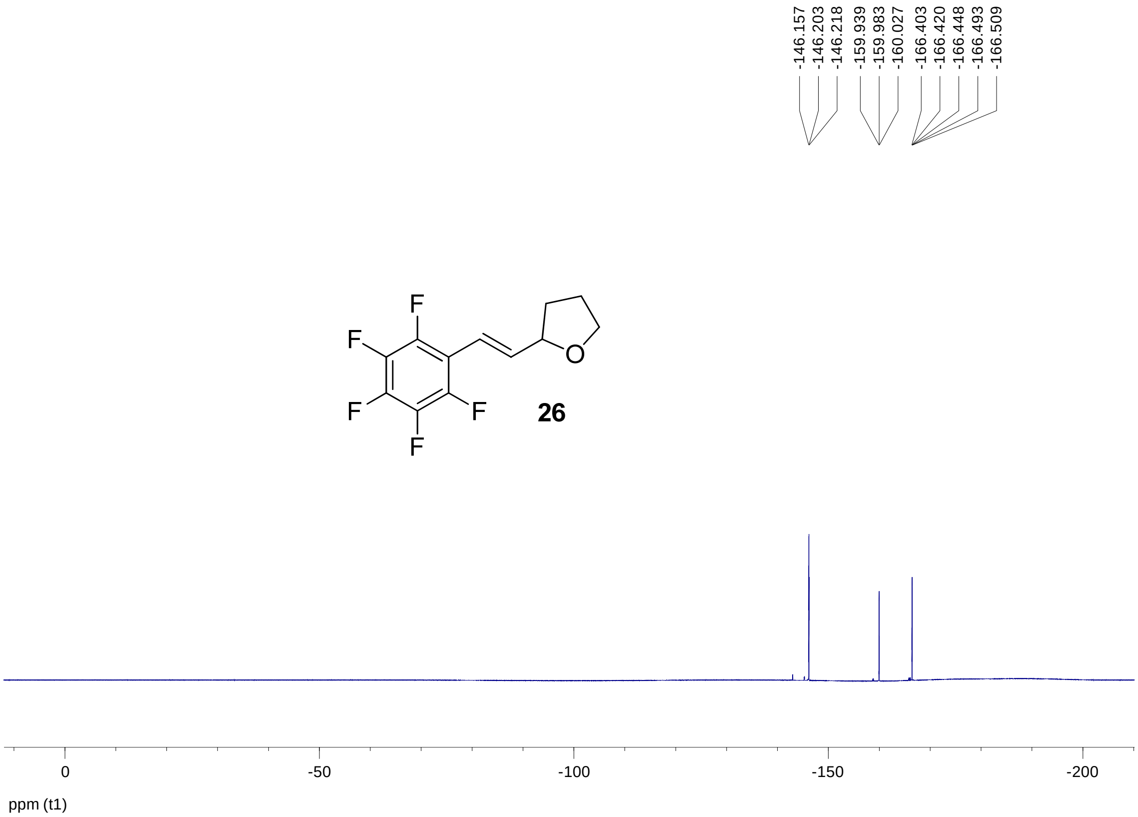

7.260
7.193
7.178
7.163
7.153
7.139
7.113
7.099
3.795
3.783
3.771
2.724
2.712
2.699
2.220
1.978
1.965
1.952
1.939
1.926
N
O
56
3.63
2.00
2.05
3.07
2.11
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


170.05
139.24
133.30
128.37
126.03
125.11
124.56
43.02
26.84
24.02
23.09
N
O
56
200
150
100
50
0
ppm (t1)


7.351
7.323
7.304
7.287
7.270
7.262
5.641
3.656
3.638
3.612
3.587
3.289
3.157
2.355
2.236
2.043
1.955
1.932
1.915
O
N
H
OMe
O
57
4.89
0.82
2.89
1.05
1.98
1.02
1.06
2.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


174.11
170.12
138.35
128.80
127.77
127.50
52.15
49.32
37.89
32.99
23.15
O
N
H
OMe
O
57
150
100
50
0
ppm (t1)

^{19}F NMR Spectrum



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