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Electronic Supplementary Information for

Zinc-Catalyzed Synthesis of 2-Alkenylfurans via Cross-Coupling of Enynones and Diazo Compounds

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General remarks.

All reactions were carried out under argon using standard Schlenck techniques. Dichloromethane and 1,2-dichloroethane were distilled from CaH_2 under nitrogen atmosphere. Solvents for column chromatography were obtained from commercial suppliers and used without further purification. TLC was performed on aluminum-backed plates coated with silica gel 60 with F254 indicator. Flash column chromatography was carried out on silica gel (230-240 mesh). ^{1}H-NMR (300, 400 MHz) and ^{13}C-NMR (75.5 and 100 MHz) spectra were recorded at room temperature in $CDCl_3$ on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts (δ) are given in ppm relative to TMS (^{1}H, 0.0 ppm) or $CDCl_3$ (^{13}C, 77.0 ppm). Carbon multiplicities were assigned by DEPT experiments. 2D-NMR experiments were recorded on a Bruker AVANCE-400 MHz. High-resolution mass spectra were recorded in an Agilent 6520Q-TOF and a Finnigan Mat95 spectrometers.

This study was carried out using enynes **1** and diazocompounds **5** (Figure S1). Enynes **1a-n**,[1] and diazoketone **5d**[2] were prepared according to literature procedures. Trifluoromethyl diazomethane **5e** was generated *in situ* as described in the literature.[3] Anhydrous zinc salts and the rest of the reagents were purchased of the best commercial grade available and used without further purification. All zinc salts were stored in Schlenk flask under an inert atmosphere of argon.

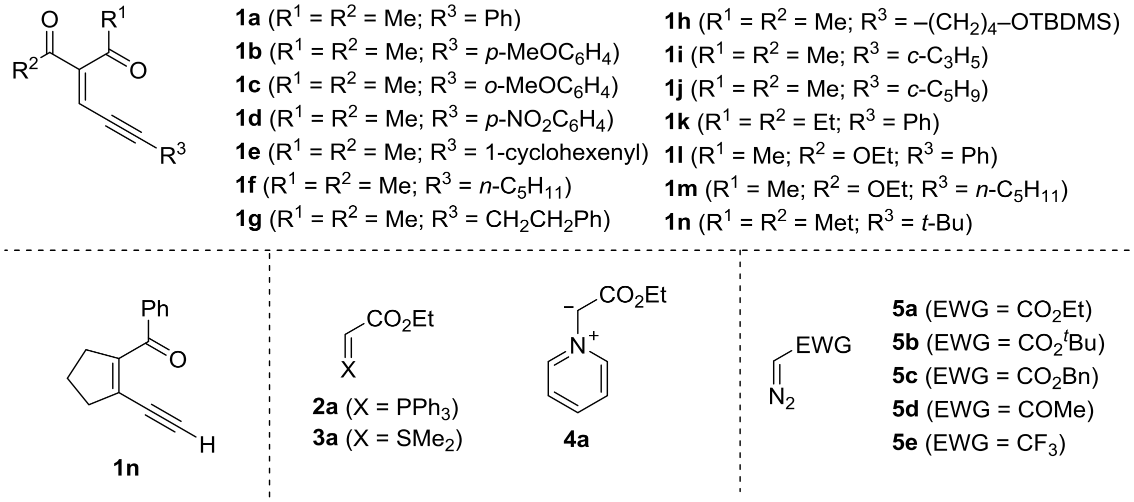

Figure S1. Starting materials used in this work.

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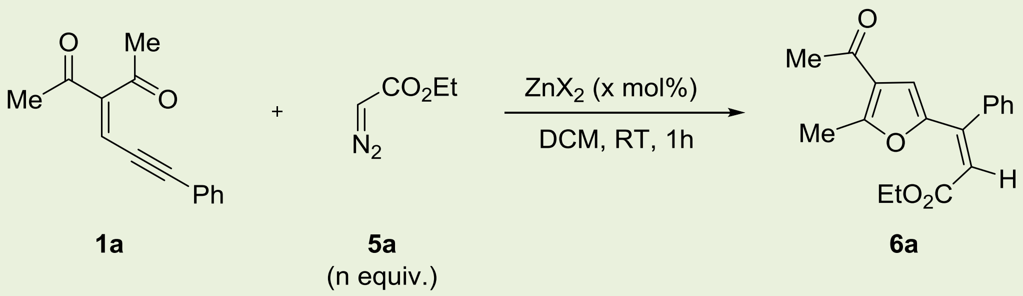
[1] Compounds **1a-m**: (a) G. Bartoli, M. Bosco, A. Carlone, R. Dalpozzo, P. Galzerano, P. Melchiorre, L. Sambri, *Tetrahedron Lett.* **2008**, *49*, 2555; (b) J. González, J. González, C. Pérez-Calleja, L. A. López, R. Vicente, *Angew. Chem. Int. Ed.* **2013**, *52*, 5853. Compound **1n**: (c) K. Miki, F. Nishino, K. Ohe and S. Uemura, *J. Am. Chem. Soc.* **2002**, *124*, 5260.

[2] M. Kitamura, N. Tashiro, T. Okauchi, *Synlett* **2009**, 2943.

[3] B. Morandi, E. M. Carreira, *Angew. Chem. Int. Ed.* **2011**, *50*, 9085.

Screening summary.

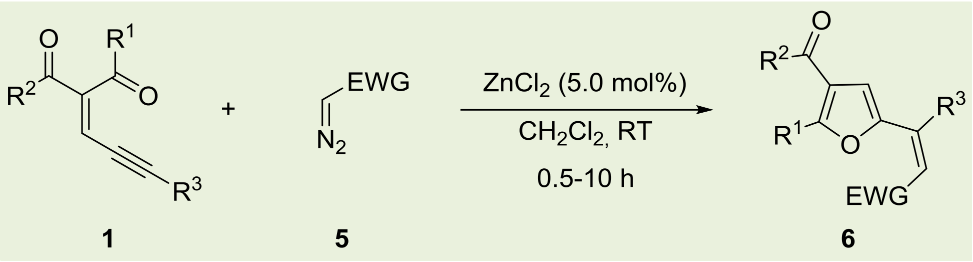


Entry	ZnX_2 (x mol%)	5a (n equiv.)	Yield 6a (*Z:E*)[a]
1	$ZnCl_2$ (10 mol%)	6.0	89 (8.5:1)
2	$ZnBr_2$ (10 mol%)	6.0	82 (6:1)
3	ZnI_2 (10 mol%)	6.0	53 (2:1)[b]
4	$Zn(OTf)_2$ (10 mol%)	6.0	n.r.
5	$ZnCl_2$ (10 mol%)	3.0	91 (8:1)
6	$ZnCl_2$ (10 mol%)	1.2	84 (7.5:1)
7	$ZnCl_2$ (5.0 mol%)	1.2	87 (6.5:1)
8	CuBr (5.0 mol%)[c]	1.2	43 (1.4:1)[b]
9	$[(IPrAu(NTf_2)]$[c] (5.0 mol%)	1.2	71 (1.7:1)[b]

[a] Isolated yield. *Z:E* ratio was determined by NMR analysis of the crude mixture and it was unaltered after purification by chromatography. [b] Estimated using CH_2Br_2 as internal standard. (n.r. = no reaction). (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). [c] 24 h.

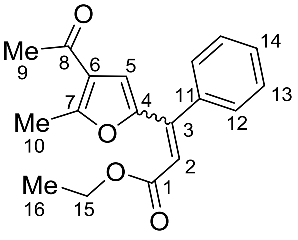
The use of lower reaction temperatures did not improve the *Z/E* selectivity but diminished yield and extended reaction times. Moreover, *Z/E* selectivity was not significantly affected during SiO_2-flash column chromatography purification.

Zinc-catalyzed synthesis of 2-alkenylfuran derivatives 6a-q.[4]



Representative procedure for zinc-catalyzed synthesis of compound 6a (Scheme 2).

To a solution of the enyne **1a** (42 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol, 1.2 equiv.) in CH_2Cl_2 (2.0 mL) was added $ZnCl_2$ (1.4 mg, 0.01 mmol, 5.0 mol%). The mixture was stirred at room temperature until disappearance of **1a** (checked by TLC; 1 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2, hexane:EtOAc = 10:1) to yield **6a** (52 mg, 87%; *Z*/*E* = 6.5:1) as a pale yellow oil. The same procedure was followed for the reaction at 10 mmol scale (**6a**, 2.56 g, 86%, *Z*/*E* = 5.8:1).



6a

Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-3-phenylacrylate (6a): **^{1}H-NMR** (300 MHz, $CDCl_3$, *Z-isomer*): 1.32 (t, *J* = 7.2 Hz, 3H, H_{16}), 2.41 (s, 3H, H_9), 2.62 (s, 3H, H_{10}), 4.25 (q, *J* = 7.2 Hz, 2H, H_{15}), 6.05 (s, 1H, H_2), 6.88 (s, 1H, H_5), 7.38-7.43 (m, 5H, H_{12-14}); (*E-isomer,* only clearly assignable signals are listed): 1.11 (t, *J* = 7.2 Hz, 3H, H_{16}), 2.31 (s, 3H, H_9), 2.67 (s, 3H, H_{10}), 4.04 (q, *J* = 7.2 Hz, 2H, H_{15}), 6.26 (s, 1H, H_2), 6.51 (s, 1H, H_5).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 14.6 (CH_3, C_{10}), 15.0 (CH_3, C_{16}), 29.5 (CH_3, C_9), 61.0 (CH_2, C_{15}), 115.3 (CH, C_5), 118.7 (CH, C_2), 123.3 (C, C_6), 128.9 (CH, C_{12}), 129.1 (CH, C_{13}), 129.9 (CH, C_{14}), 139.3 (C, C_{11}), 141.9 (C, C_3), 148.9 (C, C_4), 159.9 (C, C_7), 166.4 (C, C_1), 194.4 (C, C_8).

HR-MS (EI) calc. for $[C_{18}H_{18}O_4]^+$ 298.1205, found 298.1203.

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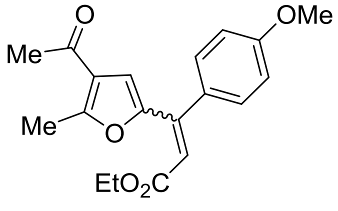
[4] The stereochemistry of compounds **6a-q** was established according to selective NOE or 2D-NOESY experiments. Selected experiments are showed in the NMR spectra section.



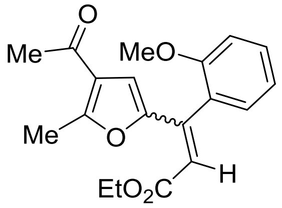
6b

Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-3-(4-methoxyphenyl)acrylate (6b): The representative procedure was followed using enyne **1b** (48 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6b** (46 mg, 70%; *Z*/*E* = 4.6:1) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$, *Z-isomer*): 1.28 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 3H), 2.61 (s, 3H), 3.84 (s, 3H), 4.21 (q, *J* = 7.2 Hz, 2H), 6.02 (s, 1H), 6.83 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H); (*E-isomer*): 1.15 (t, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 2.65 (s, 3H), 3.86 (s, 3H), 4.05 (q, J = 7.2 Hz, 2H), 6.30 (s, 1H), 6.46 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 14.2 (CH_3), 14.5 (CH_3), 29.1 (CH_3), 55.3 (CH_3), 60.4 (CH_2), 113.9 (CH), 114.6 (CH), 116.9 (CH), 122.8 (C), 130.2 (CH), 131.1 (C), 141.6 (C), 148.7 (C), 159.3 (C), 160.9 (C), 166.1 (C), 194.0 (C); (*E-isomer*): 14.1 (CH_3), 14.7 (CH_3), 55.2 (CH_3), 60.0 (CH_2), 113.3 (CH), 113.4 (CH), 114.8 (CH), 123.6 (C), 127.6 (C), 130.16 (CH), 143.5 (C), 151.8 (C), 159.8 (C), 160.4 (C), 165.9 (C), 193.6 (C) (a CH_3 signal is missing probably due to overlapping).

HR-MS (EI) calc. for $[C_{19}H_{20}O_5]^+$ 328.1311, found 328.1313.

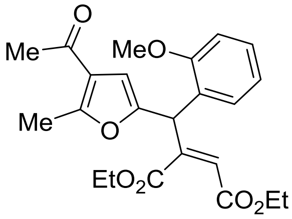


6c

Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-3-(2-methoxyphenyl)acrylate (6c): The representative procedure was followed using enyne **1c** (48 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6c** (36 mg, 55%, *Z*/*E* = 11:1, yellow oil) and compound **6c´**(9 mg, 11%, pale yellow solid, yield calculated with respect to **1c**).

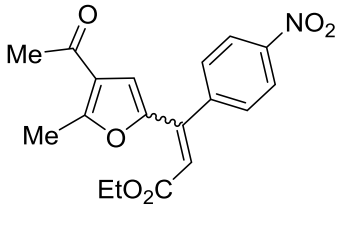
^{1}H-NMR (400 MHz, $CDCl_3$, *Z-isomer*): 1.32 (t, *J* = 8.0 Hz, 3H), 2.40 (s, 3H), 2.55 (s, 3H), 3.71 (s, 3H), 4.25 (q, *J* = 8.0 Hz, 2H), 5.91 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz 1H); (*E-isomer*, only clearly assignable signals are listed): 1.10 (t, *J* = 7.1 Hz, 3H), 2.30 (s, 3H), 2.65 (s, 3H), 3.77 (s, 3H), 4.03 (q, J = 7.1 Hz, 2H), 6.24 (s, 1H), 6.57 (s, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 14.3 (CH_3), 14.5 (CH_3), 29.1 (CH_3), 55.7 (CH_3), 60.5 (CH_2), 111.2 (CH), 114.5 (CH), 118.6 (CH), 120.5 (CH), 122.9 (C), 128.4 (C), 130.3 (CH), 130.6 (CH), 139.1 (C), 148.9 (C), 157.3 (C), 158.9 (C), 166.1 (C), 194.3 (C).
HR-MS (EI) calc. for $[C_{19}H_{20}O_5]^+$ 328.1311, found 328.1312.



6c´

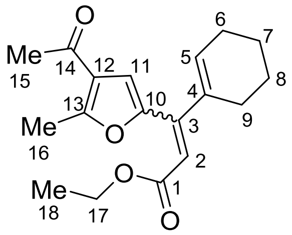
(*Z*)-Diethyl 2-((4-acetyl-5-methylfuran-2-yl)(2-methoxyphenyl)methyl)maleate (6c´): (Yellow solid, M. p. = 89-91 ºC).
^{1}H-NMR (400 MHz, $CDCl_3$): 1.24 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 2.59 (s, 3H), 3.84 (s, 3H), 4.16-4.22 (m, 4H), 5.44 (s, 1H), 5.63 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 7.26-7.34 (m, 2H), 7.41 (s, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$): 14.5 (CH_3), 14.6 (CH_3), 14.9 (CH_3), 29.5 (CH_3), 49.4 (CH), 56.0 (CH_3), 60.9 (CH_2), 61.7 (CH_2), 111.2 (CH), 114.6 (CH), 118.8 (CH), 121.2 (CH), 123.4 (C), 124.5 (C), 129.6 (CH), 129.7 (CH), 138.8 (C), 148.8 (C), 157.3 (C), 159.0 (C), 166.6 (C), 171.8 (C), 194.1 (C).
HR-MS (EI) calc. for $[C_{23}H_{26}O_7]^+$ 414.1679, found 414.1677.



6d

Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-3-(4-nitrophenyl)acrylate (6d): The representative procedure was followed using enyne **1d** (51 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 6 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6d** (56 mg, 81%, *Z*/*E* = 10:1) as a yellow solid (m. p. = 103-105 ºC).
^{1}H-NMR (300 MHz, $CDCl_3$, *Z-isomer*): 1.33 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 2.59 (s, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 6.06 (s, 1H), 7.07 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 8.27 (d, *J* = 8.7 Hz, 2H); *(E-isomer)*: 1.18 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 2.70 (s, 3H), 4.07 (q, *J* = 7.2 Hz, 2H), 6.21 (s, 1H), 6.59 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 8.34 (d, *J* = 8.7 Hz, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 14.2 (CH_3), 14.6 (CH_3), 29.1 (CH_3), 61.0 (CH_2), 116.0 (CH), 120.0 (CH), 123.1 (C), 123.7 (CH), 129.7 (CH), 139.3 (C), 145.4 (C), 147.2 (C), 148.3 (C), 160.0 (C), 165.4 (C), 193.7 (C).
HR-MS (EI) calc. for $[C_{18}H_{17}NO_6]^+$ 343.1056, found 343.1059.

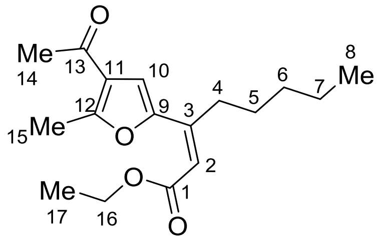


6e

Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-3-(cyclohex-1-en-1-yl)acrylate (6e): The representative procedure was followed using enyne **1e** (43 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded separately (*Z*)-**6e** (31 mg, 52%) and (*E*)-**6e** (7.0 mg, 11%) (63% combined yield, *Z:E* = 4.6:1) as pale yellow oils.

(*Z*-6e): ^{1}H-NMR (300 MHz, $CDCl_3$): 1.22 (t, *J* = 7.2 Hz, 3H, H_{18}), 1.62-1.77 (m, 4H, $H_{7\text{-}8}$), 2.21-2.23 (m, 4H, $H_{6,9}$), 2.44 (s, 3H, H_{15}), 2.63 (s, 3H, H_{16}), 4.12 (q, *J* = 7.2 Hz, 2H, H_{17}), 5.96 (s, 1H, H_2), 6.03 (br s, 1H, H_5), 6.65 (s, 1H, H_{11}).
^{13}C-NMR (100 MHz, $CDCl_3$): 14.2 (CH_3, C_{18}), 14.5 (CH_3, C_{16}), 21.8 (CH_2), 22.5 (CH_2), 26.3 (CH_2), 26.4 (CH_2), 29.1 (CH_3, C_{15}), 60.2 (CH_2, C_{17}), 111.8 (CH, C_{11}), 116.6 (CH, C_2), 122.5 (C, C_{12}), 134.7 (CH, C_5), 136.2 (C, C_4), 144.6 (C, C_3), 147.4 (C, C_{10}), 158.3 (C, C_{13}), 166.3 (C, C_1), 194.1 (C, C_{14}).
HR-MS (EI) calc. for $[C_{18}H_{22}O_4]^+$ 302.1518, found 302.1519.

(*E*-6e): ^{1}H-NMR (300 MHz, $CDCl_3$): 1.31 (t, *J* = 7.1 Hz, 3H, H_{18}), 1.72-1.81 (m, 4H, $H_{7\text{-}8}$), 2.18-2.22 (m, 4H, $H_{6,9}$), 2.43 (s, 3H, H_{15}), 2.64 (s, 3H, H_{16}), 4.19 (q, *J* = 7.1 Hz, 2H, H_{17}), 5.59-5.61 (m, 1H, H_5), 6.23 (s, 1H, H_2), 6.68 (s, 1H, H_{11}).
^{13}C-NMR (100 MHz, $CDCl_3$): 14.4 (CH_3, C_{18}), 14.8 (CH_3, C_{16}), 21.8 (CH_2), 22.8 (CH_2), 25.2 (CH_2), 28.7 (CH_2), 29.1 (CH_3, C_{15}), 59.9 (CH_2, C_{17}), 111.9 (CH, C_{11}), 113.4 (CH, C_2), 123.7 (C, C_{12}), 126.3 (CH, C_5), 134.1 (C, C_4), 146.5 (C, C_3), 151.2 (C, C_{13}), 160.4 (C, C_{13}), 165.9 (C, C_1), 193.7 (C, C_{14}).
HR-MS (EI) calc. for $[C_{18}H_{22}O_4]^+$ 302.1518, found 302.1521.



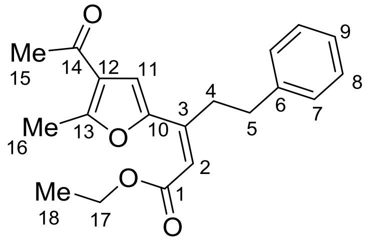
6f

(*Z*)-Ethyl 3-(4-acetyl-5-methylfuran-2-yl)oct-2-enoate (6f): The representative procedure was followed using enyne **1f** (41 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (32 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6f** (54 mg, 93%, *Z/E* > 20:1) as a colorless oil which solidifies upon standing (m. p. = 31-33 ºC).

^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (t, *J* = 7.2 Hz, 3H, H_8), 1.27-1.33 (m, 7H, $H_{6,7,17}$), 1.47-1.52 (m, 2H, H_5), 2.43 (s, 3H, H_{14}), 2.49 (t, *J* = 7.2 Hz, 2H, H_4), 2.60 (s, 3H, H_{15}), 4.18 (q, *J* = 7.2 Hz, 2H, H_{16}), 5.75 (s, 1H, H_2), 7.45 (s, 1H, H_{10}).

^{13}C-NMR (100 MHz, $CDCl_3$): 13.9 (CH_3, C_8), 14.3 (CH_3, C_{17}), 14.5 (CH_3, C_{15}), 22.4 (CH_2), 28.7 (CH_2), 29.1 (CH_3, C_{15}), 31.4 (CH_2, C_5), 36.3 (CH_2, C_4), 60.2 (CH_2, C_{16}), 114.6 (CH, C_{10}), 115.5 (CH, C_2), 122.9 (C, C_{11}), 143.1 (C, C_3), 148.8 (C, C_{12}), 158.6 (C, C_9), 166.2 (C, C_1), 194.3 (C, C_{13}).

HR-MS (EI) calc. for $[C_{17}H_{24}O_4]^+$ 292.1675, found 292.1676.



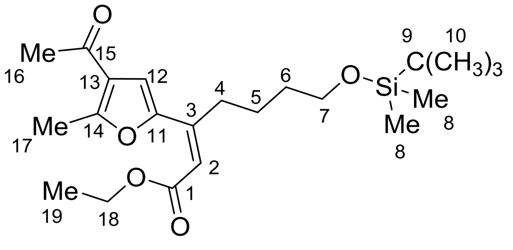
6g

Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-5-phenylpent-2-enoate (6g): The representative procedure was followed using enyne **1g** (48 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6g** (55 mg, 84%, *Z/E* = 19:1) as a white solid (m.p. = 95-97 ºC).

^{1}H-NMR (300 MHz, $CDCl_3$, *Z-isomer*): 1.32 (t, *J* = 7.1 Hz, 3H, H_{18}), 2.47 (s, 3H, H_{15}), 2.64 (s, 3H, H_{16}), 2.84 (s, 4H, H_{4-5}, accidental equivalence of the two methylene groups), 4.21 (q, *J* = 7.1 Hz, 2H, H_{17}), 5.78 (s, 1H, H_2), 7.19-7.25 (m, 3H), 7.29-7.34 (m, 2H), 7.55 (s, 1H, H_{11}); (*E-isomer*, only clearly assignable signals are listed): 6.37 (s, 1H, H_2), 6.74 (s, 1H, H_{11}).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 14.3 (CH_3, C_{18}), 14.5 (CH_3, C_{16}), 29.1 (CH_3, C_{15}), 35.6 (CH_2, C_4), 38.4 (CH_2, C_5), 60.3 (CH_2, C_{17}), 115.2 (CH, C_{11}), 115.9 (CH, C_2), 123.0 (C, C_{12}), 126.2 (CH, C_9), 128.4 (CH), 128.5 (CH), 140.9 (C, C_6), 142.0 (C, C_2), 148.5 (C, C_{10}), 158.8 (C, C_{13}), 166.0 (C, C_1), 194.2 (C, C_{14}).

HR-MS (EI) calc. for $[C_{20}H_{22}O_4]^+$ 326.1518, found 326.1520.



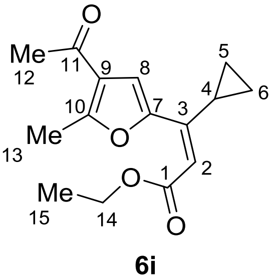
6h

(*Z*)-Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-7-((*tert*-butyldimethylsilyl)oxy)hept-2-enoate (*Z*-6h): The representative procedure was followed using enyne **1h** (64 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6h** (55 mg, 67%, %, *Z*/*E* > 20:1) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): 0.03 (s, 6H, H_8), 0.87 (s, 9H, H_{10}), 1.29 (t, *J* = 7.2 Hz, 3H, H_{19}), 1.56-1.57 (m, 4H, $H_{6\text{-}7}$), 2.43 (s, 3H, H_{16}), 2.53 (dd, *J* = 7.5, 6.9 Hz, 2H, H_5), 2.59 (s, 3H, H_{17}), 3.61 (t, *J* = 5.6 Hz, 2H, H_4), 4.18 (q, *J* = 7.2 Hz, 2H, H_{18}), 5.76 (s, 1H, H_2), 7.46 (s, 1H, H_{12}).

^{13}C-NMR (100 MHz, $CDCl_3$): -5.3 (CH, C_8), 14.2 (CH_3, C_{19}), 14.5 (CH_3, C_{16}), 18.3 (C, C_9), 25.4 (CH_2), 25.9 (CH_3, C_{10}), 29.1 (CH_3, C_{17}), 32.3 (CH_2, C_4), 36.1 (CH_2), 60.2 (CH_2, C_{18}), 62.7 (CH_2, C_7), 114.7 (CH, C_{12}), 115.7 (CH, C_2), 122.9 (C, C_{13}), 142.8 (C, C_3), 148.7 (C, C_{14}), 158.6 (C, C_{11}), 166.1 (C, C_1), 194.2 (C, C_{15}).

HR-MS (EI) calc. for $[C_{22}H_{36}O_5Si]^+$ 408.2332, found 408.2333.

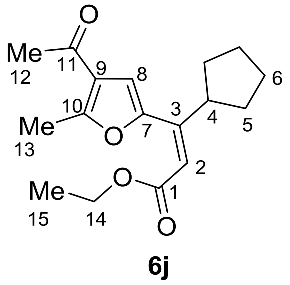


6i

(*Z*)-Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-3-cyclopropylacrylate (6i): The representative procedure was followed using enyne **1i** (35 mg, 0.2 mmol) and ethyl diazoacetate (**2a**) (27 mg, 0.24 mmol) at 0º C. After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6i** (40 mg, 76%, *Z*/*E* > 20:1) as a pale yellow oil. (*Note: A 5% of an unknown byproduct with identical mass (GC-MS analysis) was observed in the ^{1}H NMR spectra. Although the structure is unknown, we believe that this byproduct could arise from the nucleophilic attack of the diazocompound with a concomitant cyclopropane ring opening*).

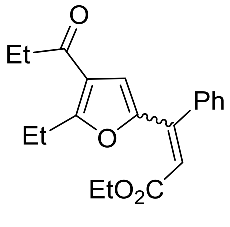
^{1}H-NMR (400 MHz, $CDCl_3$): 0.66-0.69 (m, 2H), 0.86-0.91 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H, H_{15}), 1.79-1.86 (m, 1H, H_4), 2.41 (s, 3H, H_{12}), 2.58 (s, 3H, H_{13}), 4.14 (q, *J* = 7.2 Hz, 2H, H_{14}), 5.59 (s, 1H, H_2), 7.25 (s, 1H, H_8).

^{13}C-NMR (100 MHz, $CDCl_3$): 7.4 (CH_2, $C_{5,6}$), 14.2 (CH_3, C_{15}), 14.5 (CH_3, C_{13}), 16.0 (CH, C_4), 29.1 (CH_3, C_{12}), 60.2 (CH_2, C_{14}), 113.2 (CH, C_8), 113.3 (CH, C_2), 122.7 (C, C_9), 143.5 (C, C_3), 149.2 (C, C_7), 158.7 (C, C_{10}), 166.5 (C, C_1), 194.1 (C, C_{11}).
HR-MS (EI) calc. for $[C_{15}H_{18}O_4]^+$ 262.1205, found 262.1205.



6j

(*Z*)-Ethyl 3-(4-acetyl-5-methylfuran-2-yl)-3-cyclopentylacrylate (*Z*-6j): The representative procedure was followed using enyne **1j** (41 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6j** (46 mg, 80%, *Z*/*E* > 20:1) as a colourless oil.
^{1}H-NMR (400 MHz, $CDCl_3$): 1.25 (t, *J* = 7.2 Hz, 3H, H_{15}), 1.46-1.51 (m, 2H), 1.61-1.75 (m, 4H), 1.90-1.93 (m, 2H), 2.41 (s, 3H, H_{12}), 2.58 (s, 3H, H_{13}), 2.99 (quint, *J* = 8.8 Hz, 1H, H_4), 4.15 (q, *J* = 7.2 Hz, 2H, H_{14}), 5.81 (s, 1H, H_2), 7.11 (s, 1H, H_8).
^{13}C-NMR (100 MHz, $CDCl_3$): 14.2 (CH_3, C_{15}), 14.5 (CH_3, C_{13}), 25.0 (CH_2, C_6), 29.1 (CH_3, C_{12}), 32.1 (CH_2, C_5), 45.0 (CH, C_4), 60.3 (CH_2, C_{14}), 112.8 (CH, C_8), 114.5 (CH, C_2), 122.6 (C, C_9), 146.0 (C, C_3), 149.2 (C, C_7), 158.3 (C, C_{10}), 166.7 (C, C_1), 194.1 (C, C_{11}).
HR-MS (EI) calc. for $[C_{17}H_{22}O_4]^+$ 290.1518, found 290.1519.



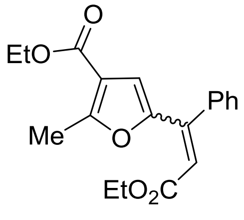
6k

Ethyl 3-(5-ethyl-4-propionylfuran-2-yl)-3-phenylacrylate (6k): The representative procedure was followed using enyne **1k** (48 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6k** (48 mg, 74%, *Z*/*E* = 5.8:1) as a colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$, *Z-isomer*): 1.14 (t, *J* = 7.3 Hz, 3H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 2.74 (q, *J* = 7.3 Hz, 2H), 3.04 (q, *J* = 7.5 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 6.02 (s, 1H), 6.89 (s, 1H), 7.37-7.42 (m, 5H); (*E-isomer,* only clearly assignable signals are listed): 1.07 (t, *J* =

7.3 Hz, 3H, overlapped signal), 1.10 (t, *J* = 7.2 Hz, 3H, overlapped signal), 2.60 (q, *J* = 7.3 Hz, 2H), 3.08 (q, *J* = 7.6 Hz, 2H, overlapped signal), 4.02 (q, *J* = 7.1 Hz, 2H), 6.24 (s, 1H), 6.49 (s, 1H), 7.26-7.29 (m, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 7.7 (CH_3), 11.9 (CH_3), 14.2 (CH_3), 21.9 (CH_2), 34.4 (CH_2), 60.5 (CH_2), 114.6 (CH), 117.9 (CH), 121.4 (C), 128.4 (CH), 128.7 (CH), 129.4 (CH), 139.0 (C), 141.5 (C), 148.4 (C), 164.3 (C), 166.0 (C), 196.9 (C); (*E-isomer,* only clearly assignable signals are listed): 7.6 (CH_3), 14.0 (CH_3), 22.0 (CH_2), 34.3 (CH_2), 60.0 (CH_2), 113.5 (CH), 128.0 (CH), 128.6 (CH), 143.1 (C), 143.8 (C), 151.4 (C).

HR-MS (EI) calc. for $[C_{20}H_{22}O_4]^+$ 326.1518, found 326.1522.



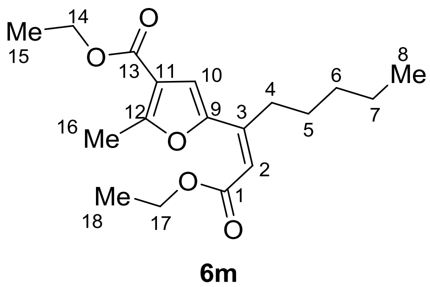
6l

Ethyl 3-(4-ethoxycarbonyl-5-methylfuran-2-yl)-3-phenylacrylate (6l): The representative procedure was followed using enyne **1l** (48 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6l** (54 mg, 83%, *Z/E* = 7.5:1) as a colorless oil. (*Note: a byproduct of unknown structure was detected in the ^{1}H NMR, estimated in ca. 3%*).

^{1}H-NMR (400 MHz, $CDCl_3$, *Z-isomer*): 1.29 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 2.60 (s, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 6.02 (s, 1H), 6.82 (s, 1H), 7.40-7.46 (m, 5H); (*E-isomer,* only clearly assignable signals are listed): 1.09 (t, *J* = 7.2 Hz, 3H), 2.64 (s, 3H), 4.02 (q, *J* = 7.2 Hz, 2H), 6.31 (s, 1H), 6.49 (s, 1H), 7.21-7.28 (bs, 5H).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 13.9 (CH_3), 14.2 (CH_3), 14.3 (CH_3), 60.2 (CH_2), 60.5 (CH_2), 115.1 (CH), 115.4 (C), 118.1 (CH), 128.4 (CH), 128.7 (CH), 129,4 (CH), 138.9 (C), 141.3 (C), 148.6 (C), 160.1 (C), 163.7 (C), 166.1 (C).

HR-MS (EI) calc. for $[C_{19}H_{20}O_5]^+$ 328.1311, found 328.1309.



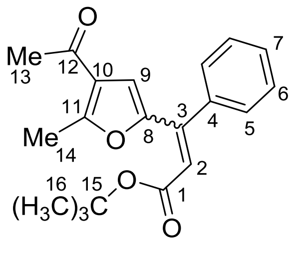
6m

Ethyl 3-(4-ethoxycarbonyl-5-methylfuran-2-yl)oct-2-enoate (6m): The representative procedure was followed using enyne **1m** (47 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6m** (41 mg, 63%, *Z*/*E* > 20:1) as a colorless oil. (*Note: a byproduct of unknown structure was detected in the* ^{1}*H NMR, estimated in ca. 3%*).

^{1}H-NMR (400 MHz, $CDCl_3$): 0.88-0.92 (m, 3H, H_8), 1.30-1.39 (m, 10H, $H_{6\text{-}7,15,18}$), 1.49-1.54 (m, 2H, H_5), 2.48 (dd, *J* = 7.8, 7.3 Hz, 2H, H_4), 2.60 (s, 3H, H_{16}), 4.21 (q, *J* = 7.1 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 5.75 (s, 1H, H_2), 7.28 (s, 1H, H_{10}).

^{13}C-NMR (100 MHz, $CDCl_3$): 13.9 (CH_3, C_8), 14.2 (CH_3), 14.4 (CH_3), 22.4 (CH_2), 28.6 (CH_2), 31.4 (CH_2), 36.1 (CH_2, C_4), 60.2 (CH_2, $C_{14,17}$), 114.1 (CH, C_{10}), 115.3 (C, C_{11}), 115.7 (CH, C_2), 142.2 (C, C_3), 149.0 (C, C_9), 159.3 (C, C_{12}), 163.8 (C), 166.4 (C) (a CH_3 signal is missing due to overlapping).

HR-MS (EI) calc. for $[C_{18}H_{26}O_5]^+$ 322.1780, found 322.1777.



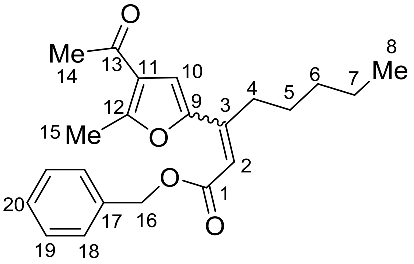
6n

***tert*-Butyl 3-(4-ethoxycarbonyl-5-methylfuran-2-yl)-3-phenylacrylate (6n):** The representative procedure was followed using enyne **1a** (42 mg, 0.2 mmol) and *tert*-butyl diazoacetate (**5b**) (34 mg, 0.24 mmol). After 5 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6n** (55 mg, 84%, *Z*/*E* = 17:1) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$, *Z-isomer*): 1.51 (s, 9H, H_{16}), 2.39 (s, 3H, H_{13}), 2.62 (s, 3H, H_{14}), 6.00 (s, 1H, H_2), 6.73 (s, 1H, H_9), 7.38 (bs, 5H); (*E-isomer,* only clearly assignable signals are listed): 1.25 (s, 9H, H_{16}), 2.29 (s, 3H, H_{13}), 2.65 (s, 3H, H_{14}), 6.19 (s, 1H, H_2), 6.43 (s, 1H, H_9).

^{13}C-NMR (100 MHz, $CDCl_3$): 14.6 (CH_3, C_{14}), 28.1 (CH_3, C_{16}), 29.1 (CH_3, C_{13}), 80.9 (C, C_{15}), 113.9 (CH, C_9), 120.6 (CH, C_2), 122.9 (C, C_{10}), 128.4 (CH), 128.6 (CH), 129.3 (CH, C_7), 139.0 (C, C_4), 139.8 (C, C_3), 148.9 (C, C_8), 159.2 (C, C_{11}), 165.4 (C, C_1), 193.9 (C, C_{12}); (*E-isomer,* only clearly assignable signals are listed): 27.8 (CH_3), 114.2 (CH), 116.2 (CH), 128.0 (CH), 128.8 (CH).

HR-MS (EI) calc. for $[C_{20}H_{22}O_4]^+$ 326.1518, found 326.1517.



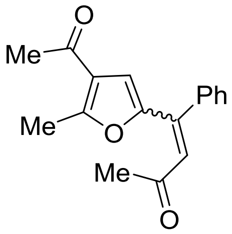
6o

Benzyl 3-(4-acetyl-5-methylfuran-2-yl)oct-2-enoate (6o): The representative procedure was followed using enyne **1f** (41 mg, 0.2 mmol) and benzyl diazoacetate (**5c**) (42 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6o** (55 mg, 77%, *Z/E* = 16:1) as a pale yellow oil which solidifies upon standing (m. p. = 30-32 ºC)

^{1}H-NMR (300 MHz, $CDCl_3$, *Z-isomer*): 0.89-0.93 (m, 3H, H_8), 1.33-1.36 (m, 4H, $H_{6,7}$), 1.50-1.56 (m, 2H, H_5), 2.43 (s, 3H, H_{14}), 2.53 (dd, *J* = 8.0 and 7.2 Hz, 2H, H_4), 2.58 (s, 3H, H_{15}), 5.20 (s, 2H, H_{16}), 5.84 (s, 1H, H_2), 7.35-7.39 (m, 5H), 7.51 (s, 1H, H_{10}); (*E-isomer*, only clearly assignable signals are listed): 2.45 (s, 3H, H_{14}), 2.63 (s, 3H, H_{15}), 2.92 (dd, *J* = 7.9 and 7.9 Hz, 2H, H_4), 6.40 (s, 1H, H_2), 6.86 (s, 1H, H_{10}).

^{13}C-NMR (75 MHz, $CDCl_3$): 13.9 (CH_3, C_8), 14.4 (CH_3, C_{15}), 22.4 (CH_2, C_6), 28.8 (CH_2, C_7), 29.1 (CH_3, C_{14}), 31.4 (CH_2, C_5), 36.4 (CH_2, C_4), 66.1 (CH_2, C_{16}), 115.0 (CH, C_{10}+C_2), 122.9 (C, C_{11}), 128.2 (CH), 128.6 (CH), 136.0 (C, C_{17}), 144.0 (C, C_3), 148.7 (C, C_9), 158.7 (C, C_{12}), 165.9 (C, C_1), 194.2 (C, C_{13}) (an aromatic CH signal is overlapped).

HR-MS (EI) calc. for $[C_{22}H_{26}O_4]^+$ 354.1831, found 354.2836.



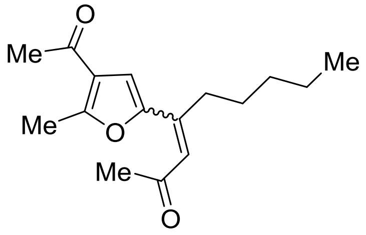
6p

4-(4-Acetyl-5-methylfuran-2-yl)-4-phenylbut-3-en-2-one (3p): The representative procedure was followed using enyne **1a** (42 mg, 0.2 mmol) and 1-diazopropan-2-one (**5d**) (20 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6p** (45 mg, 84%, *Z/E* = 4:1) as a pale yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$, *Z-isomer*): 2.27 (s, 3H), 2.41 (s, 3H), 2.61 (s, 3H), 6.26 (s, 1H), 6.92 (s, 1H), 7.38-7.43 (m, 5H); (*E-isomer*): 1.89 (s, 3H), 2.31 (s, 3H), 2.67 (s, 3H), 6.28 (s, 1H), 6.75 (s, 1H), 7.29-7.33 (m, 2H), 7.43-7.47 (m, 3H, overlapped signal).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 14.9 (CH_3), 29.5 (CH_3), 31.0 (CH_3), 115.7 (CH), 123.5 (C), 127.5 (CH), 128.9 (CH), 129.2 (CH), 129.9 (CH), 139.4 (C), 139.6 (C), 149.1 (C), 160.3 (C), 194.2 (C), 199.5 (C); (*E-isomer*, only clearly assignable signals are listed): 15.1 (CH_3), 31.1 (CH_3), 115.9 (CH), 123.5 (CH), 129.4 (CH).

HR-MS (EI) calc. for $[C_{17}H_{16}O_3]^+$ 268.1099, found 268.1103.



6q

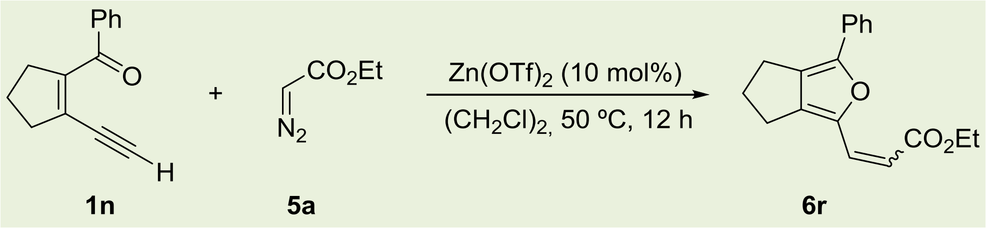
4-(4-Acetyl-5-methylfuran-2-yl)-non-3-en-2-one (6q): The representative procedure was followed using enyne **1f** (41 mg, 0.2 mmol) and 1-diazopropan-2-one (**5d**) (20 mg, 0.24 mmol). After 1 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6q** (47 mg, 89%, *Z*/*E* = 7.4:1) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$, *Z-isomer*): 0.85-0.88 (m, 3H), 1.28-1.34 (m, 4H) 1.47-1.51 (m, 2H), 2.21 (s, 3H), 2.41 (s, 3H), 2.46 (dd, *J* = 8.0, 7.4 Hz, 2H), 2.57 (s, 3H), 6.02 (s, 1H), 7.55 (s, 1H); (*E-isomer,* only clearly assignable signals are listed): 2.26 (s,3H), 2.61 (s, 3H), 2.79 (dd, *J* = 8.0, 7.8 HZ, 2H), 6.66 (s, 1H), 6.85 (s, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$, *Z-isomer*): 13.9 (CH_3), 14.5 (CH_3), 22.3 (CH_2), 28.9 (CH_2), 29.0 (CH_3), 31.1 (CH_3), 31.4 (CH_2), 36.3 (CH_2), 114.9 (CH), 122.9 (C), 124.3 (CH), 140.7 (C), 149.2 (C), 159.1 (C), 194.2 (C), 198.6 (C); (*E-isomer*, only clearly assignable signals are listed): 14.0 (CH_3), 14.7 (CH_3), 22.4 (CH_2), 28.7, 29.8, 32.1, 32.4 (CH_2), 112.2 (CH), 118.9 (CH), 193.4 (C).

HR-MS (EI) calc. for $[C_{16}H_{22}O_3]^+$ 262.1569, found 262.1566.

Zinc-catalyzed synthesis of 2-alkenylfuran derivative 6r (Scheme 3).



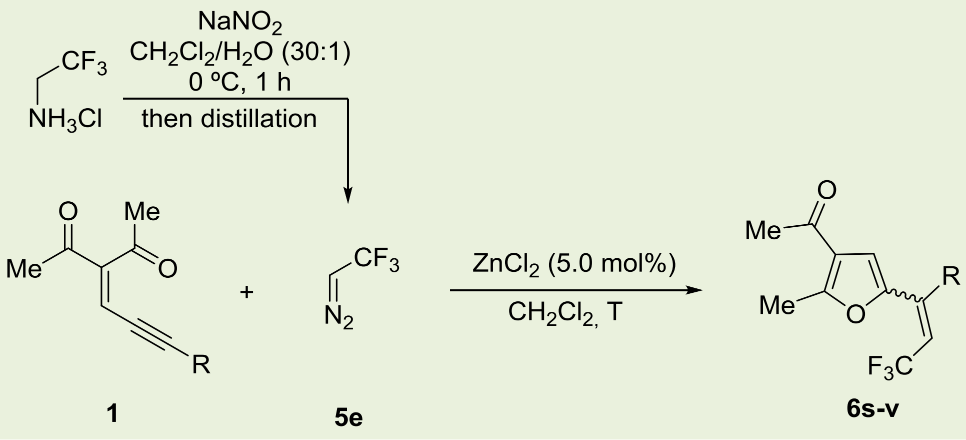
To a solution of the enyne **1n** (39 mg, 0.2 mmol) and ethyl diazoacetate (**5a**) (27 mg, 0.24 mmol) in $(CH_2Cl)_2$ (2 mL) was added $Zn(OTf)_2$ (7.3 mg, 0.02 mmol, 10 mol%). The mixture was stirred at 50 ºC until disappearance of **1n** (checked by TLC; 12 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO_2, hexane:EtOAc = 10:1) to yield **6r** (28 mg, 49%; *Z*/*E* = 1.2:1) as a pale yellow oil.

Ethyl 3-(3-phenyl-5,6-dihydro-4*H*-cyclopenta[*c*]furan-1-yl)acrylate (6r): ^{1}H-NMR (300 MHz, $CDCl_3$, only clearly distinguishable signals are assigned for*Z/E* isomers): 1.29-1.39 (m, 6H, *Z+E*), 2.42-2.54 (m, 4H, *Z+E*), 2.65-2.80 (m, 4H, *Z+E*), 2.84-2.91 (m, 4H, *Z+E*), 4.23-4.34 (m, 4H, *Z+E*), 5.71 (d, *J* = 12.6 Hz, 1H, *Z*), 5.71 (d, *J* = 15.6 Hz, 1H, *E*), 5.71 (d, *J* = 12.6 Hz, 1H, *Z*), 7.21-7.30 (m, 2H, *Z+E*), 7.35-7.47 (m, 5H, *Z+E*), 7.62-7.68 (m, 4H, *Z+E*).

^{13}C-NMR (75 MHz, $CDCl_3$): 14.36 (CH_3), 14.40 (CH_3), 24.1 (CH_2), 25.3 (CH_2), 25.4 (CH_2), 31.8 (CH_2), 60.3 (CH_2), 113.5 (CH), 113.6 (CH), 124.4 (CH), 127.11 (CH), 127.14 (CH), 127.4 (CH), 128.67 (CH), 128.74 (CH), 130.5 (CH), 130.6 (C), 130.9 (C), 131.5 (C), 132.0 (C), 140.3 (C), 140.9 (C), 141.3 (C), 141.5 (C), 145.4 (C), 145.8 (C), 166.4 (C), 167.6 (C) (missing signals are probably overlapped).

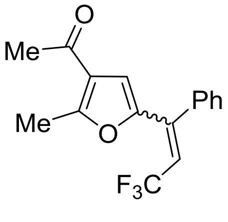
HR-MS (EI) calc. for $[C_{18}H_{18}O_3]^+$ 282.1256, found 282.1260.

Zinc-catalyzed synthesis of trifluoromethyl substituted 2-alkenylfuran derivatives 6s-v.[5]



Representative procedure for zinc-catalyzed synthesis of compound 6s (Scheme 4).

A solution of NaNO$_2$ (331 mg, 4.8 mmol, 24 equiv.) and trifluoroethylamine hydrochloride (542 mg, 4.0 mmol, 20 equiv.) in CH$_2$Cl$_2$/H$_2$O (30:1, 10 mL) was stirred at 0 °C during 1 h. The resulting yellow solution was carefully distilled by a steam of Ar and collected in a precooled Schlenk flask (-78 ºC). To this solution were added the enyne **1a** (42 mg, 0.2 mmol) and ZnCl$_2$ (27 mg, 0.2 mmol, 1.0 equiv) at room temperature and the flask was closed with a teflon-tape-wrapped glass stopper. The mixture was stirred until disappearance of **1a** (checked by TLC, 48 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (SiO$_2$, hexane:EtOAc = 10:1) to yield **6s** (48 mg, 81%; *Z*/*E* = 4:1) as a pale yellow oil.



6s

1-(4-Acetyl-5-methylfuran-2-yl)-3,3,3-trifluoro-1-phenylprop-1-ene (6s): **^{1}H-NMR** (300 MHz, CDCl$_3$, *Z-isomer*): 2.40 (s, 3H), 2.67 (s, 3H), 5.77 (q, *J* = 9.0 Hz, 1H), 6.65 (s, 1H), 7.31-7.50 (m, 5H, overlapped with signals from the *E-isomer*); (*E-isomer*, only clearly assignable signals are listed): 2.32 (s, 3H), 2.68 (s, 3H), 6.34 (q, *J* = 8.3 Hz, 1H), 6.38 (s, 1H).

^{13}C-NMR (75 MHz, CDCl$_3$, *Z-isomer*): 14.9 (CH$_3$), 29.5 (CH$_3$), 115.8 (q, *J* = 36.4 Hz, CH), 116.0 (CH), 123.4 (C), 123.8 (q, *J* = 270.3 Hz, C), 128.6 (CH), 129.0 (CH), 130.0 (CH), 138.6 (C), 140.4 (q, *J* = 6.0 Hz, C), 147.8 (C), 160.9 (C), 194.0 (C); (*E-isomer,* only clearly assignable signals are listed) 112.6 (q, *J* = 34.4 Hz, CH), 114.6 (CH), 121.9 (C), 123.7 (q, *J* = 269.9 Hz, C), 123.9 (C), 129.2 (CH), 129.3 (CH), 134.2 (C), 140.0 (q, *J* = 5.7 Hz, C), 150.8 (C), 160.7 (C), 193.9 (C).

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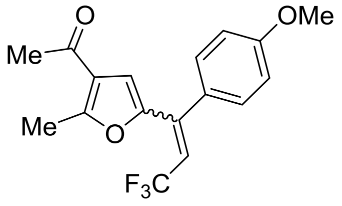
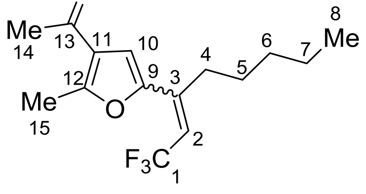
[5] The stereochemistry of compounds **6s-v** was established according to selective NOE or 2D-NOESY experiments. Selected experiments are showed in the NMR spectra section.

^{19}F-NMR (282 MHz, $CDCl_3$): -57.0 (s, *Z-isomer*), -55.3 (s, *E-isomer*).
HR-MS (EI) calc. for $[C_{16}H_{13}F_3O_2]^+$ 294.0868, found 294.0871.



6t

1-(4-Acetyl-5-methylfuran-2-yl)-3,3,3-trifluoro-1-(4-methoxypheyl)prop-1-ene (6t): The representative procedure was followed using enyne **1b** (48 mg, 0.2 mmol) and $ZnCl_2$ (27 mg, 0.2 mmol, 1.0 equiv) at 0 ºC. After 10 h, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6t** (52 mg, 80%, *Z/E* = 3:1) as a colorless oil.
^{1}H-NMR (300 MHz, $CDCl_3$, *Z-isomer*): 2.41 (s, 3H), 2.66 (s, 3H), 3.87 (s, 3H), 5.74 (q, *J* = 8.9 Hz, 1H), 6.67 (s, 1H), 6.94 (d, *J* = 8.7 Hz, 2H, signal overlapped with the corresponding from *E-isomer*), 7.32 (d, *J* = 8.7 Hz, 2H, signal overlapped with the corresponding from *E-isomer*); (*E-isomer,* only clearly assignable signals are listed): 2.33 (s, 3H), 2.68 (s, 3H), 3.88 (s, 3H), 6.25 (s, 1H), 6.29 (q, *J* = 8.4 Hz, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$, only clearly distinguishable signals are assigned for *Z/E isomers*): 14.54 (CH_3, *Z-isomer*), 14.60 (CH_3, *E-isomer*), 29.1 (CH_3, signal from both isomers overlapping), 55.3 (CH_3, *E-isomer*), 55.4 (CH_3, *Z-isomer*), 111.97 (q, *J* = 34.1 Hz, CH, *E-isomer*), 113.6 (CH), 113.98 (CH, *Z-isomer*, signal overlapped), 114.04 (q, *J* = 36.2 Hz, CH, *Z-isomer*), 115.3 (CH), 122.8 (q, *J* = 270.1 Hz, C, *Z-isomer*), 122.9 (C, *Z-isomer*), 123.42 (q, *J* = 269.8 Hz, C, *E*-isomer), 123.46 (C, *E-isomer*), 130.0 (CH, *Z-isomer*), 130.2 (CH), 130.4 (C, *Z-isomer*), 139.36 (d, *J* = 6.0 Hz, C, signal overlapping with the corresponding of the *Z-isomer*), 139.55 (q, *J* = 6.1 Hz, C, signal overlapping with the corresponding of the *E-isomer*), 147.6 (C, *Z-isomer*), 150.5 (C, *E-isomer*), 160.1 (C, *E-isomer*), 160.2 (C, *E-isomer*), 160.4 (C, *Z-isomer*), 160.9 (C, *Z-isomer*), 193.6 (C, *E-isomer*), 193.7 (C, *Z-isomer*).
^{19}F-NMR (282 MHz, $CDCl_3$): -56.6 (s, *Z-isomer*), -55.1 (s, *E-isomer*).
HR-MS (EI) calc. for $[C_{17}H_{15}F_3O_3]^+$ 324.0973, found 324.0975.



6u

3-(4-Acetyl-5-methylfuran-2-yl)-1,1,1-trifluorooct-2-ene (6u): The representative procedure was followed using enyne **1f** (41 mg, 0.2 mmol) and $ZnCl_2$ (5.5 mg, 0.04 mmol, 20 mol%). After

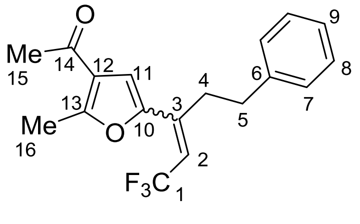
4 days, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6u** (37 mg, 65%, *Z*/*E* = 16:1) as a colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$, *Z-isomer*): 0.84-0.95 (m, 3H, H_8), 1.27-1.41 (m, 4H, $H_{5,7}$), 1.47-1.57 (m, 2H, H_5), 2.37-2.49 (m, 2H, overlapped signal, H_4), 2.44 (s, 3H, overlapped signal, H_{14}), 2.64 (s, 3H, H_{15}), 5.54 (q, *J* = 9.1 Hz, 1H, H_2), 6.85 (s, 1H, H_{10}); (*E-isomer,* only clearly assignable signals are listed): 6.10 (q, *J* = 8.9 Hz, 1H, H_2), 6.75 (s, 1H, H_{10}).

^{13}C-NMR (75 MHz, $CDCl_3$, *Z-isomer*): 13.9 (CH_3, C_8), 14.5 (CH_3, C_{15}), 22.3 (CH_2, C_7), 28.38 (q, *J* = 0.9 Hz, CH_2, C_4), 29.0 (CH_3, C_{14}), 31.2 (CH_2, C_6), 35.5 (CH_2, C_5), 112.6 (q, *J* = 2.7 Hz, CH, C_{10}), 113.7 (q, *J* = 36.3 Hz, CH, C_2), 122.8 (q, *J* = 270.1 Hz, C, C_1), 123.0 (C, C_{11}), 139.9 (q, *J* = 6.1 Hz, C, C_3), 147.4 (q, *J* = 1.3 Hz, C, C_9), 159.4 (C, C_{12}), 193.6 (C, C_{13}).

^{19}F-NMR (282 MHz, $CDCl_3$): -57.2 (s, *Z-isomer*), -56.1 (s, *E-isomer*).

HR-MS (EI) calc. for $[C_{15}H_{19}F_3O_2]^+$ 288.1337, found 288.1340.



6v

3-(4-Acetyl-5-methylfuran-2-yl)-5-phenyl-1,1,1-trifluoropent-2-ene (6v): The representative procedure was followed using enyne **1g** (48 mg, 0.2 mmol) and $ZnCl_2$ (5.5 mg, 0.04 mmol, 20 mol%). After 4 days, purification by flash chromatography (SiO_2, hexane:EtOAc = 10:1) yielded **6v** (31 mg, 48%, *Z*/*E* = 19:1) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$, *Z-isomer*): 2.44 (s, 3H, H_{15}), 2.64 (s, 3H, H_{16}), 2.73-2.80 (m, 2H), 2.81-2.88 (m, 2H), 5.48 (q, *J* = 9.0 Hz, 1H, H_2), 6.87 (s, 1H, H_{11}), 7.17 (d, *J* = 7.1 Hz, 2H), 7.21-7.25 (m, 1H, H_9), 7.30-7.33 (m, 2H); (*E-isomer,* only clearly assignable signals are listed): 6.17 (q, *J* = 8.9 Hz, 1H, H_2), 6.71 (s, 1H, H_{11}).

^{13}C-NMR (75 MHz, $CDCl_3$, *Z-isomer*): 14.6 (CH_3, C_{16}), 29.1 (CH_3, C_{15}), 35.1 (q, *J* = 1.2 Hz, CH_2, C_4), 37.4 (CH_2, C_5), 112.9 (q, *J* = 2.8 Hz, CH, C_{11}), 114.2 (q, *J* = 36.4 Hz, CH, C_2), 122.6 (q, *J* = 270.3 Hz, C, C_1), 123.0 (C, C_{12}), 126.4 (CH), 128.4 (CH, C_9), 128.5 (CH), 138.7 (q, *J* = 6.1 Hz, C), 140.3 (C, C_{10}), 147.1 (q, *J* = 1.3 Hz, C, C_3), 159.6 (C, C_{13}), 193.7 (C, C_{14}).

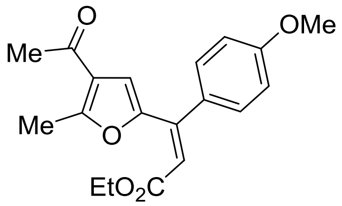
^{19}F-NMR (282 MHz, $CDCl_3$): -57.5 (s, *Z-isomer*), -56.3 (s, *E-isomer*).

HR-MS (EI) calc. for $[C_{18}H_{17}F_3O_2]^+$ 322.1181, found 322.1186.

Calculated relative stabilities of 2-alkenylfurans 6.

To gain insights into the origin of the *Z/E* selectivity in the formation of 2-alkenylfurans **6**, the geometry of *Z/E*-isomer from two representative alkenylfuran derivatives were fully optimized at the B3LYP/6-31G* level of theory, and each stationary point was shown to be a minimum by performing the calculation of the harmonic vibrational frequencies (Total energy (HF) and Free energy (G, at 298.150 K and 1.0 Atm) are in Hartrees).

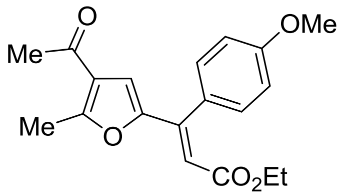
The computational study indicates that for both compounds (bearing an aryl or an alkyl substituents) *E*-isomer is thermodynamically more stable. According to the selectivity observed, which is in favour of *Z*-isomers, the stereochemical outcome is likely dependent on kinetic control.



(*Z*)-6b

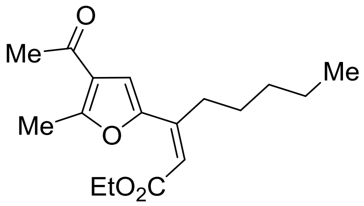
G=-1111.870297 au

$\Delta G = +1.4$ **kcal mol^{-1}**



(*E*)-6b

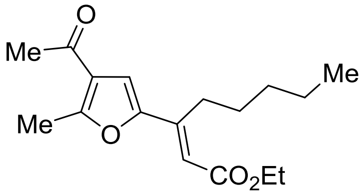
GP-1111.872532 au



(*Z*)-6f

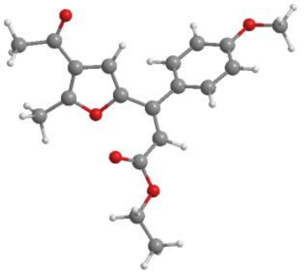
G=-962.832644 au

$\Delta G = +7.2$ **kcal mol^{-1}**



(*E*)-6f

G=-962.844062 au



(*Z*)-6b

O	-1.8373	-1.7321	-0.1484
C	-2.5242	-2.8853	-0.2964
C	-1.7685	-3.7850	-1.0286
C	-0.5423	-3.1102	-1.3330
C	-0.6281	-1.8557	-0.7985
C	-3.8663	-2.9093	0.3559
H	0.2751	-3.5250	-1.9035
C	0.2817	-0.7158	-0.8036
C	-0.1244	0.5839	-0.8393
C	-2.0581	-5.1701	-1.4533
H	0.6171	1.3584	-0.6747
C	-1.4723	1.0901	-1.1577
C	-3.4015	-5.7909	-1.1070
O	-1.2203	-5.8053	-2.0798
H	-3.9202	-3.6564	1.1567
H	-4.6595	-3.1396	-0.3633
H	-4.0708	-1.9260	0.7858
H	-4.2247	-5.2213	-1.5553
H	-3.5664	-5.8035	-0.0230
H	-3.4223	-6.8137	-1.4878
O	-2.3998	0.4860	-1.6627
O	-1.5372	2.4181	-0.8559
C	-2.7816	3.0694	-1.1759
C	-2.6484	4.5292	-0.7821
H	-3.5942	2.5720	-0.6351
H	-2.9823	2.9498	-2.2461
H	-3.5778	5.0636	-1.0080
H	-1.8324	5.0095	-1.3318
H	-2.4454	4.6281	0.2893
C	1.7326	-1.0285	-0.7491
C	2.6583	-0.2543	-1.4652
C	4.0279	-0.5079	-1.4095
C	4.5051	-1.5624	-0.6201
C	3.5946	-2.3527	0.0985
C	2.2351	-2.0921	0.0280
H	2.2975	0.5472	-2.1029
H	4.7053	0.1060	-1.9918
O	5.8163	-1.9042	-0.4914
H	3.9804	-3.1649	0.7065
H	1.5475	-2.7100	0.5962
C	6.7858	-1.1448	-1.1986
H	6.7758	-0.0914	-0.8901
H	6.6313	-1.2058	-2.2837
H	7.7516	-1.5858	-0.9465

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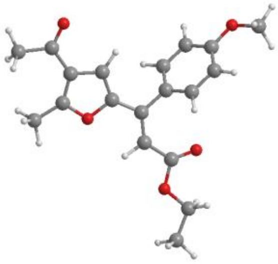
G= -1111.870297



(*E*)-6b

O	-1.8024	0.4675	0.0870
C	-3.1188	0.1493	0.0265
C	-3.2565	-1.2168	-0.1300
C	-1.9259	-1.7481	-0.1664
C	-1.0626	-0.6968	-0.0307
C	-4.0548	1.3063	0.1429
H	-1.6741	-2.7896	-0.2920
C	0.3907	-0.5881	-0.0289
C	0.9546	0.6462	-0.1307
C	-4.4680	-2.0575	-0.2502
H	0.3005	1.5039	-0.2371
C	2.3838	0.9850	-0.0292
C	-5.8384	-1.4020	-0.2084
O	-4.3582	-3.2684	-0.3820
H	-4.7517	1.1834	0.9791
H	-4.6534	1.4384	-0.7660
H	-3.4787	2.2201	0.3076
H	-5.9483	-0.6604	-1.0087
H	-5.9970	-0.8807	0.7435
H	-6.5993	-2.1756	-0.3256
O	3.3356	0.2379	0.1030
O	2.5213	2.3410	-0.0911
C	3.8702	2.8358	0.0132
C	3.8106	4.3490	-0.0900
H	4.4756	2.3937	-0.7856
H	4.2987	2.5065	0.9660
H	4.8198	4.7688	-0.0153
H	3.2010	4.7719	0.7152
H	3.3783	4.6589	-1.0470
C	1.1231	-1.8806	0.0593
C	2.0878	-2.2369	-0.8899
C	2.7453	-3.4642	-0.8341
C	2.4527	-4.3622	0.2004
C	1.4921	-4.0193	1.1629
C	0.8331	-2.8008	1.0840
H	2.3287	-1.5454	-1.6896
H	3.4813	-3.7052	-1.5922
O	3.0376	-5.5832	0.3569
H	1.2798	-4.7239	1.9606
H	0.0928	-2.5488	1.8374
C	4.0294	-5.9801	-0.5775
H	4.8853	-5.2927	-0.5731
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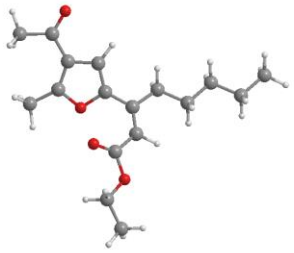

(*Z*)-6f

O	-2.3444	-0.9246	0.3321
C	-3.5808	-1.4640	0.2599
C	-3.5035	-2.7238	-0.3067
C	-2.1155	-2.9434	-0.5856
C	-1.4415	-1.8180	-0.2023
C	-4.6765	-0.6052	0.7977
H	-1.7142	-3.8369	-1.0399
C	-0.0256	-1.4679	-0.2181
C	0.4658	-0.2097	-0.3030
C	-4.5537	-3.7202	-0.5995
H	1.5334	-0.0617	-0.1902
C	-0.2701	1.0347	-0.6181
C	-6.0035	-3.3910	-0.2843
O	-4.2518	-4.7991	-1.0929
H	-5.1612	-1.0574	1.6712
H	-5.4533	-0.4253	0.0467
H	-4.2590	0.3598	1.0940
H	-6.3381	-2.5107	-0.8466
H	-6.1379	-3.1673	0.7808
H	-6.6235	-4.2477	-0.5548
O	-1.3563	1.1488	-1.1507
O	0.5011	2.1058	-0.2810
C	-0.0534	3.3984	-0.5965
C	0.9558	4.4467	-0.1651
H	-1.0103	3.5123	-0.0758
H	-0.2597	3.4447	-1.6712
H	0.5715	5.4484	-0.3871
H	1.9051	4.3167	-0.6949
H	1.1509	4.3828	0.9103
C	0.8969	-2.6727	-0.0927
C	2.4047	-2.4198	-0.1857
H	0.6113	-3.3897	-0.8765
H	0.6679	-3.1839	0.8534
H	2.7221	-1.7563	0.6305
H	2.6345	-1.8930	-1.1218
C	3.2206	-3.7182	-0.1209
C	4.7351	-3.4863	-0.1972
H	2.9141	-4.3830	-0.9420
H	2.9827	-4.2551	0.8094
H	5.0421	-2.8273	0.6273
H	4.9715	-2.9441	-1.1237
C	5.5474	-4.7840	-0.1439
H	5.2885	-5.4484	-0.9774
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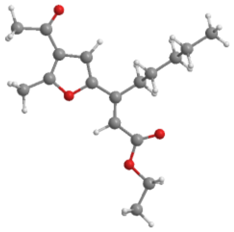
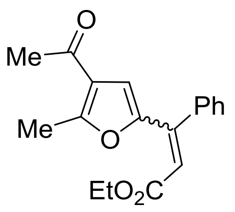
G=-962.832644



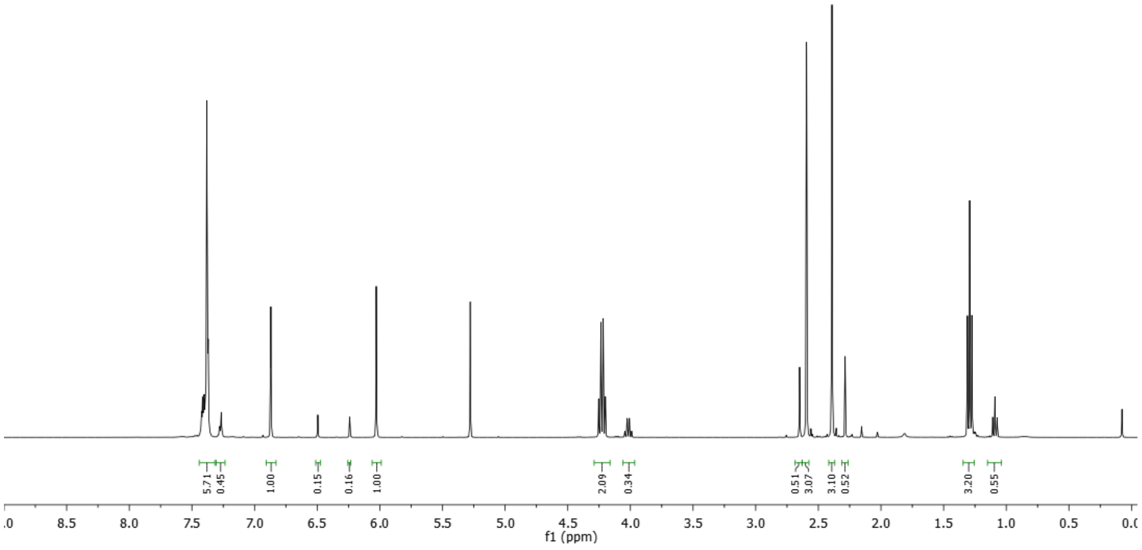
(*E*)-6f

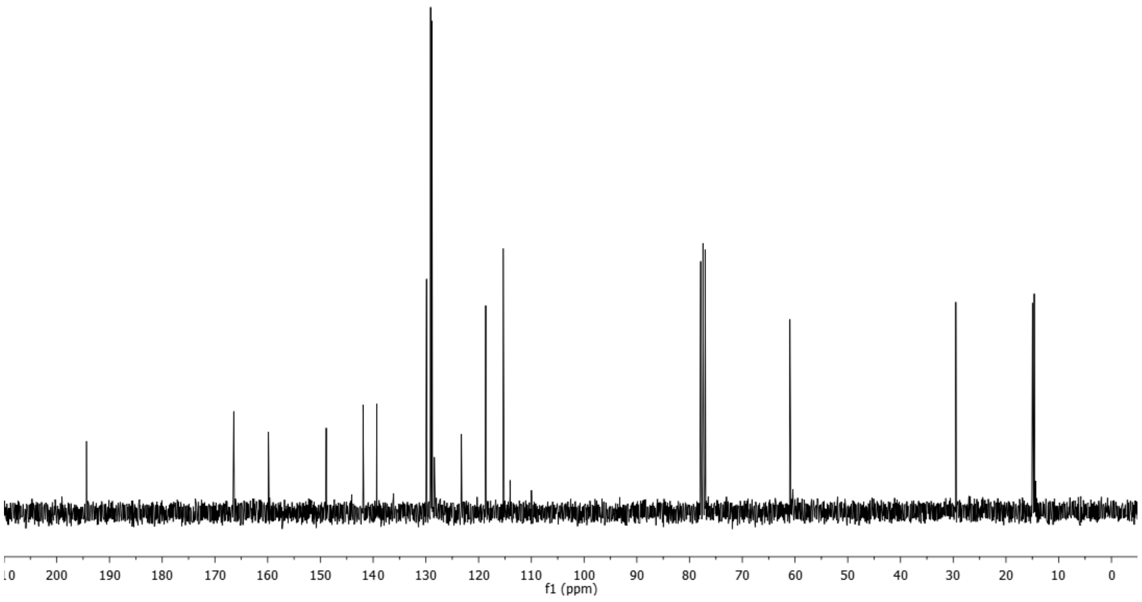
O	-3.1010	-0.8005	-0.2226
C	-4.4524	-0.7536	-0.1308
C	-4.8990	0.4917	-0.5298
C	-3.7280	1.2362	-0.8872
C	-2.6476	0.4221	-0.6886
C	-5.0967	-2.0043	0.3675
H	-3.7339	2.2554	-1.2422
C	-1.2171	0.6055	-0.8585
C	-0.3709	-0.4147	-0.5626
C	-6.2659	1.0522	-0.6070
H	-0.7739	-1.3625	-0.2247
C	1.0941	-0.3625	-0.6701
C	-7.4511	0.1907	-0.2054
O	-6.4300	2.2013	-0.9929
H	-4.3438	-2.7929	0.4412
H	-5.8918	-2.3468	-0.3026
H	-5.5412	-1.8645	1.3605
H	-7.3482	-0.1760	0.8227
H	-7.5364	-0.6868	-0.8583
H	-8.3611	0.7877	-0.2884
O	1.7897	0.6016	-0.9490
O	1.6199	-1.5871	-0.3987
C	3.0574	-1.6797	-0.4587
C	3.4381	-3.1046	-0.1008
H	3.4905	-0.9520	0.2357
H	3.3899	-1.4072	-1.4662
H	4.5271	-3.2193	-0.1346
H	2.9945	-3.8166	-0.8044
H	3.0957	-3.3590	0.9075
C	-0.7762	1.9744	-1.3332
C	-0.4937	2.9460	-0.1674
H	-1.5508	2.3996	-1.9822
H	0.1342	1.8695	-1.9254
H	0.3015	2.5181	0.4543
H	-1.3864	3.0314	0.4678
C	-0.0713	4.3368	-0.6552
C	0.2101	5.3199	0.4885
H	-0.8559	4.7530	-1.3054
H	0.8270	4.2403	-1.2818
H	0.9901	4.9015	1.1401
H	-0.6894	5.4162	1.1132
C	0.6425	6.7058	-0.0013
H	-0.1327	7.1650	-0.6272
H	1.5585	6.6449	-0.6018
H	0.8382	7.3840	0.8372

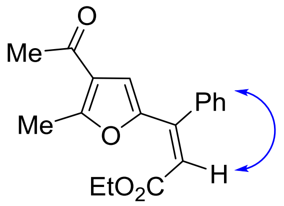
HF=-963.1702961
G=-962.844060


O
Me
Me
O
Ph
EtO2C

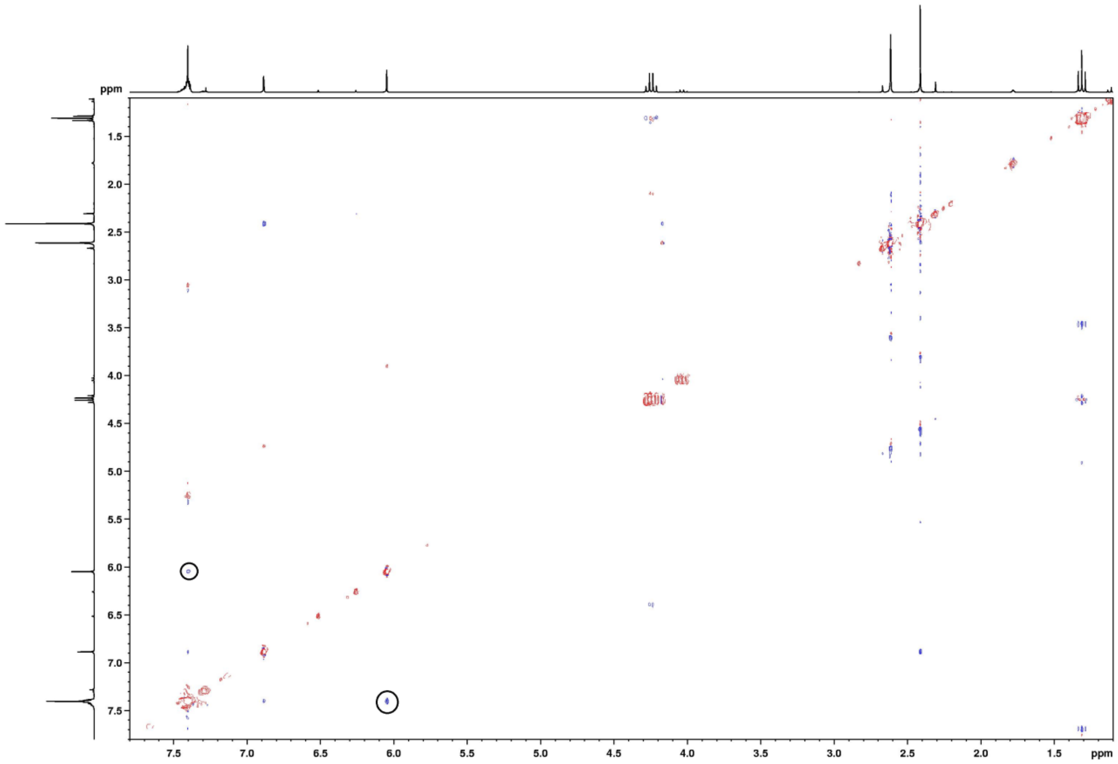
6a

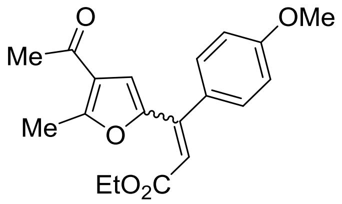

5.71
0.45
1.00
0.15
0.16
1.00
2.09
0.34
0.51
3.07
3.10
0.52
3.20
0.55
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

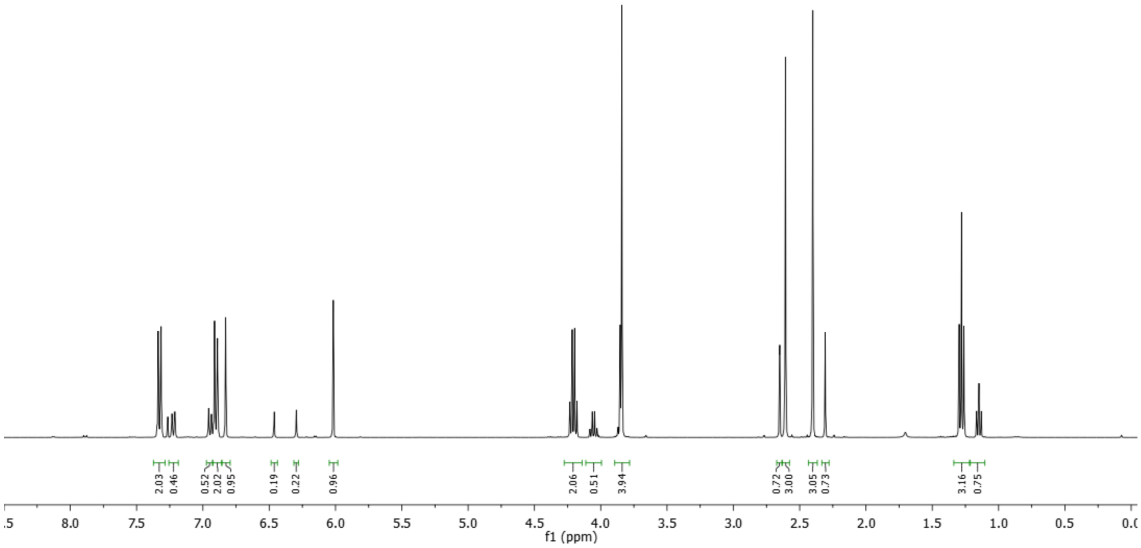

O
Me
Ph
Me
O
H
EtO$_2$C

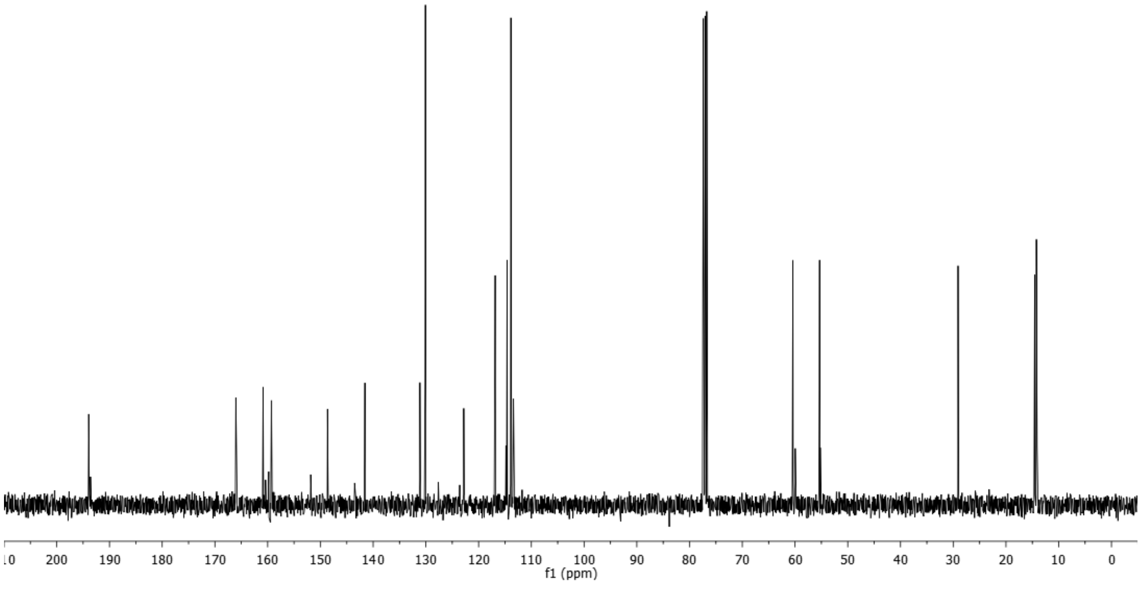
6a

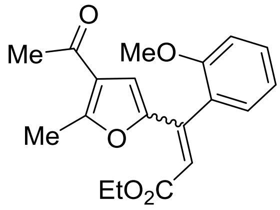

ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


O
OMe
Me
Me
O
EtO2C

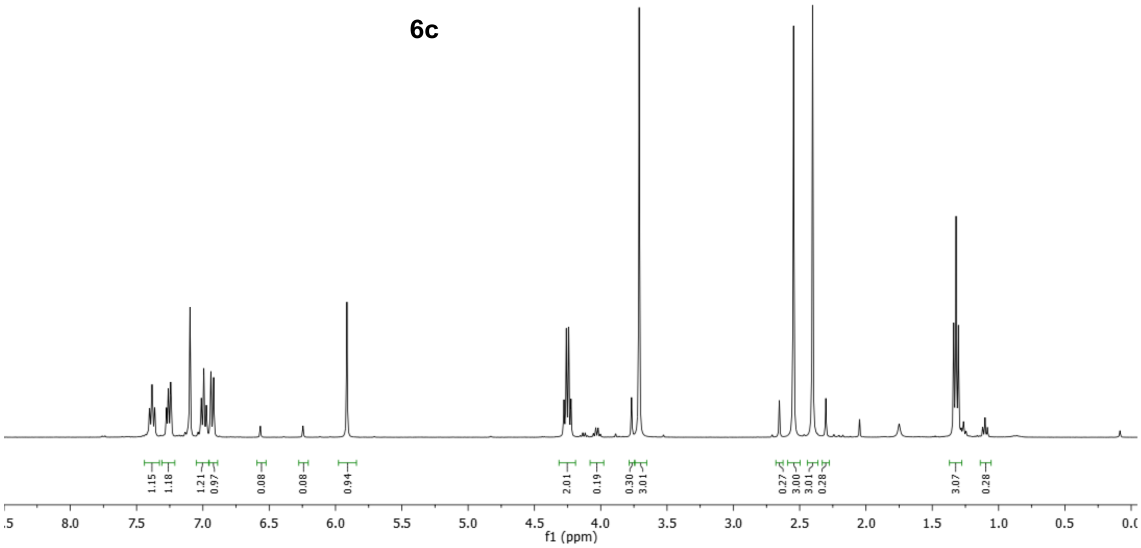
6b

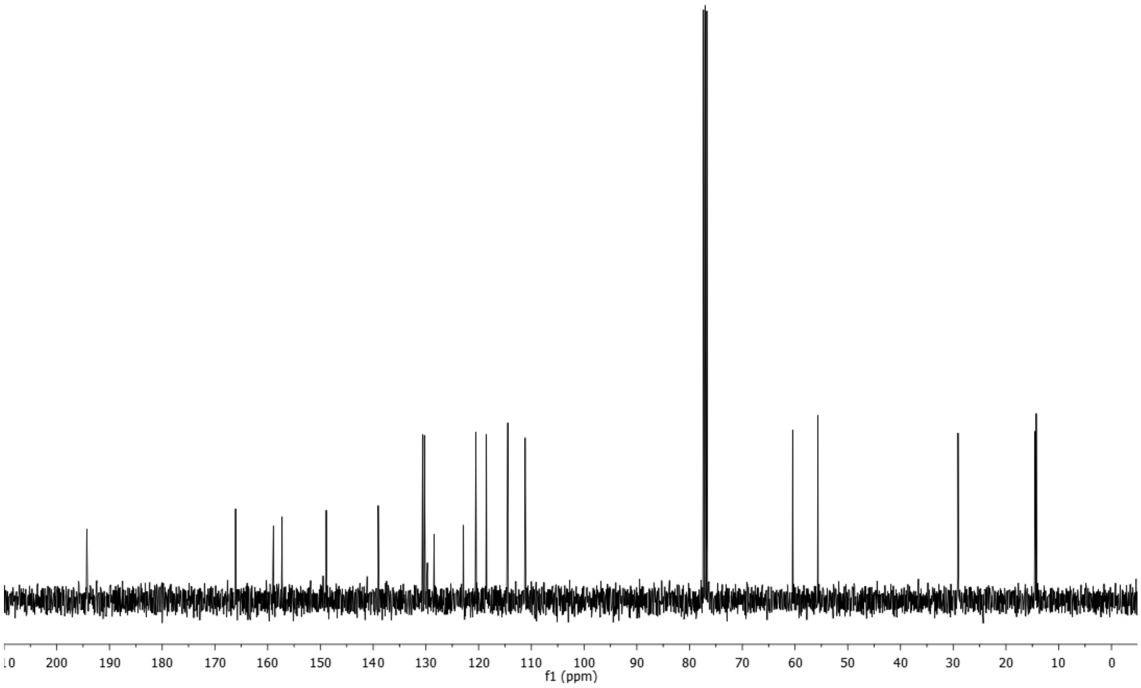

2.03
0.46
0.52
2.02
0.95
0.19
0.22
0.96
2.06
0.51
3.94
0.72
3.00
3.05
0.73
3.16
0.75
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)

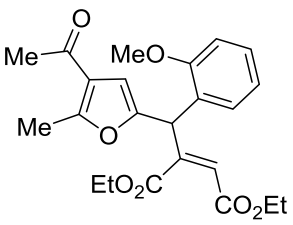

.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
MeO
Me
O
O
EtO2C

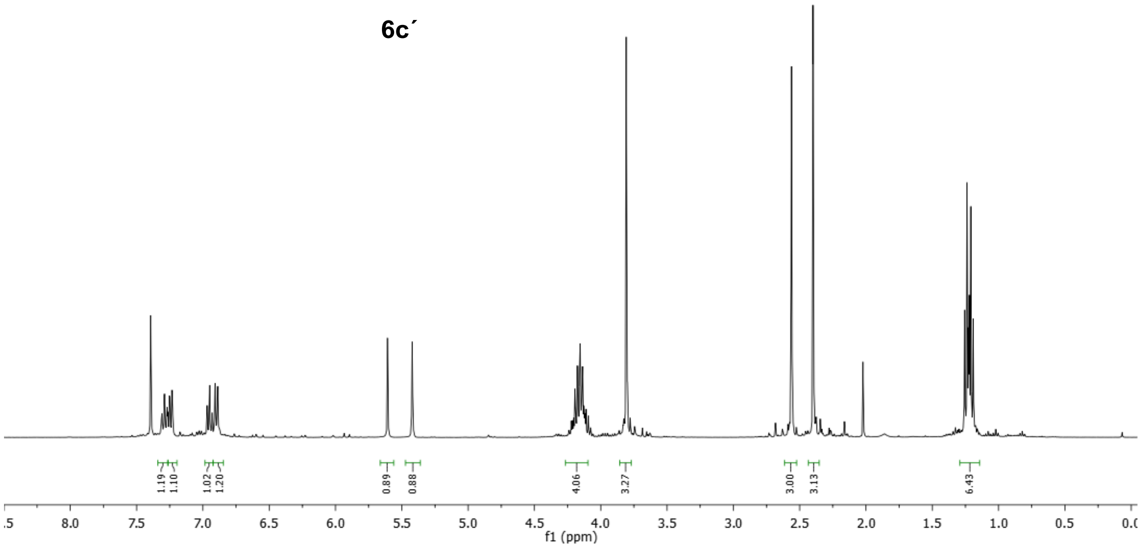
6c

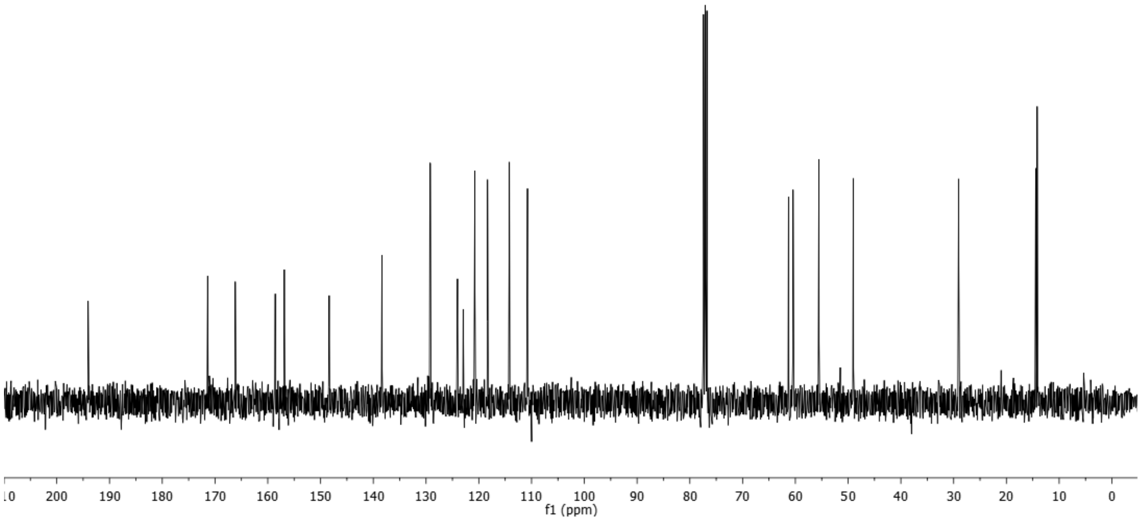

1.15
1.18
1.21
0.97
0.08
0.08
0.94
2.01
0.19
0.30
3.01
0.27
3.00
3.01
0.28
3.07
0.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

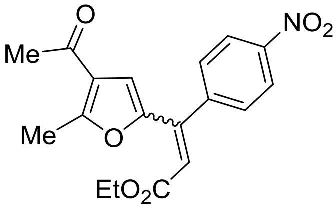

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
MeO
Me
O
EtO2C
CO2Et

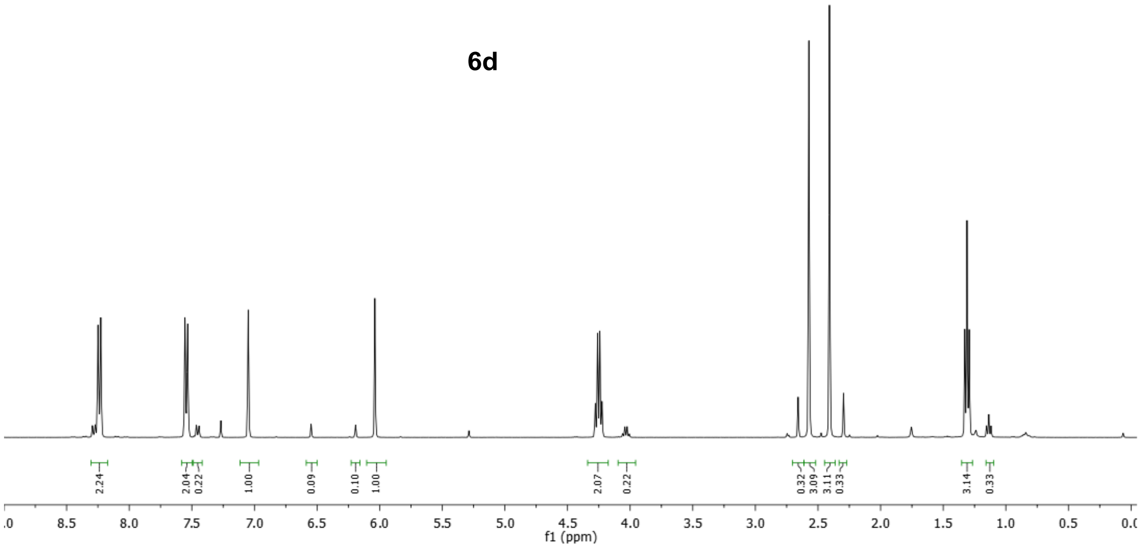
6c´

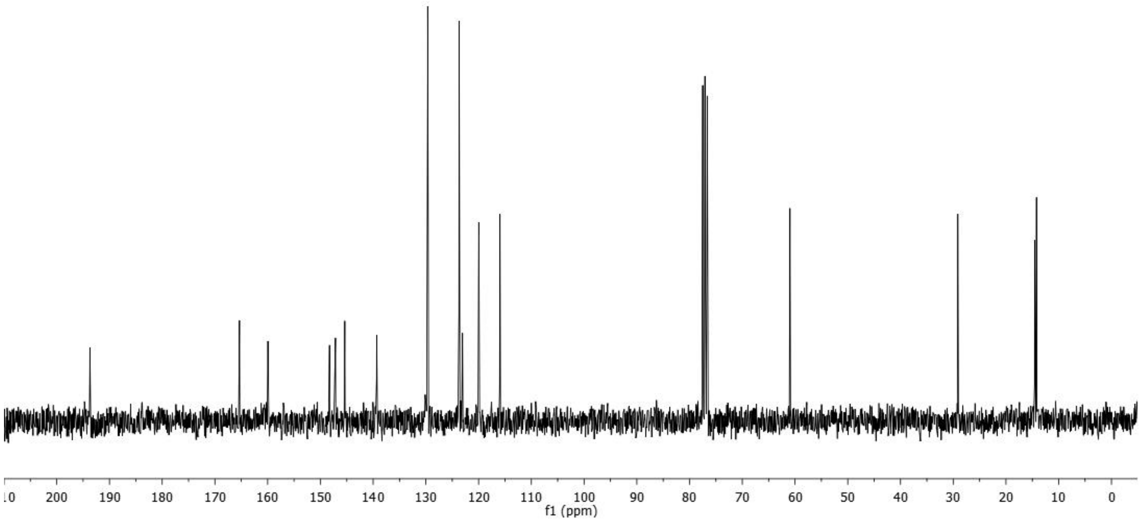

1.19
1.10
1.02
1.20
0.89
0.88
4.06
3.27
3.00
3.13
6.43
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

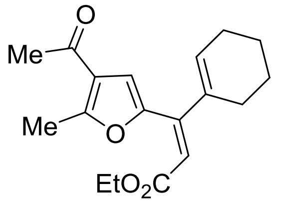

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



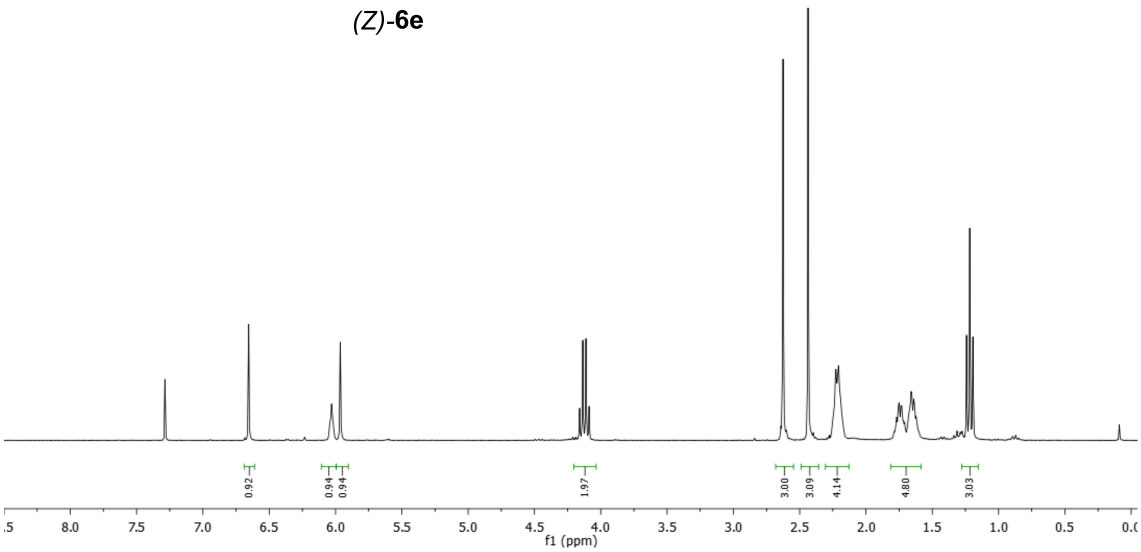
6d

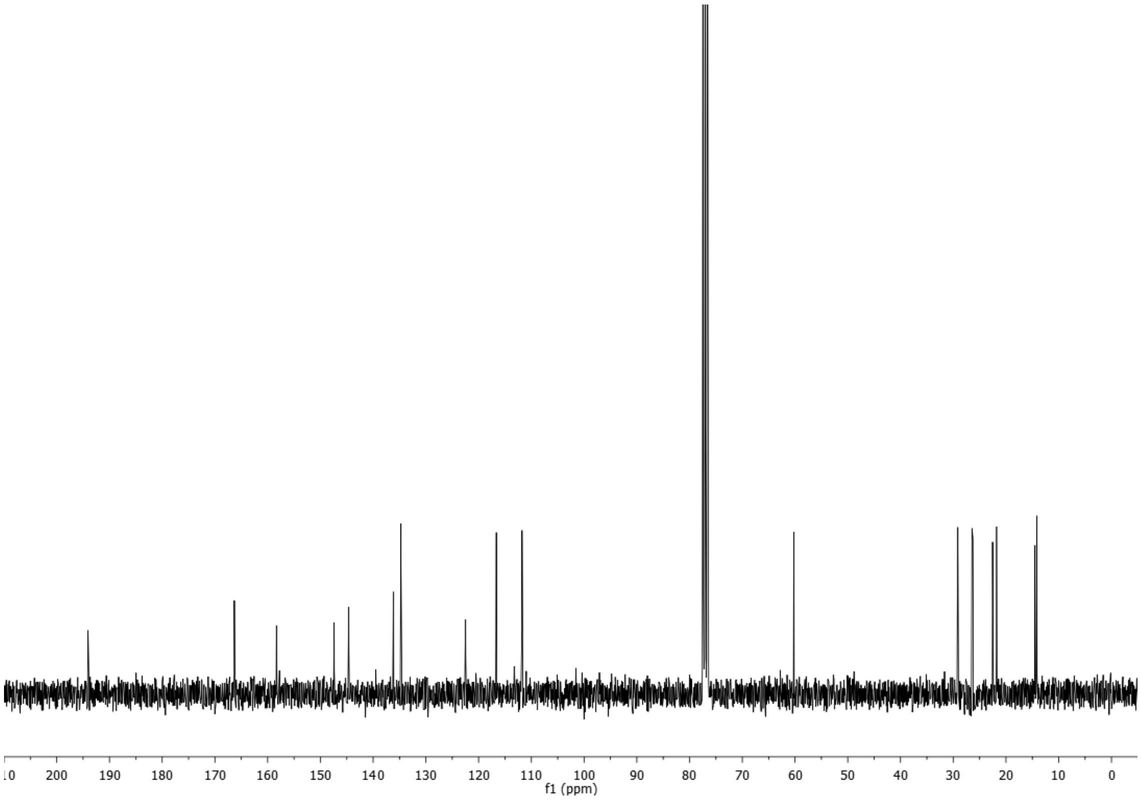

2.24
2.04
0.22
1.00
0.09
0.10
1.00
2.07
0.22
0.32
3.09
3.11
0.33
3.14
0.33
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

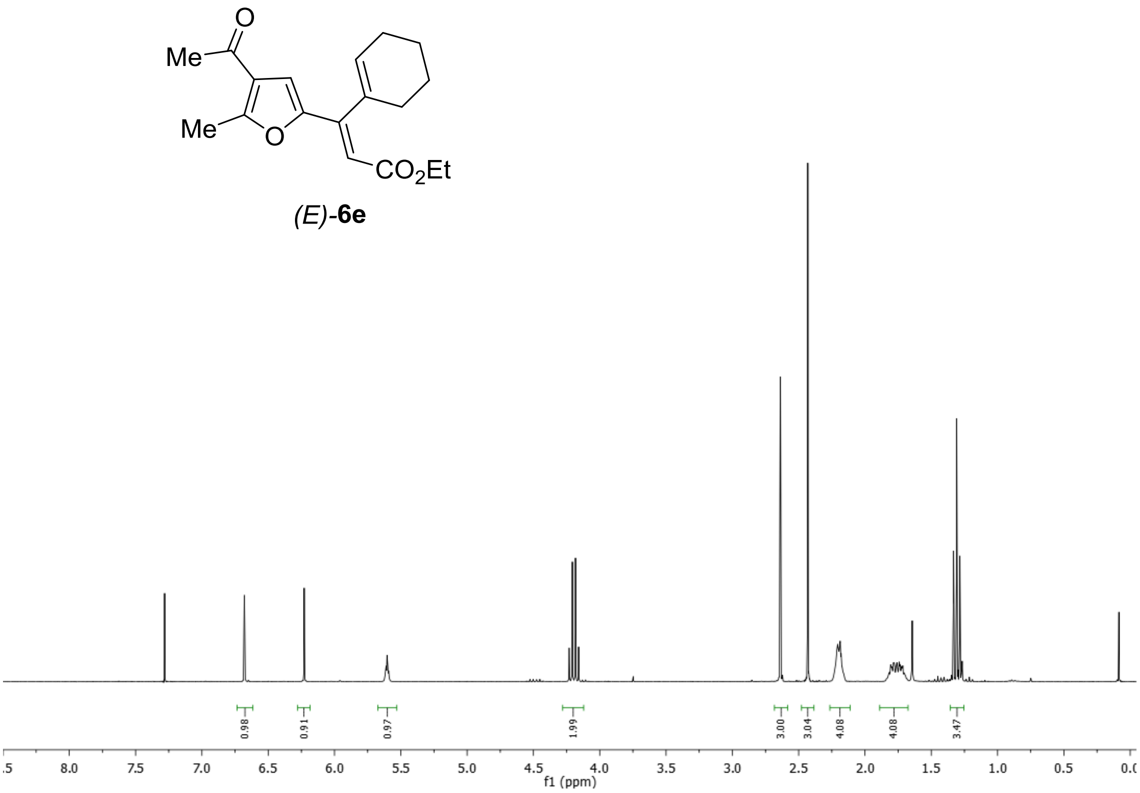

10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Me
Me
O
EtO2C

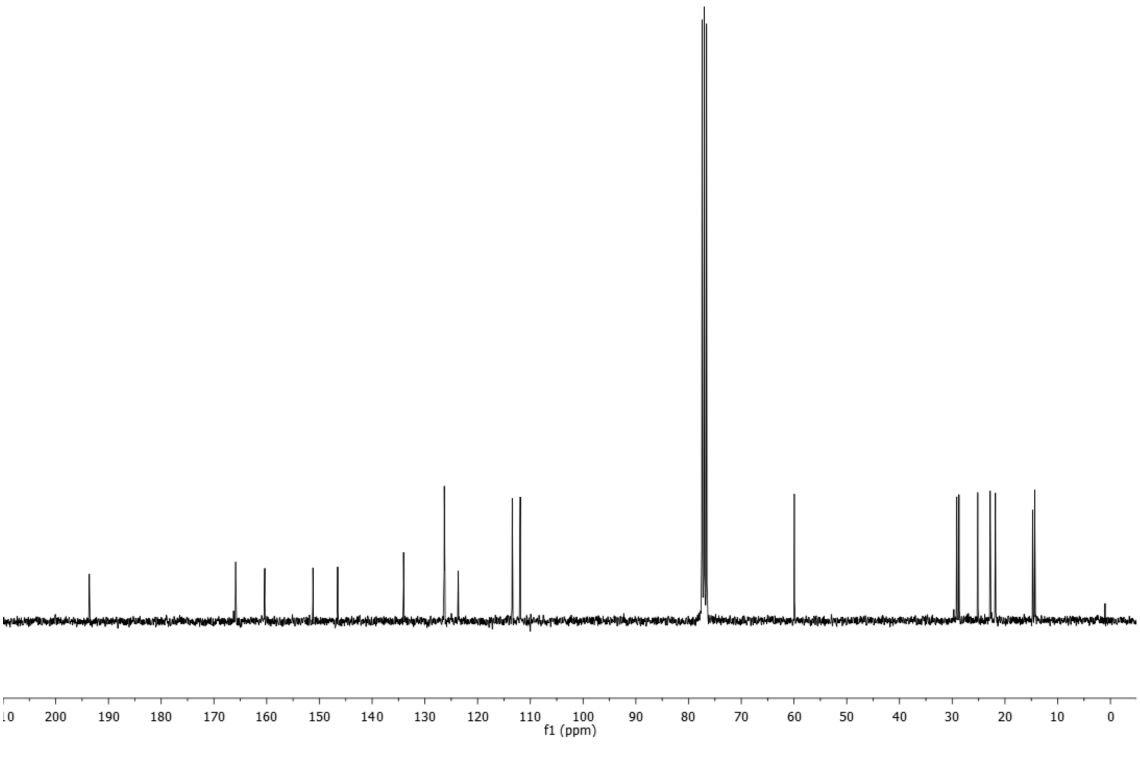
(Z)-**6e**

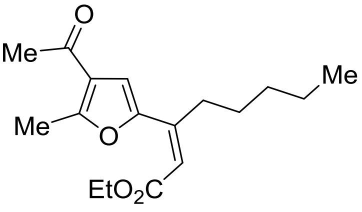

0.92
0.94
0.94
1.97
3.00
3.09
4.14
4.80
3.03
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

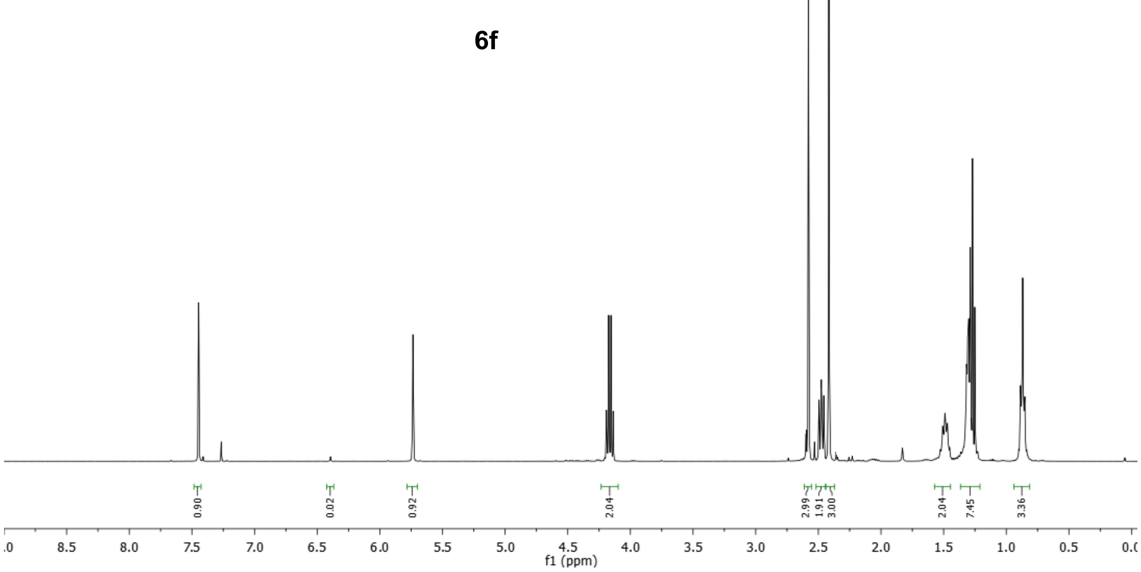

Me
Me
O
O
CO2Et
0.98
0.91
0.97
1.99
3.00
3.04
4.08
4.08
3.47
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

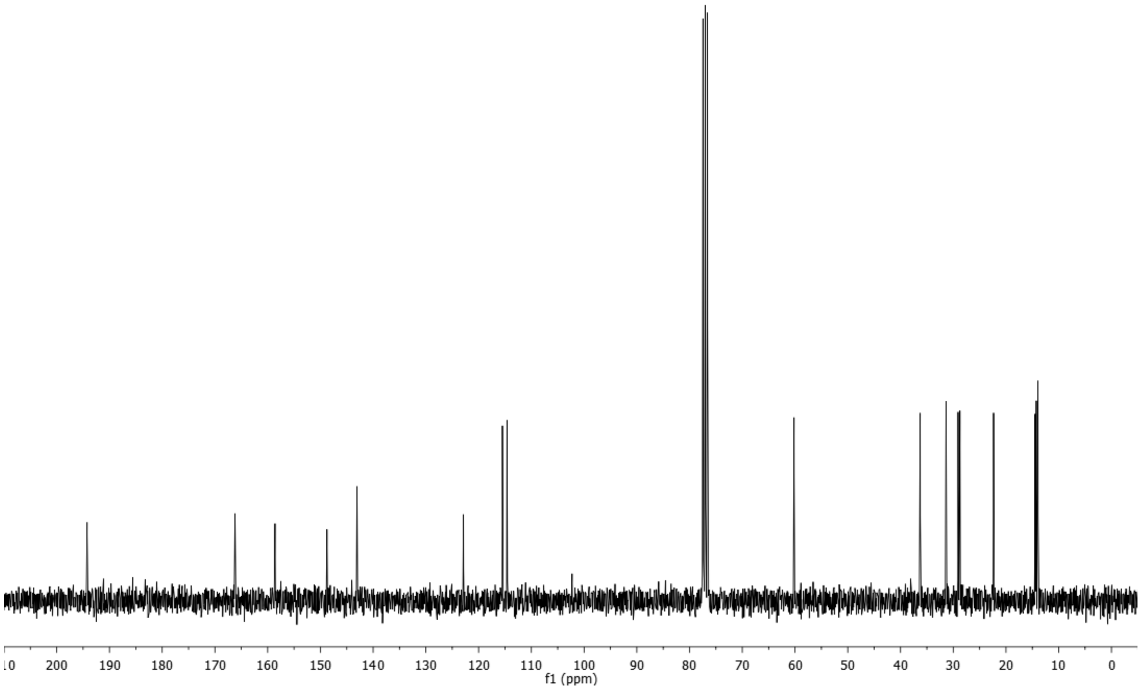
(E)-**6e**

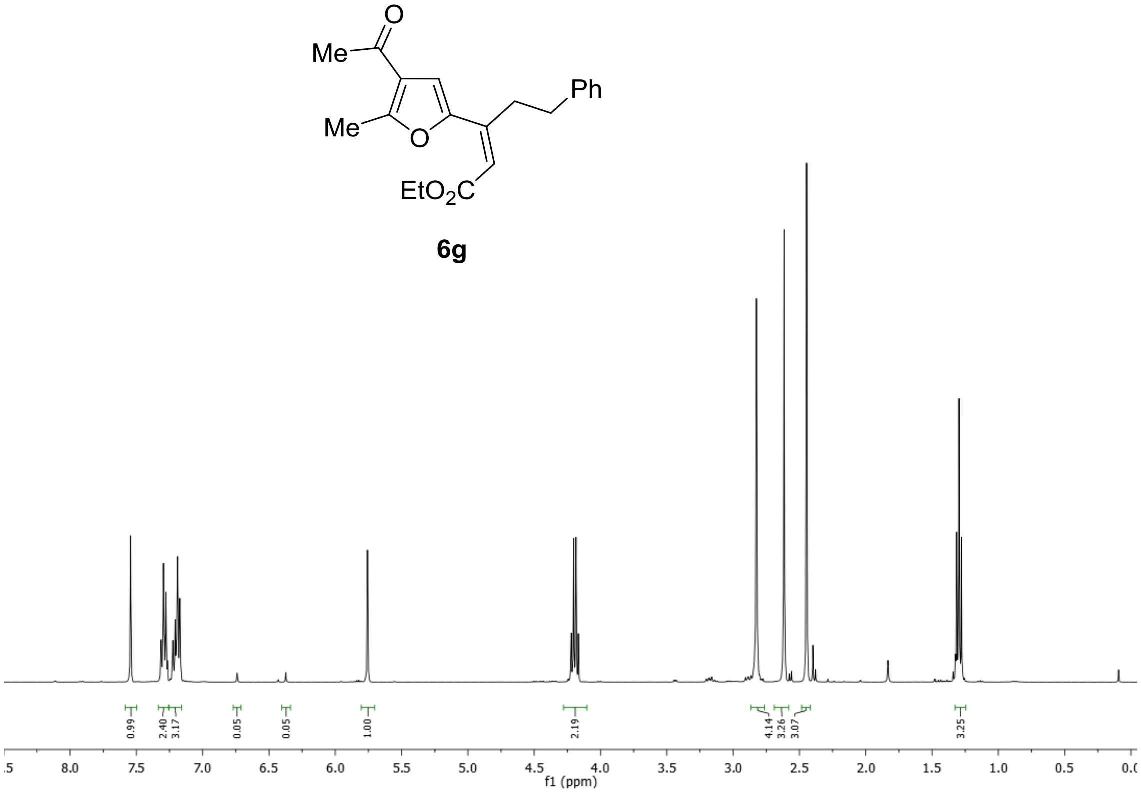

.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

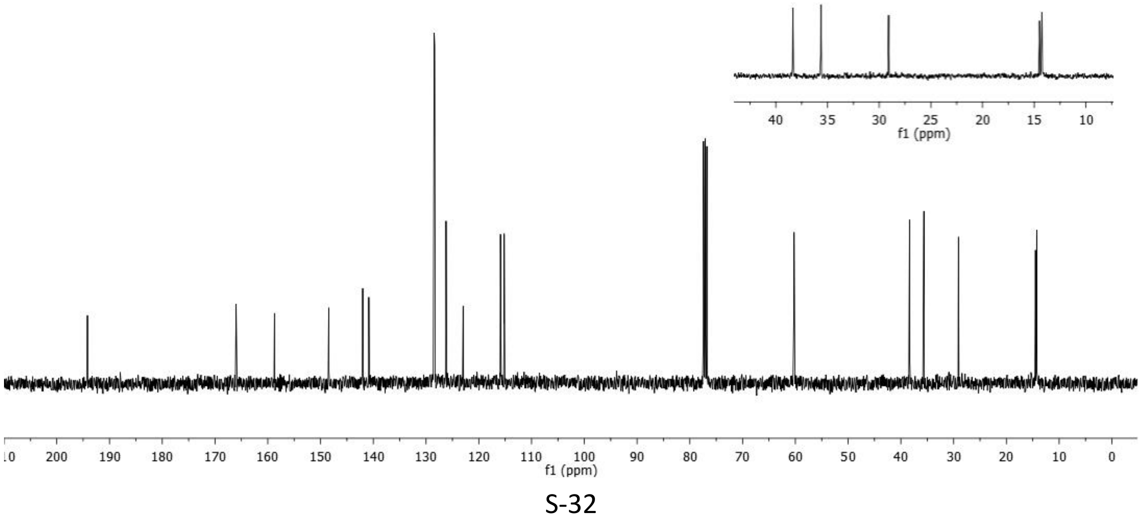

O
Me
Me
Me
O
EtO2C

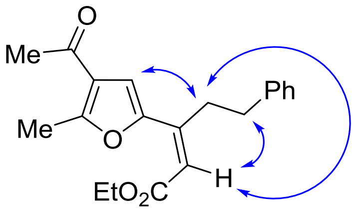
6f


0.90
0.02
0.92
2.04
2.99
1.91
3.00
2.04
7.45
3.36
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)

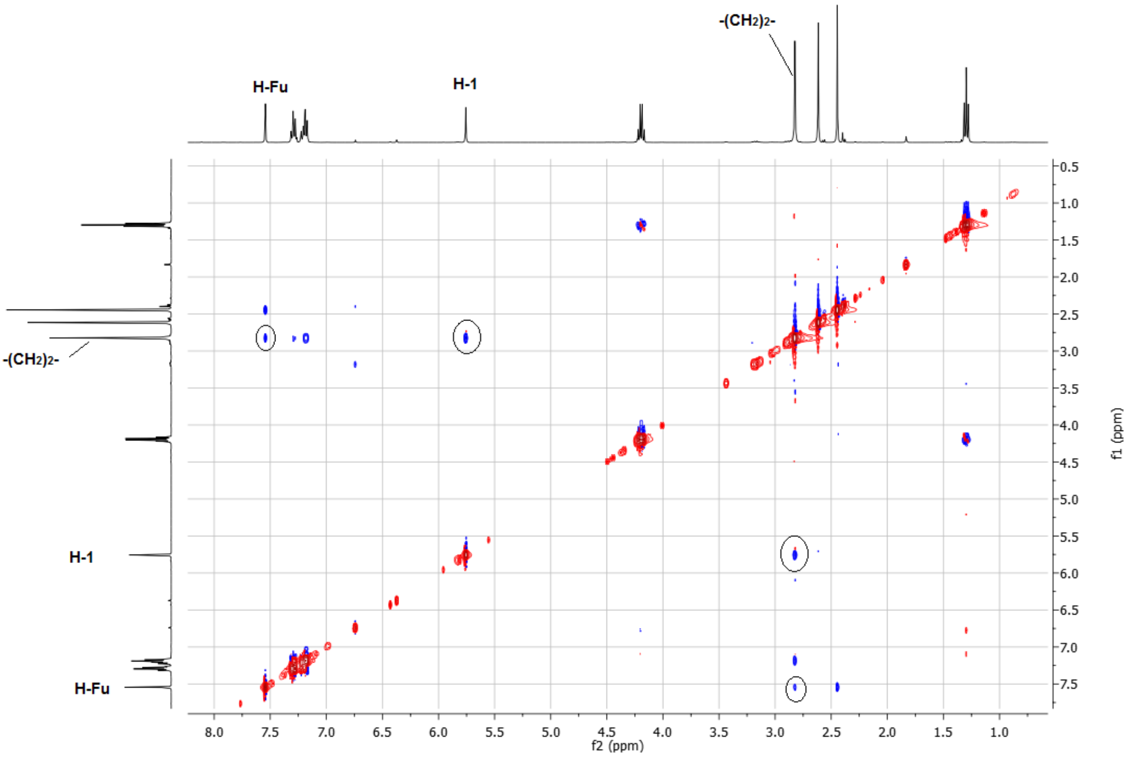

.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

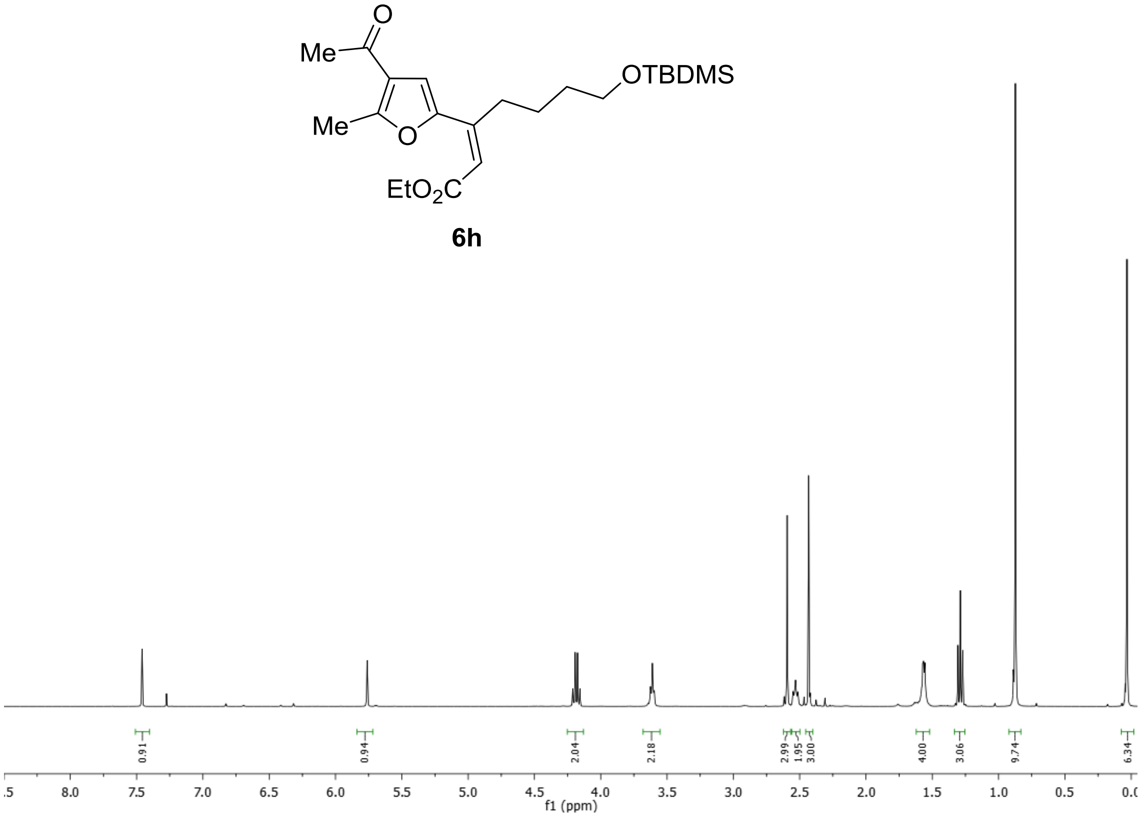

Me
O
Me
O
Ph
EtO2C
6g
0.99
2.40
3.17
0.05
0.05
1.00
2.19
4.14
3.26
3.07
3.25
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)


40
35
30
25
20
15
10
f1 (ppm)
.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Me
Me
O
Ph
H
EtO2C

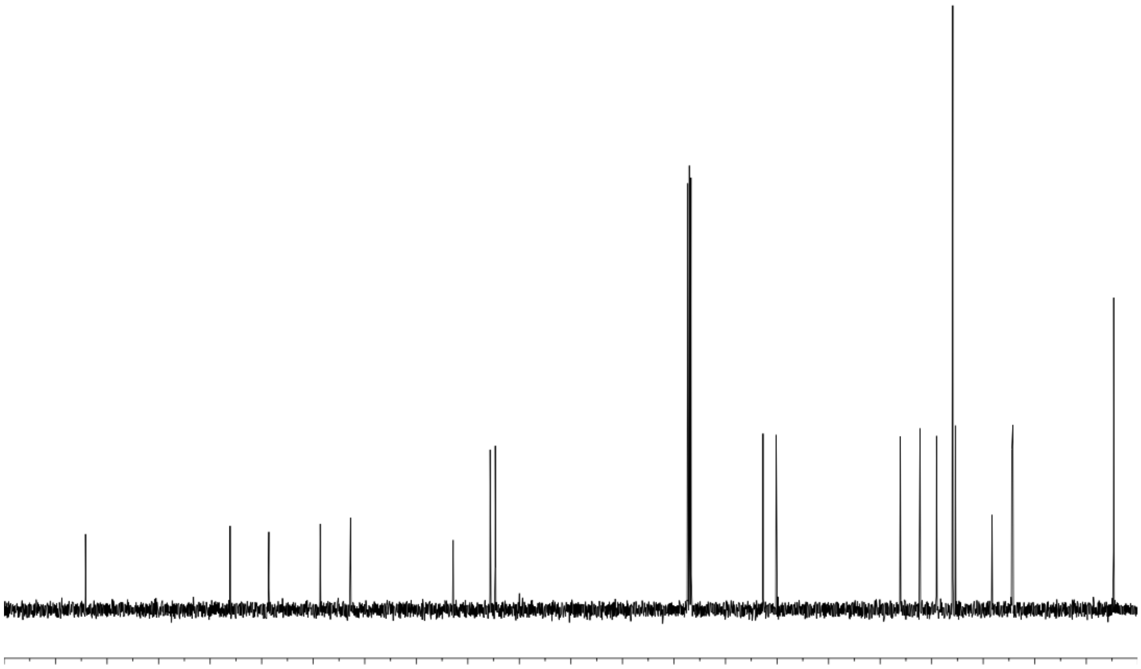
6g

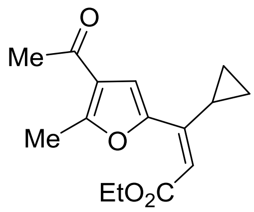

H-Fu
H-1
-(CH2)2-
-(CH2)2-
H-1
H-Fu
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)


O
Me
Me
O
OTBDMS
EtO2C

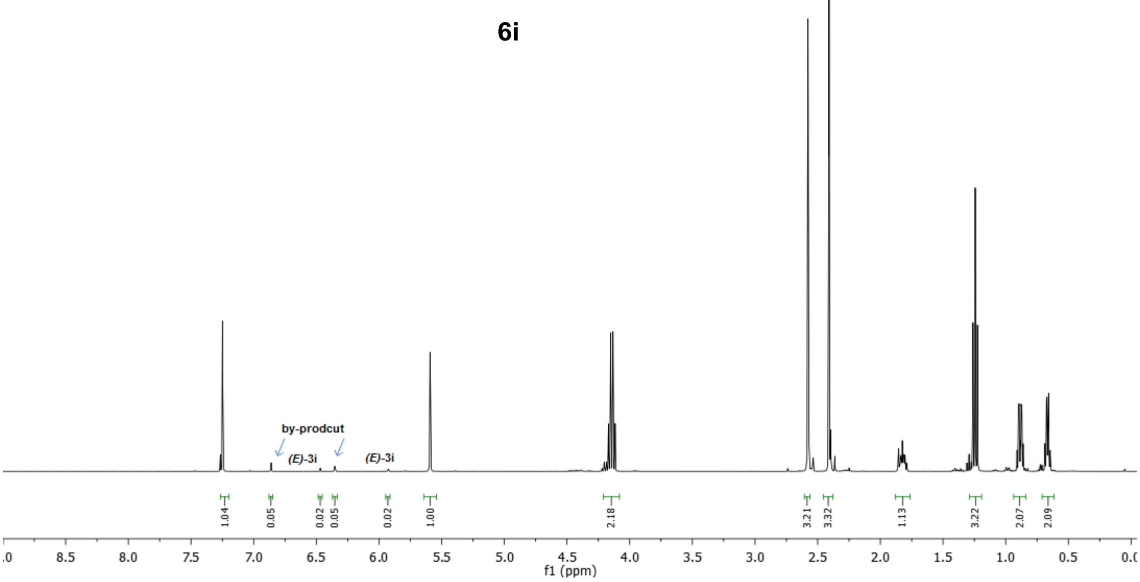
6h

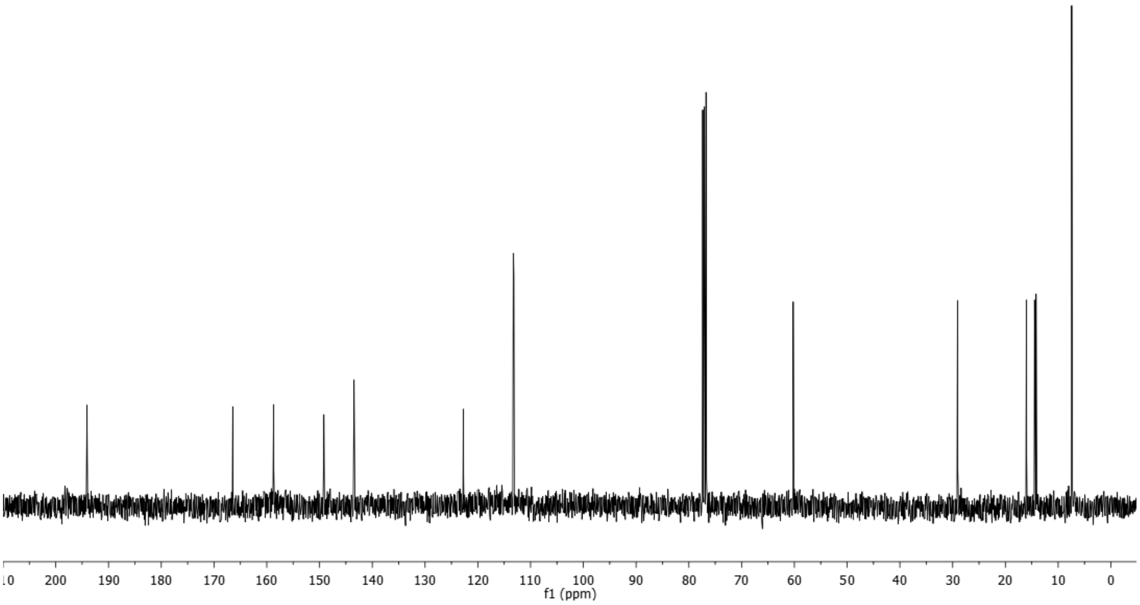
0.91
0.94
2.04
2.18
2.99
1.95
3.00
4.00
3.06
9.74
6.34
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)


.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


O
Me
Me
O
EtO2C

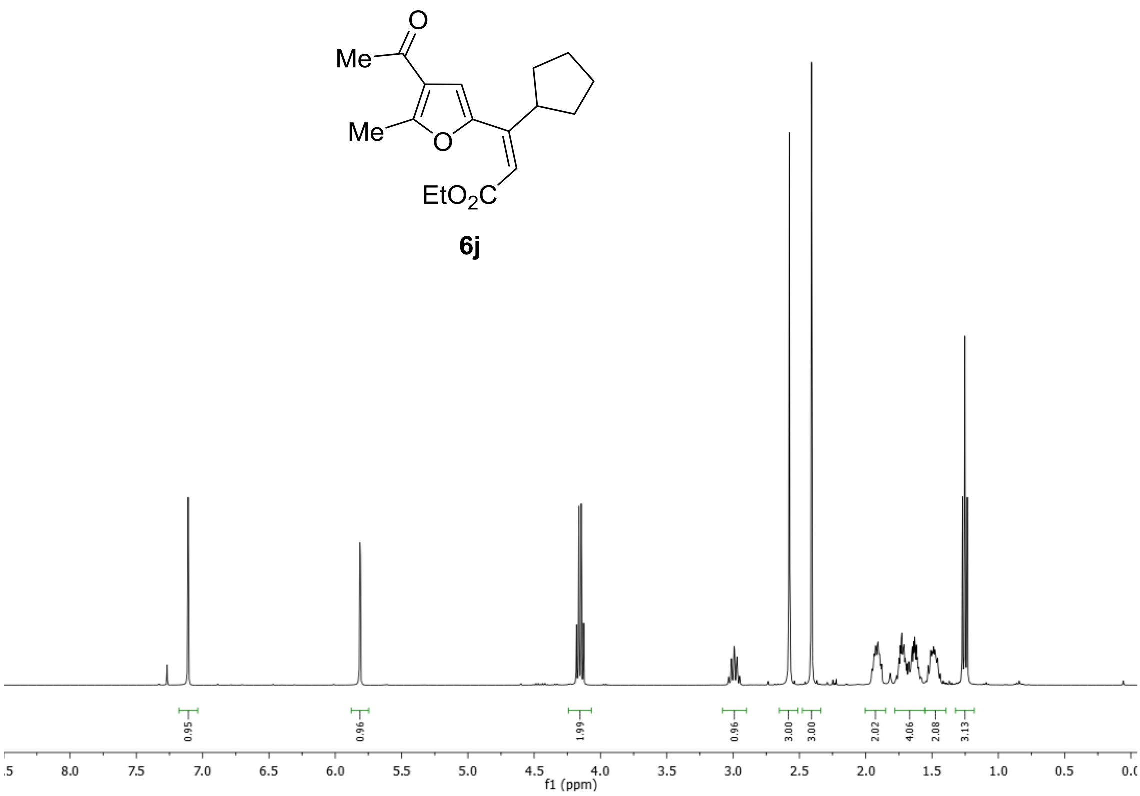
6i

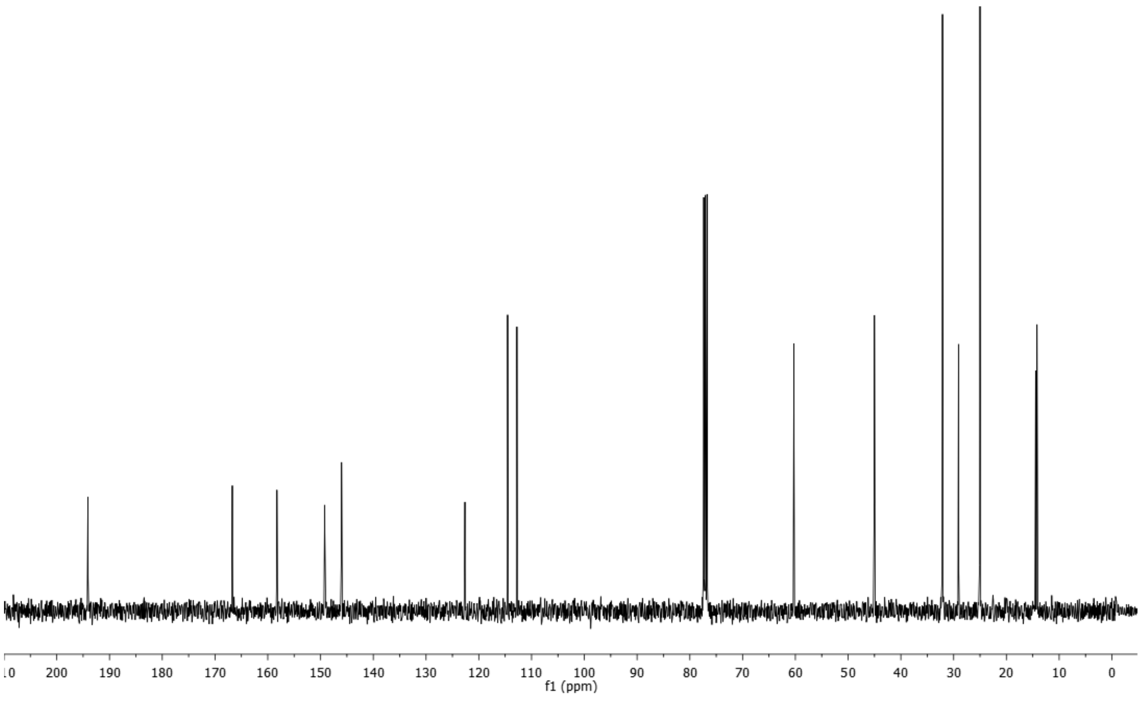

by-prodcut
(E)-3i
(E)-3i
1.04
0.05
0.02
0.05
0.02
1.00
2.18
3.21
3.32
1.13
3.22
2.07
2.09
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)

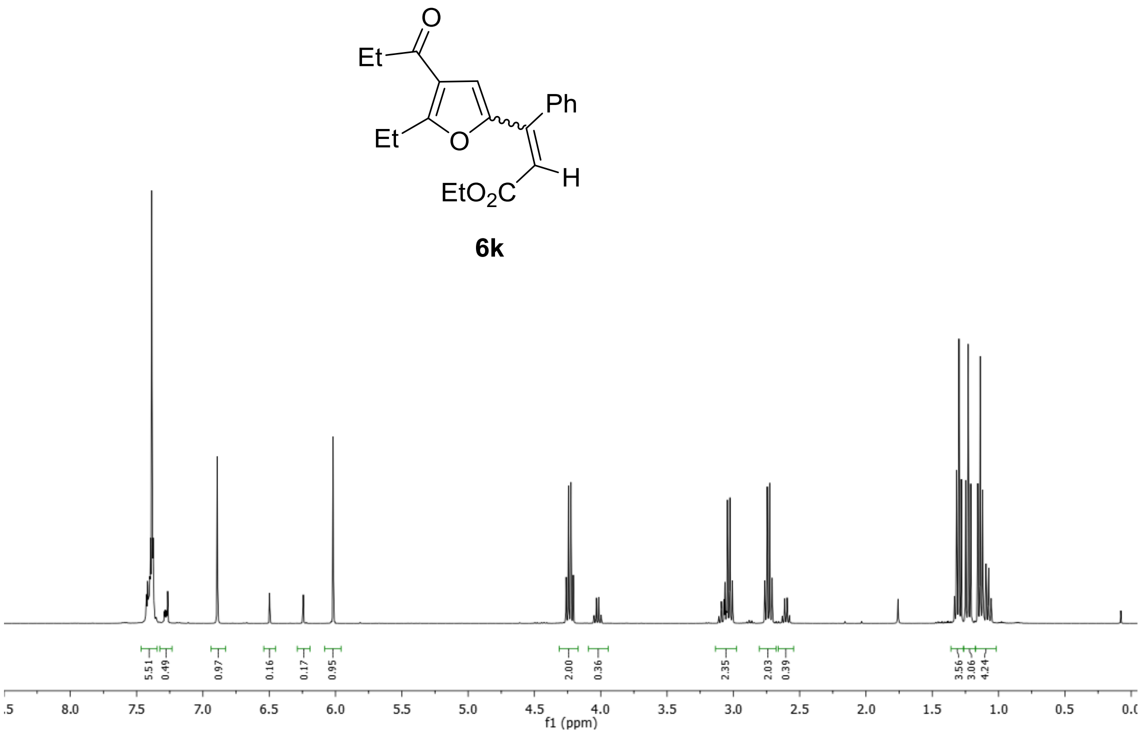

.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

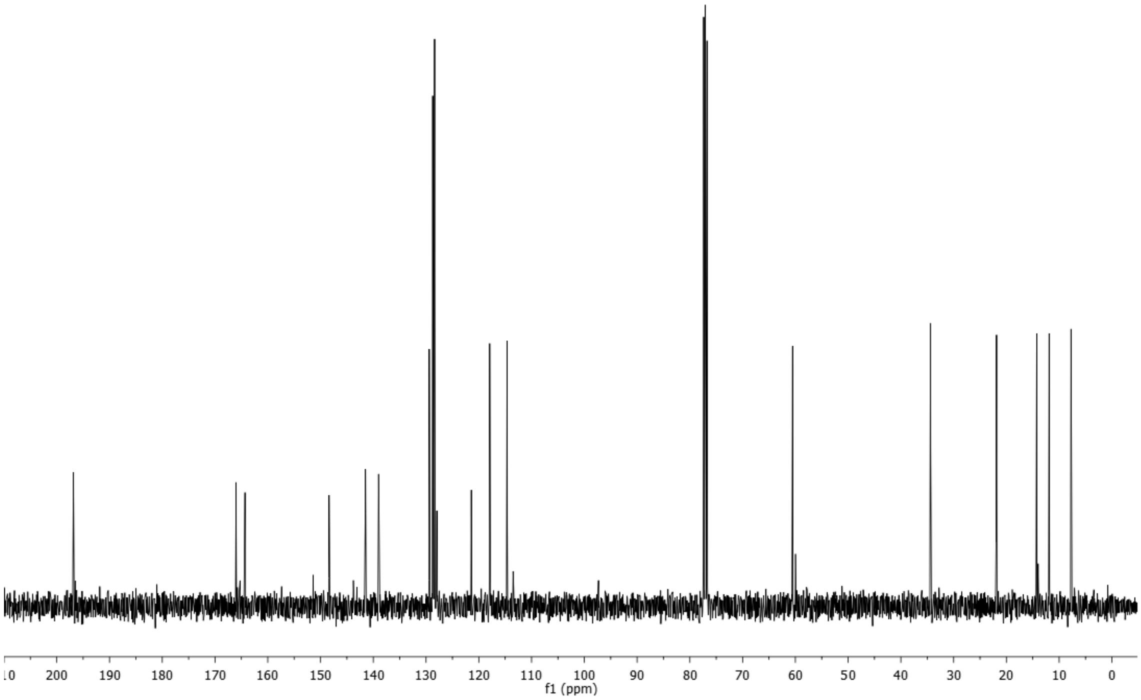
Me
Me
O
O
EtO$_2$C

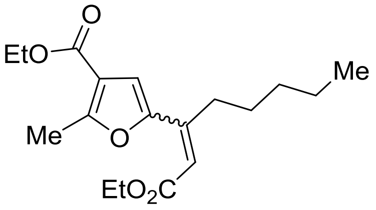
6j


0.95
0.96
1.99
0.96
3.00
3.00
2.02
4.06
2.08
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

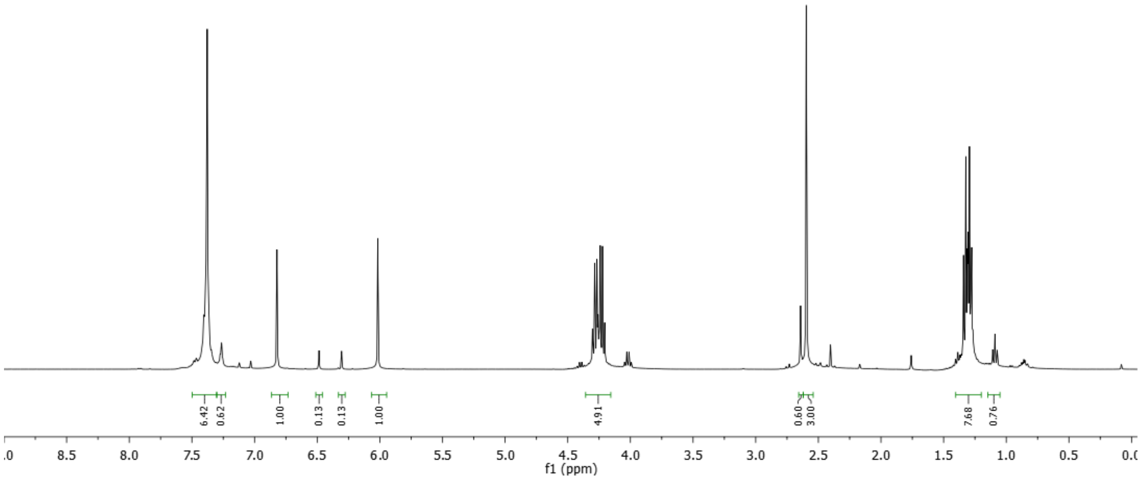

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

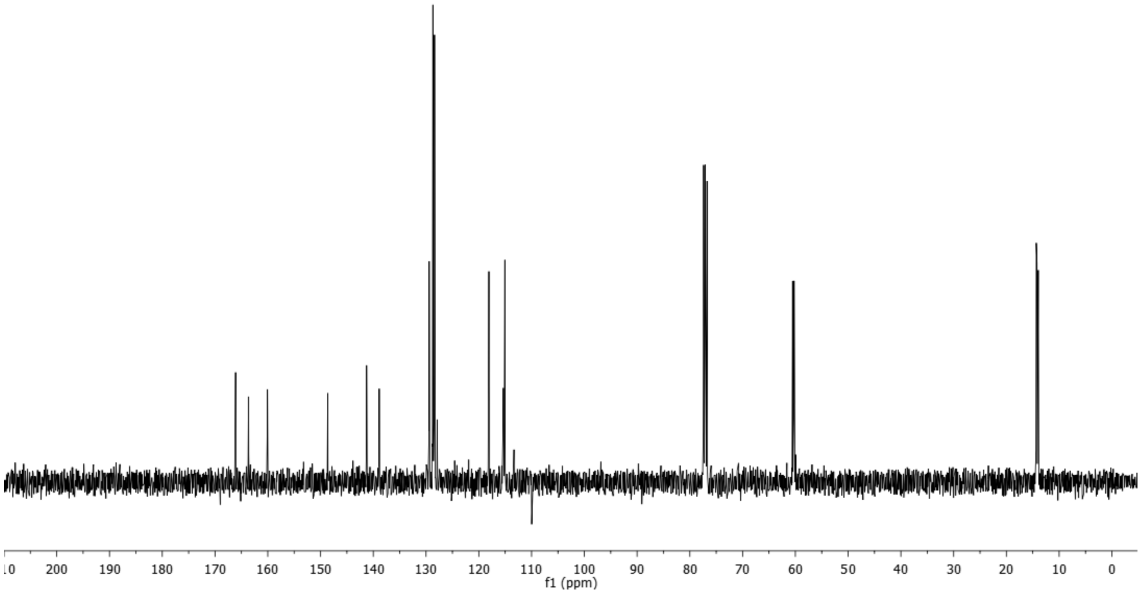

O
Et
Ph
Et
O
H
EtO$_2$C
6k
5.51
0.49
0.97
0.16
0.17
0.95
2.00
0.36
2.35
2.03
0.39
3.56
3.06
4.24
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)

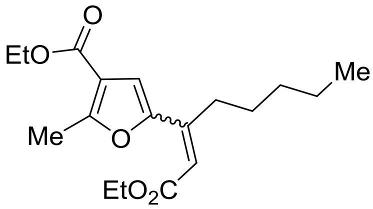

.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
EtO
Me
Me
O
EtO$_2$C

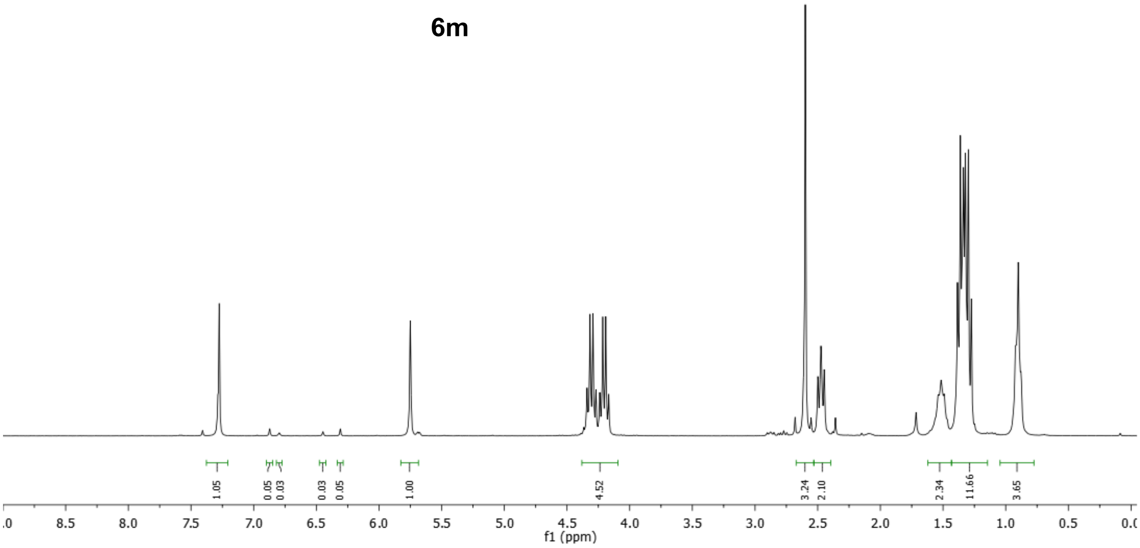
6l

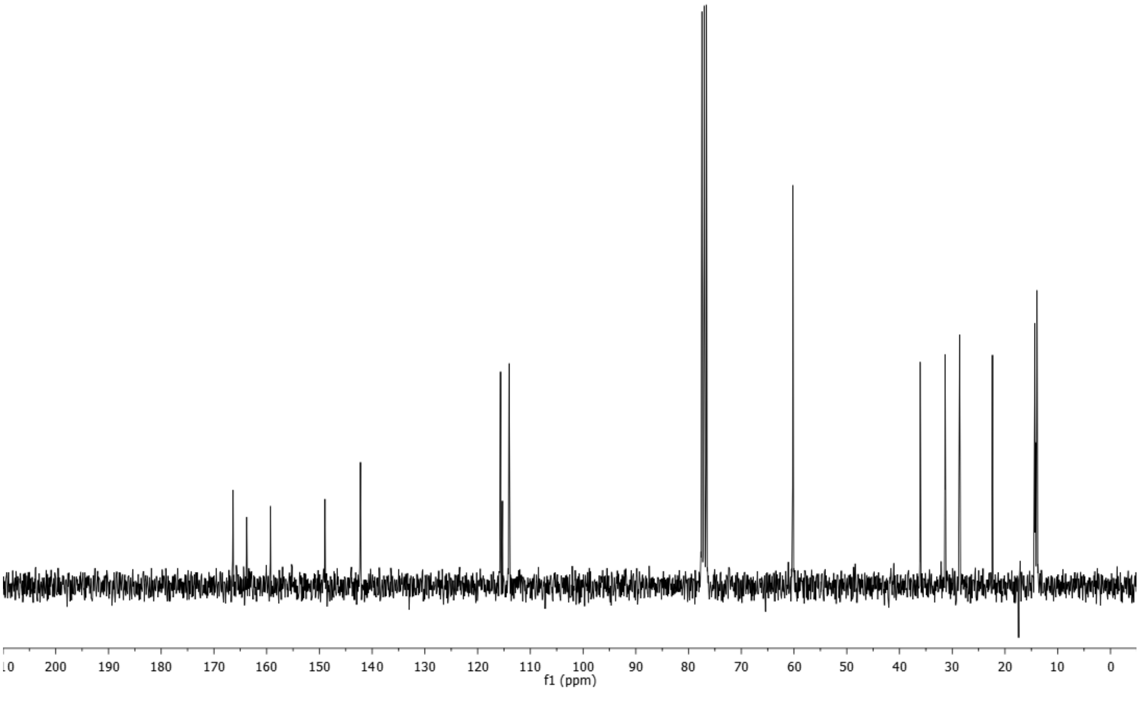

6.42
0.62
1.00
0.13
0.13
1.00
4.91
0.60
3.00
7.68
0.76
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

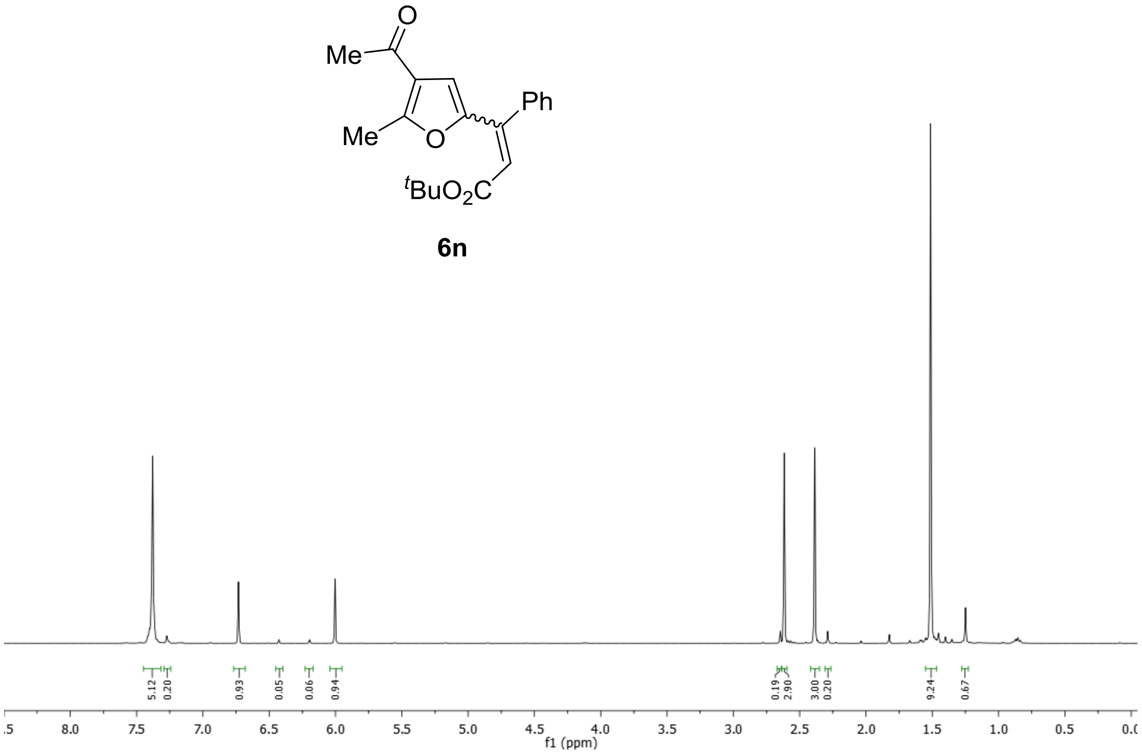

.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


EtO
O
Me
Me
O
EtO$_2$C

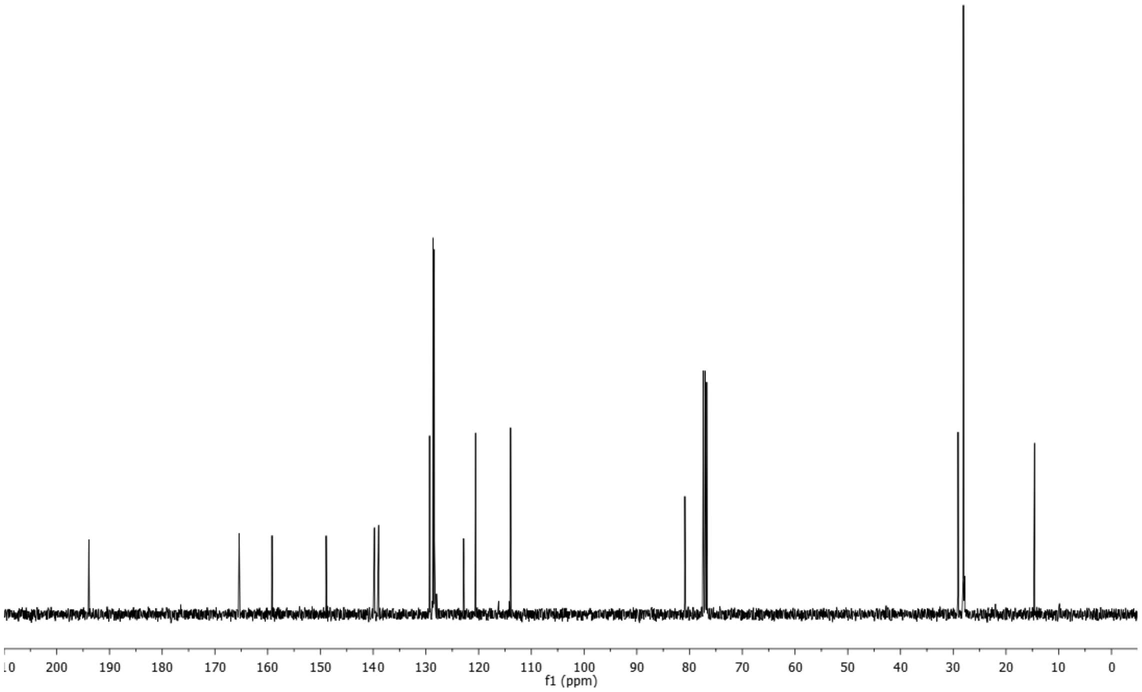
6m

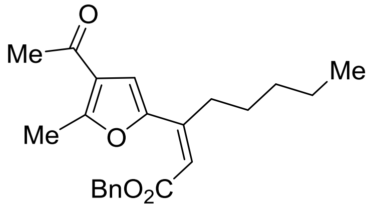

1.05
0.05
0.03
0.03
0.05
1.00
4.52
3.24
2.10
2.34
11.66
3.65
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)


.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

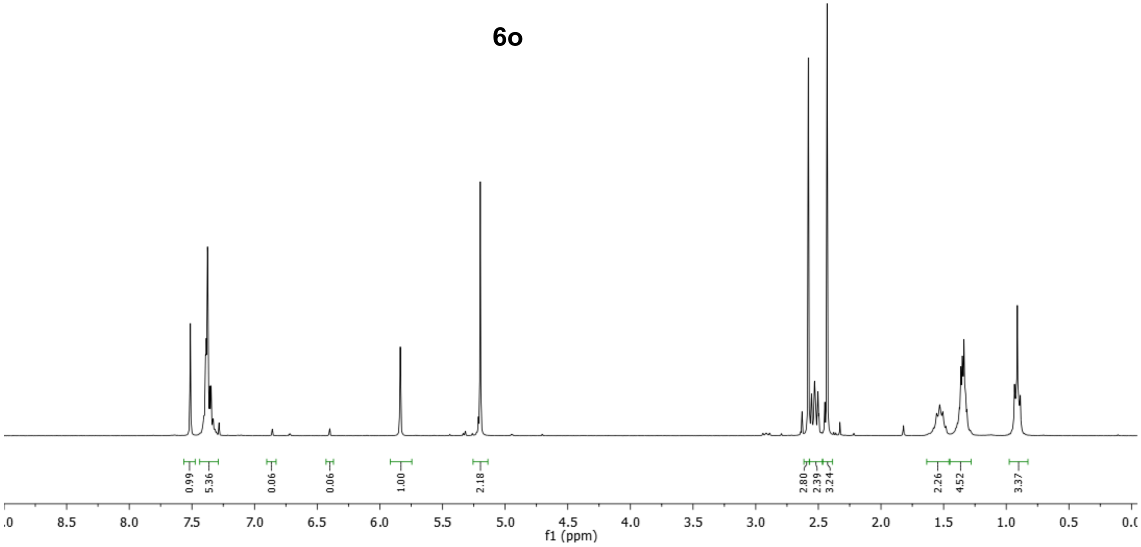

Me
O
Me
O
Ph
^{t}BuO$_2$C
5.12
0.20
0.93
0.05
0.06
0.94
0.19
2.90
3.00
0.20
9.24
0.67
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)

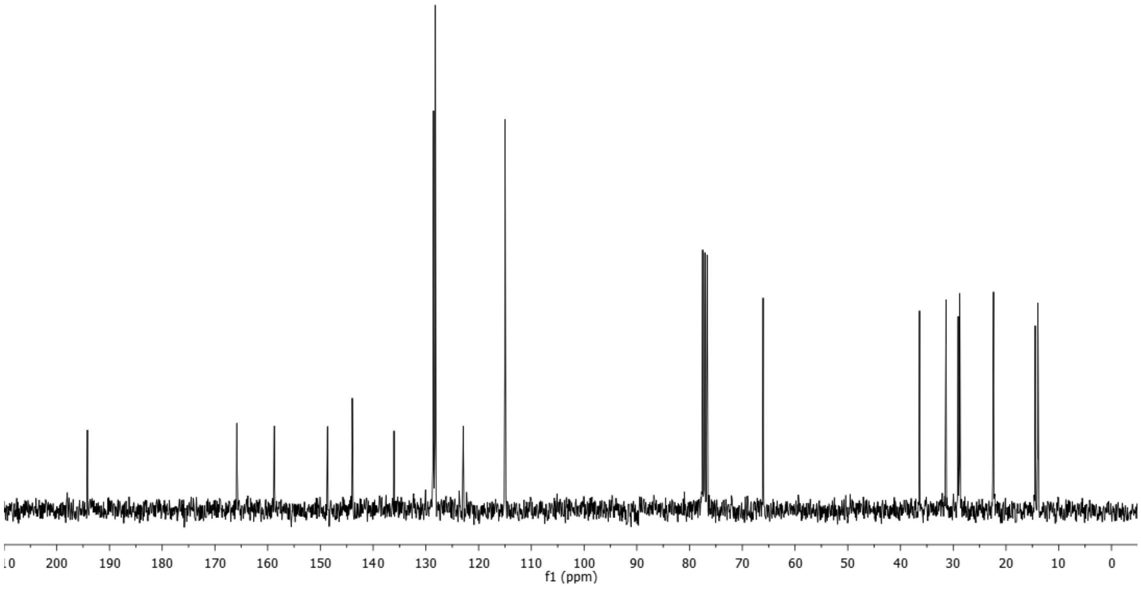
6n

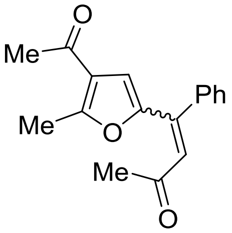

.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Me
Me
Me
O
BnO$_2$C

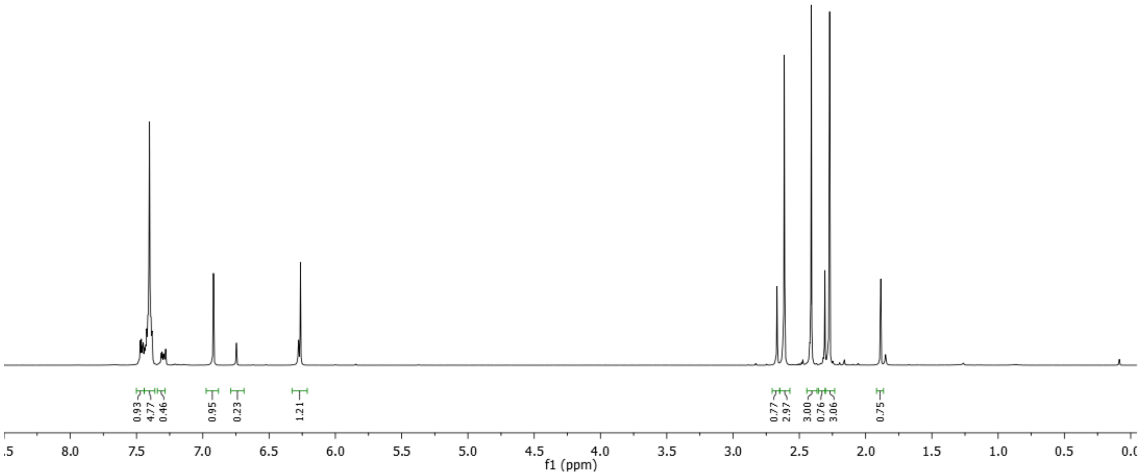
6o

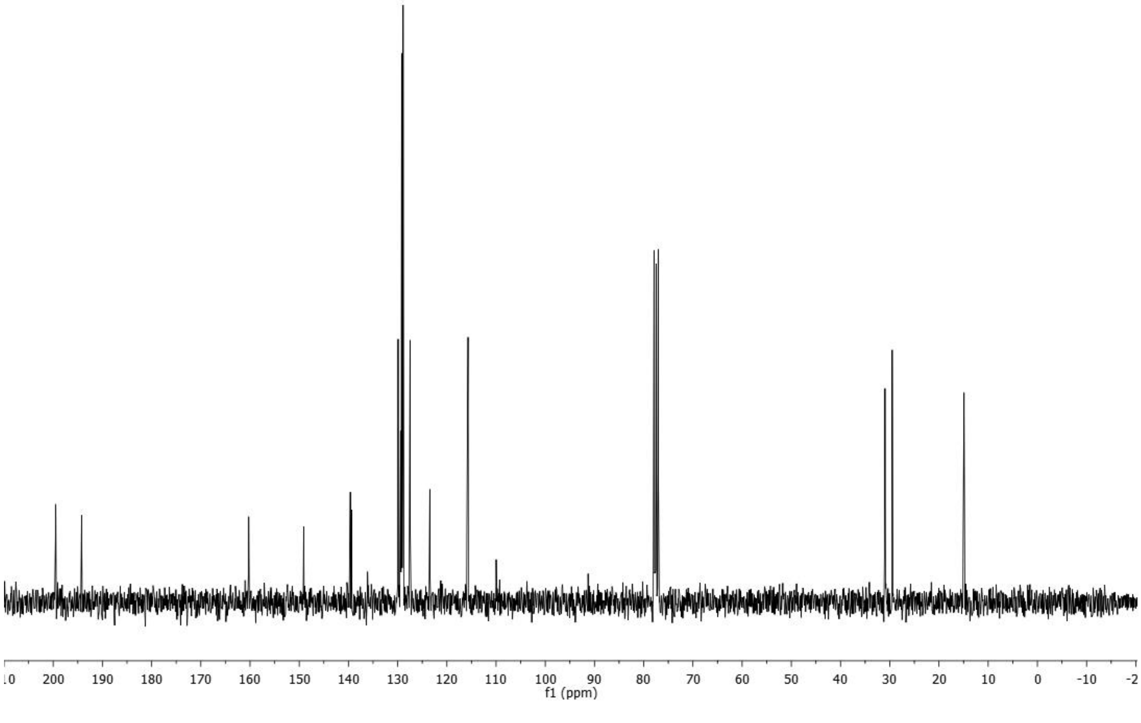

0.99
5.36
0.06
0.06
1.00
2.18
2.80
2.39
3.24
2.26
4.52
3.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

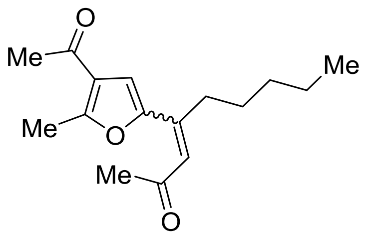

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Me
Ph
Me
O
Me
O

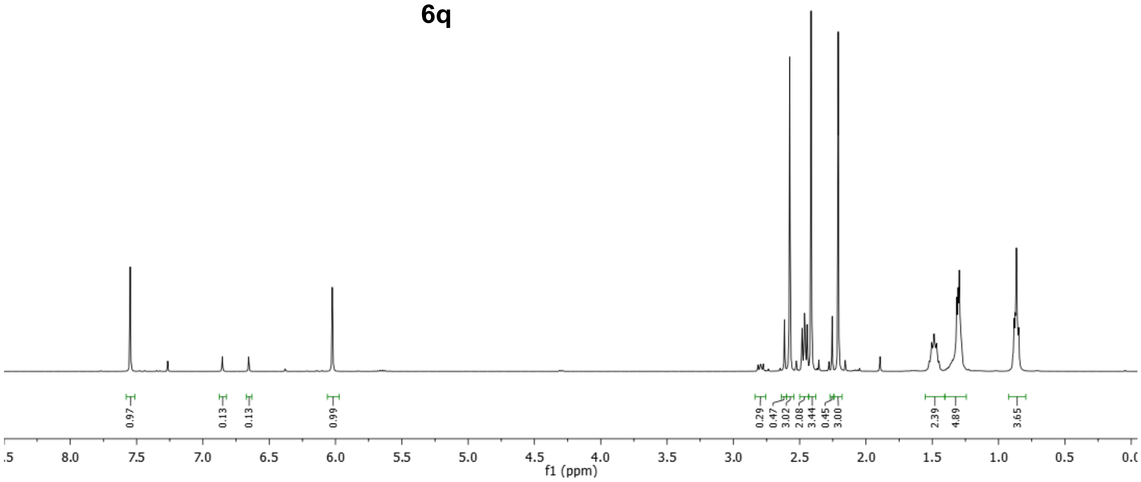
6p

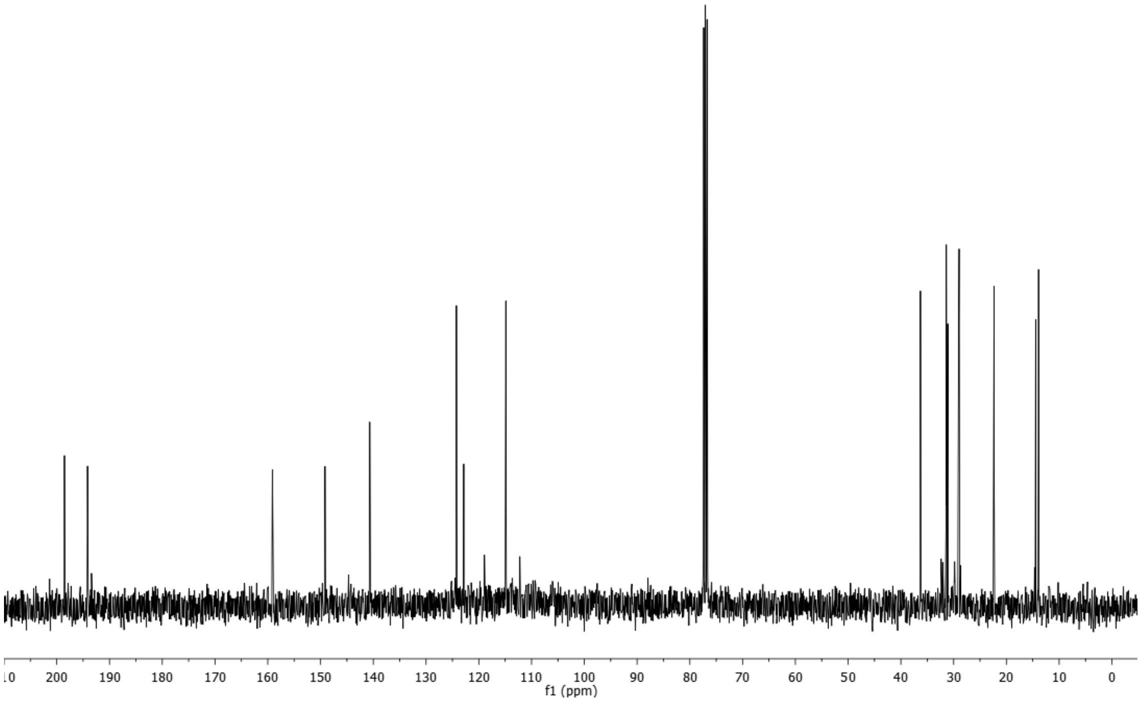

0.93
4.77
0.46
0.95
0.23
1.21
0.77
2.97
3.00
0.76
3.06
0.75
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

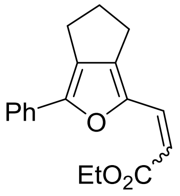

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
Me
Me
O
Me
O
O

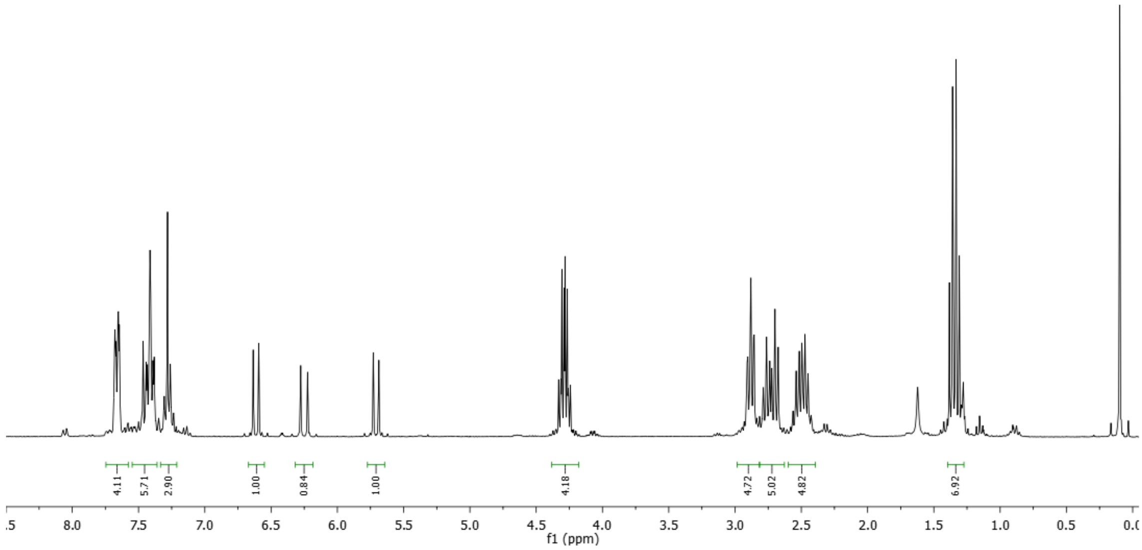
6q

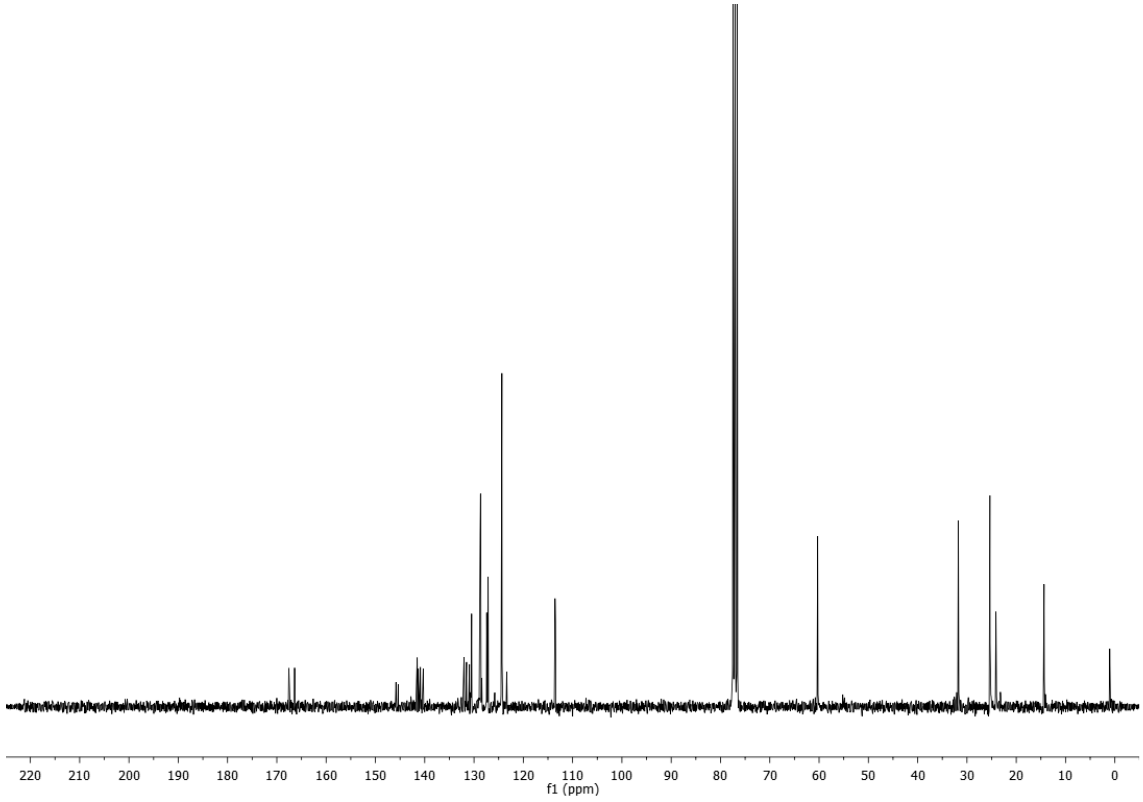

0.97
0.13
0.13
0.99
0.29
0.47
3.02
2.08
3.44
0.45
3.00
2.39
4.89
3.65
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)

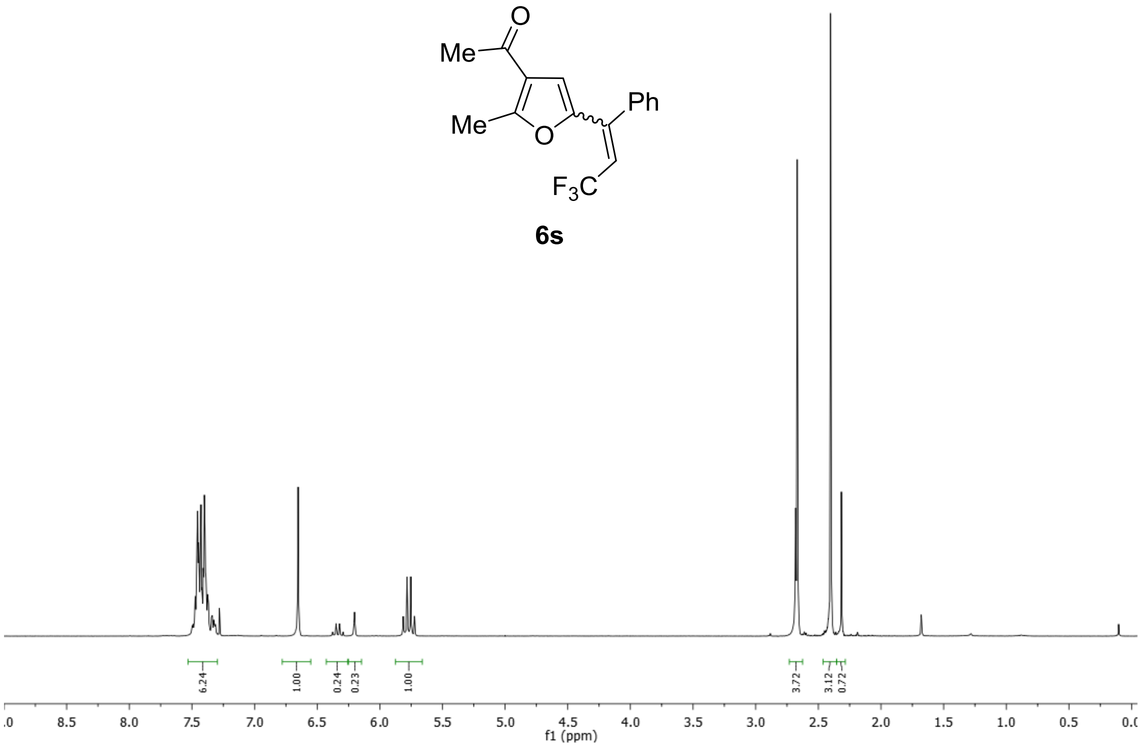

.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
O
EtO$_2$C

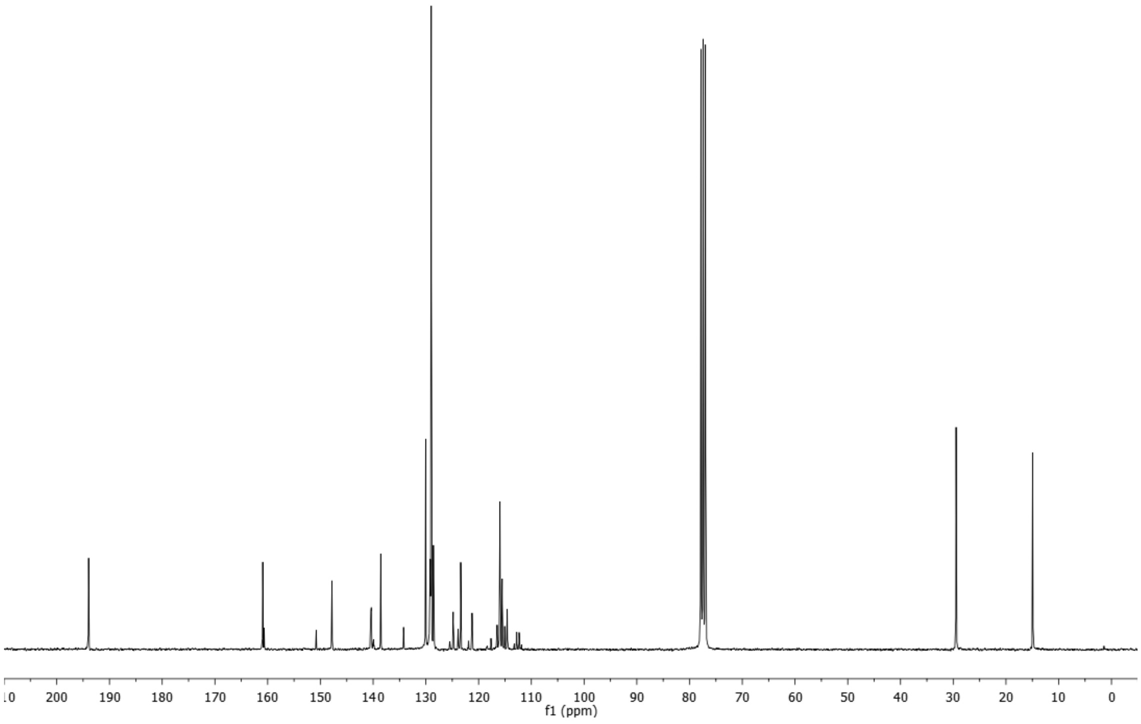
6r


4.11
5.71
2.90
1.00
0.84
1.00
4.18
4.72
5.02
4.82
6.92
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

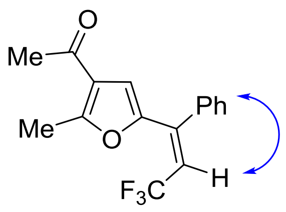

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6s

Me
O
Me
O
Ph
F3C
6.24
1.00
0.24
0.23
1.00
3.72
3.12
0.72
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)

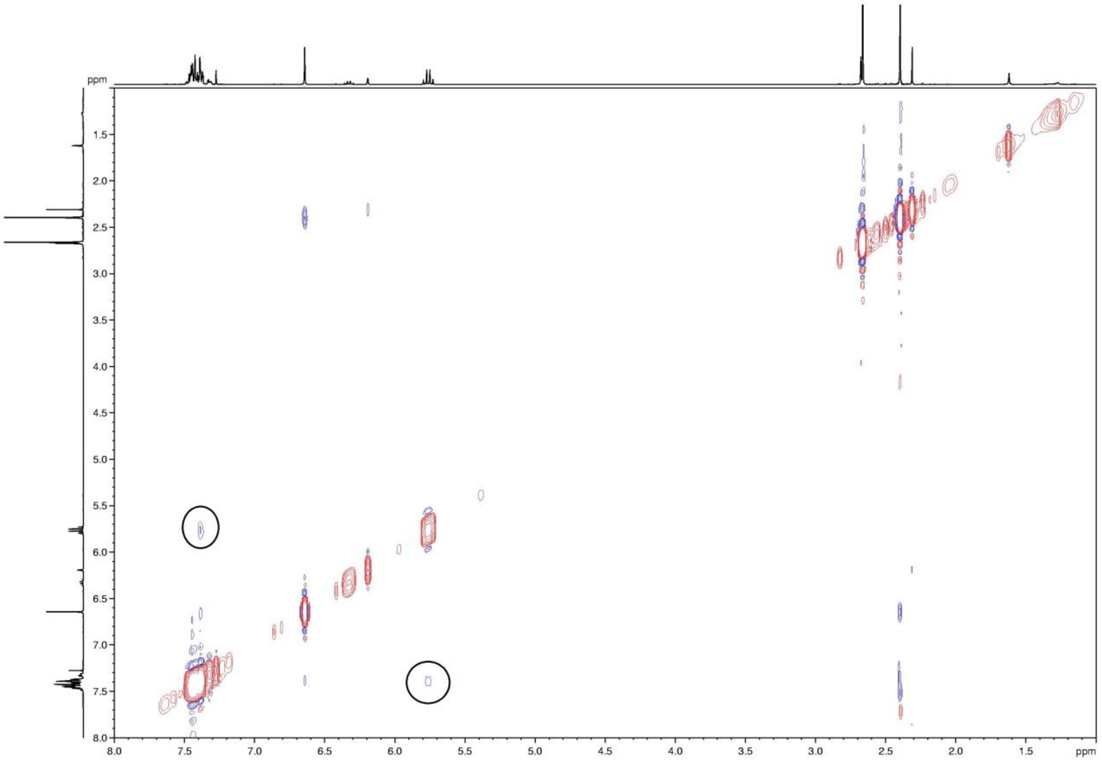


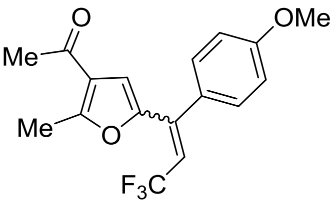
.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



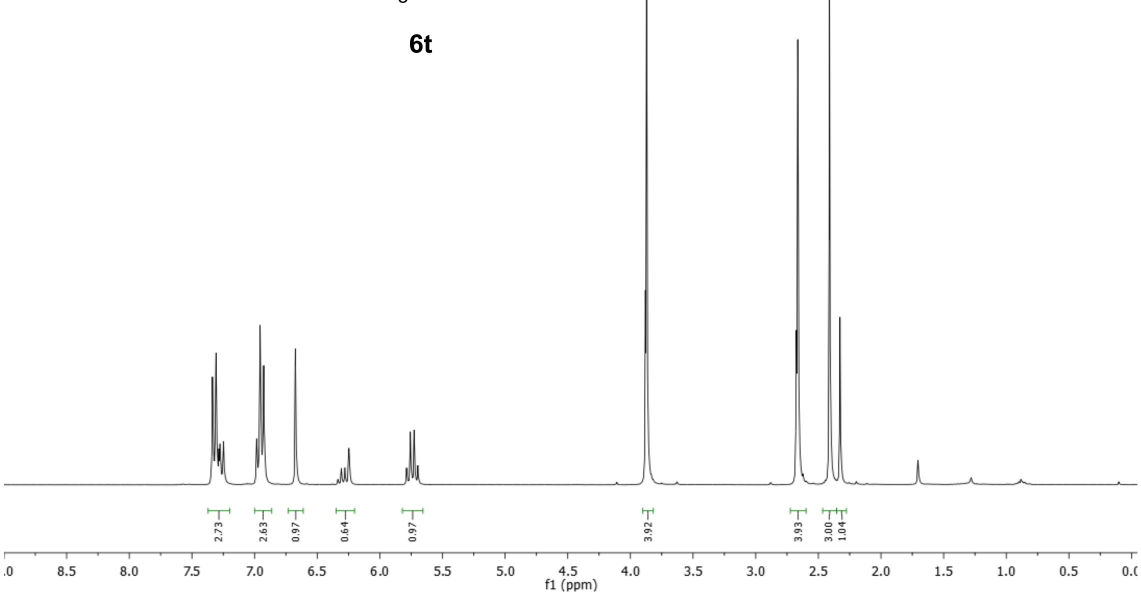
6s

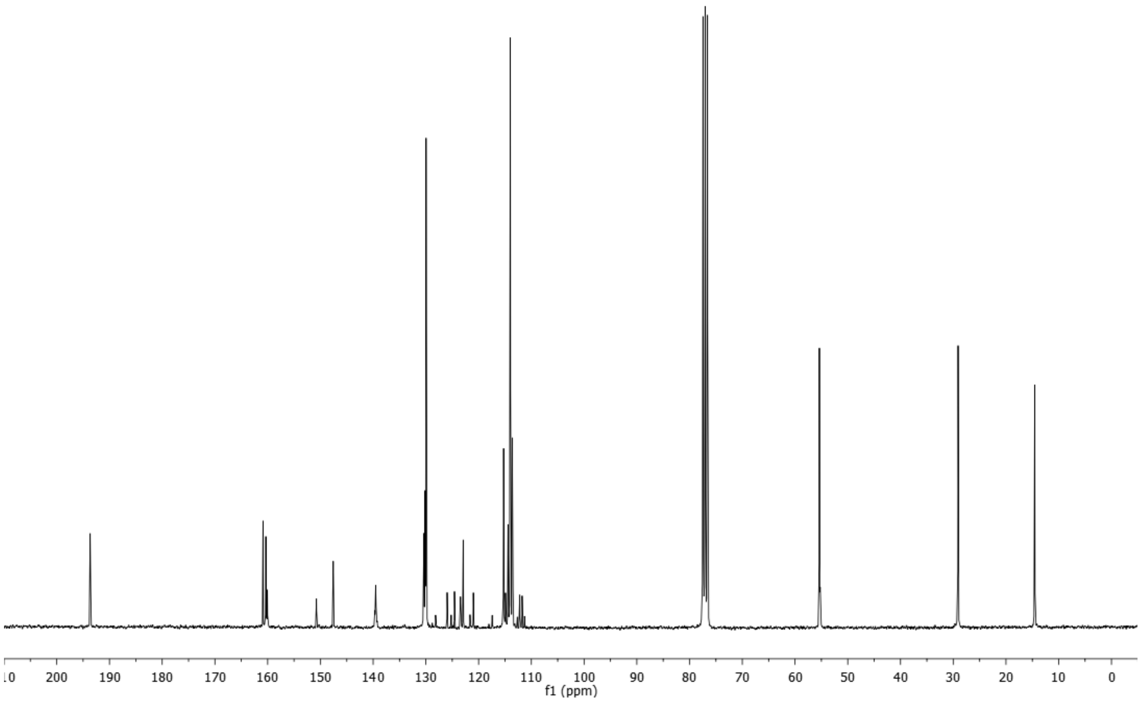
Z-isomer (major isomer)

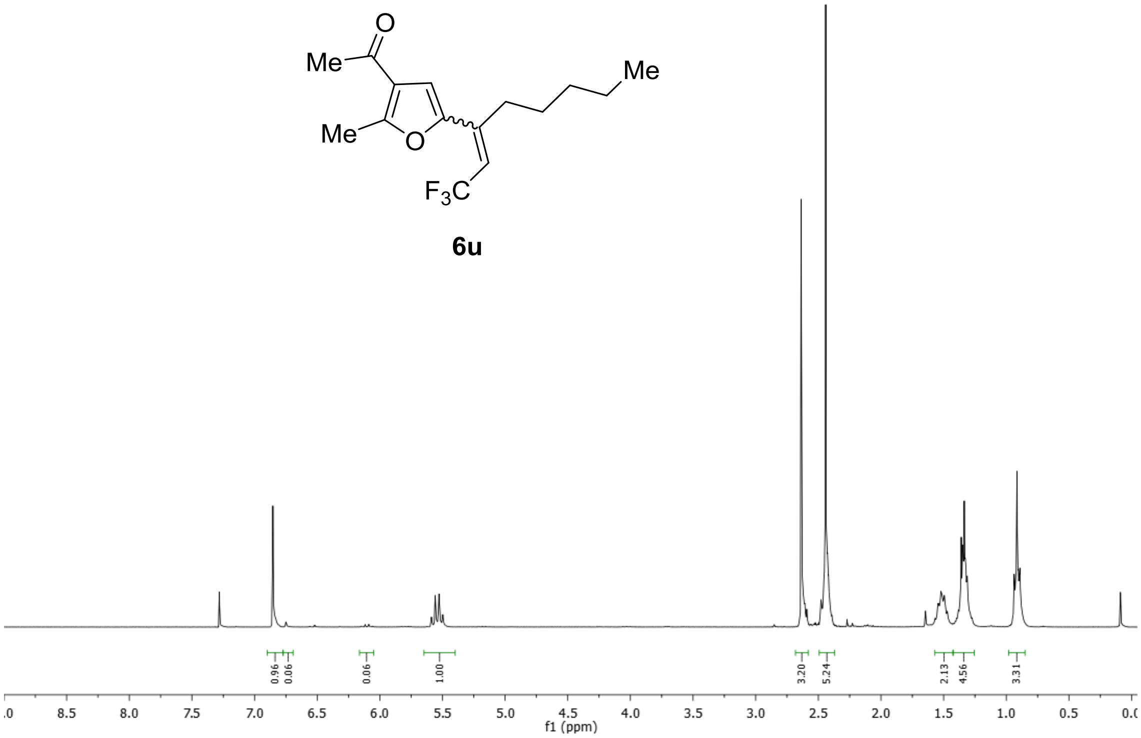



O
Me
OMe
Me
O
F3C

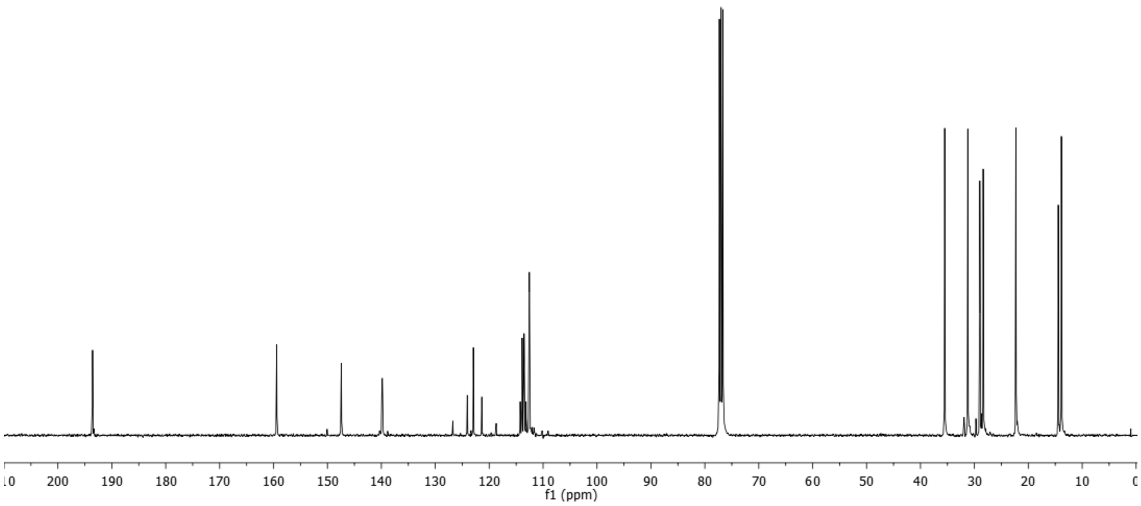
6t

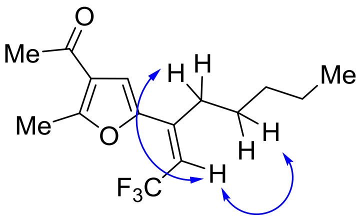

2.73
2.63
0.97
0.64
0.97
3.92
3.93
3.00
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

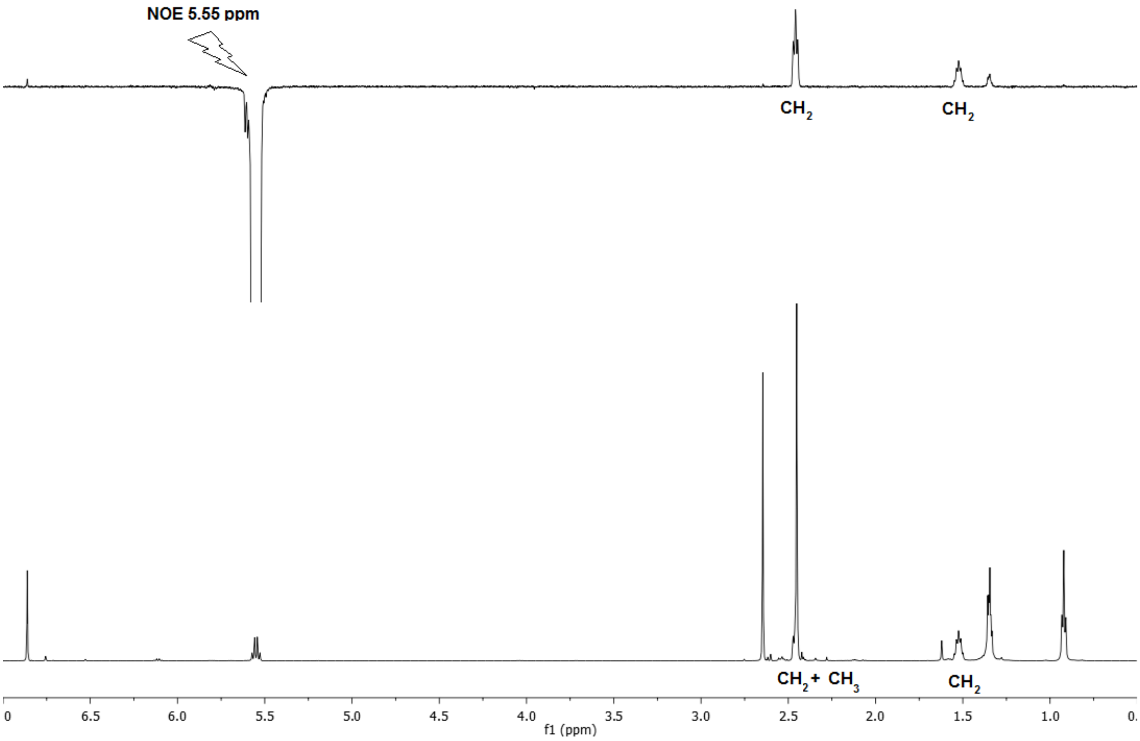

Me
O
Me
Me
O
F3C
0.96
0.06
0.06
1.00
3.20
5.24
2.13
4.56
3.31
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)

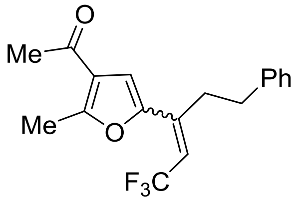
6u


.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(
f1 (ppm)

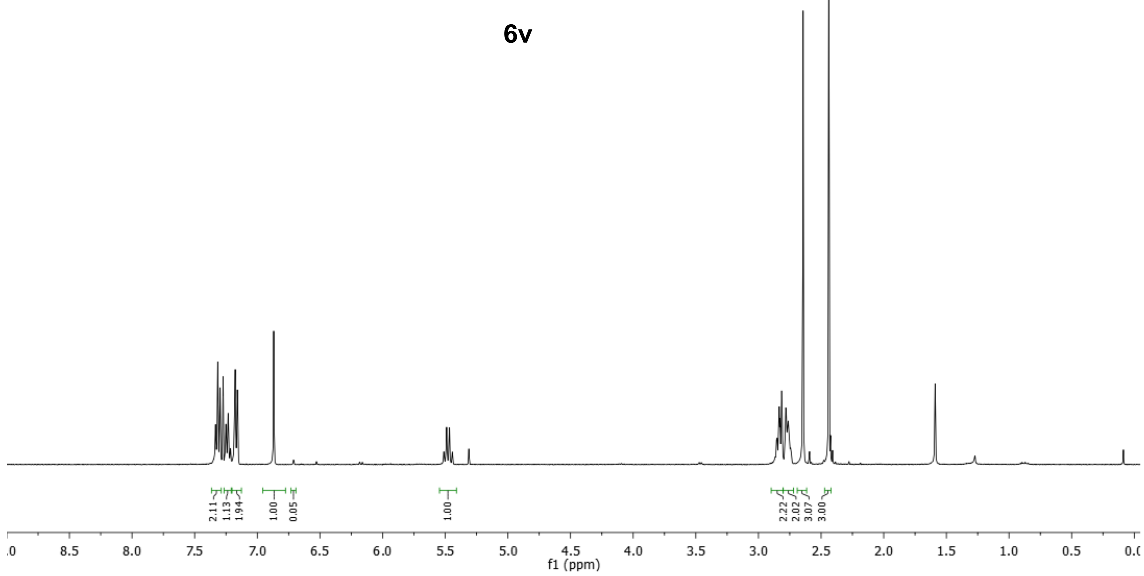

O
Me
Me
O
H
H
Me
H
H
F3C
H

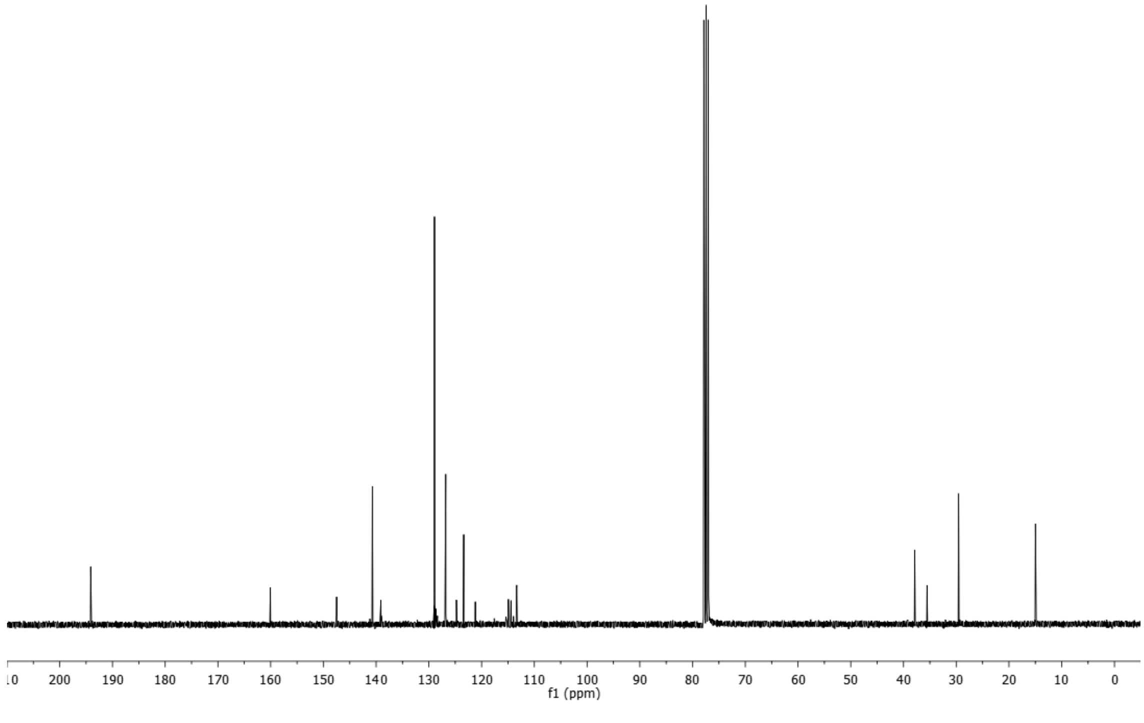
6u


NOE 5.55 ppm
CH2
CH2
CH2 + CH3
CH2
0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)


O
Me
Ph
Me
O
F3C

6v


2.11
1.13
1.94
1.00
0.05
1.00
2.22
2.02
3.07
3.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.(
f1 (ppm)


.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)