Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

## Zinc-mediated CH-activation of tetrahydrofuran under mild conditions for the regioselective addition to aryl-propiolates

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## Content



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## Experimental

### General

All experiments were carried out under an atmosphere of argon in dried flasks and anhydrous solvents. All used reagents and reactants were purchased and used as received or previously synthesized. The solvents were dried using common procedures, distilled and then stored over molecular sieves (MS 4Å) under an atmosphere of argon.

### General procedure for the CH-activation of THF

**A:** Zinc powder (99.999% purity; 78.5 mg; 1.2 mmol), 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (256 mg, 1.0 mmol) and *p*-toluenesulfonic acid monohydrate (3.8 mg, 0.02 mmol) were dissolved in 1.0 mL of THF and after stirring for 2 minutes at room temperature the alkyne (0.40 mmol) was added. The reaction mixture was then stirred at 40 °C until either alkyne or dibromocyclopropane were consumed. The reaction was monitored by GC/MS spectroscopy and after complete conversion the mixture was cooled to 0 °C, 2 mL of 1 M HCl were added, stirred for 15 min, warmed to room temperature, diluted with water (20 mL) and extracted three times with diethyl ether. The organic layers were combined, dried over magnesium sulphate, the solvent was evaporated and the crude product was purified by column chromatography to give the pure alkenes and in some cases unconsumed alkyne.

**B:** Iron(II)bromide (10 Mol%), zinc powder (≥98.5% purity; 3.0 eq.), 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (2.0 eq.) and triphenylphosphine (15 Mol%) were dissolved in THF (0.4 M) and conc. hydrobromic acid (2 µL/mmol alkyne) was added. The mixture was stirred for 2 minutes at room temperature before the alkyne (1.0 eq.) was added. The reaction mixture was then stirred at 40 °C until either alkyne or dibromocyclopropane were consumed. The reaction was monitored by GC/MS spectroscopy and after complete conversion the mixture was cooled to 0 °C, 4 mL of 1 M HCl (4.0 eq.) were added, stirred for 15 min, warmed to room temperature, diluted with water (30 mL) and extracted three times with diethyl ether. The organic layers were combined, dried over magnesium sulphate, the solvent was evaporated and the crude product was purified by column chromatography to give the pure alkenes and in some cases unconsumed alkyne; or (without quenching) passed through a short pad of silica and then purified by column chromatography.

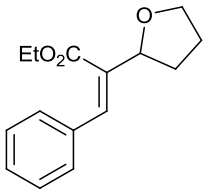
Note: To all reported eluents 1% of dichloromethane was added.

**Synthesis of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane**

The synthesis of dibromocyclopropane **5** was performed adopting a protocol published by *Spyvee*.[1] To a solution of 2,3-dimethylbutene (4.21 g, 50.0 mmol) in *n*-pentane (15 mL) potassium *tert*-butylate (6.17 g, 55.0 mmol) was added and the mixture was cooled to 0 °C. Then $CHBr_3$ (4.6 mL, 52.5 mmol) was added dropwise over a period of 20 min. The mixture was stirred for 1 h at 0 °C and 1 h at room temperature. The reaction mixture was then diluted with *n*-pentane (75 mL) and washed with water. The organic phase was dried over magnesium sulphate, the solvent was evaporated, and the residue was purified by column chromatography using *n*-pentane as eluent to give the desired product as white crystals (10.5 g, 41.0 mmol, 82%).

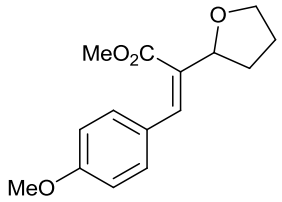
[1] C. Frost, P. Linnane, P. Magnus, M. Spyvee *Tetrahedon Lett.* **1996**, *51*, 9139-9142.

**Synthesis of ethyl 3-phenyl-2-(tetrahydrofuran-2-yl)acrylate (6a)**



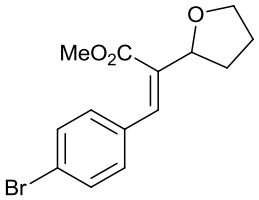

The title compound was prepared according to the general procedure **A** from ethyl 3-phenylpropiolate (69.7 mg, 0.40 mmol) and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 11:1) as colorless oil (81.1 mg, 0.33 mmol, 82%, *E*/*Z* = 38:62). $^1$H NMR data of the *E*-isomer: **$^1$H NMR (300 MHz, $CDCl_3$)**: δ = 7.73 (s, 1 H), 7.42-7.22 (m, 5H), 4.88 (dd, *J* = 8.2, 7.7 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.08-3.95 (m, 1H), 3.92-3.77 (m, 1H), 2.37-1.87 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 3H). $^1$H NMR data of the *Z*-isomer: **$^1$H NMR (300 MHz, $CDCl_3$)**: δ = 7.42-7.22 (m, 5H), 6.88 (d, *J* = 1.4 Hz, 1H), 4.77-4.70 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.08-3.95 (m, 1H), 3.92-3.77 (m, 1H), 2.37-1.87 (m, 4H), 1.12 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 168.4, 167.0, 141.2, 135.7, 135.0, 133.7, 131.4, 129.2, 128.4, 128.3 (2 C), 128.0, 127.8, 79.5, 74.9, 69.1, 68.7, 60.6, 60.5, 31.7, 31.1, 27.2, 25.6, 14.2, 13.7, (1 $C_{sp2}$ is overlapping and not resolved). **IR (film):** 2977, 2873, 1711, 1637, 1491, 1449, 1377, 1294, 1234, 1205, 1127, 1056, 1027, 928, 870, 753, 696, 480. **MS (EI):** *m*/*z* (%) = 246 ([$M^+$], 4), 200 (7), 173 (100), 131 (30), 115 (9), 103 (11). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{15}H_{18}O_3$+$Na^+$: 269.1159; found: 269.1147.

**Synthesis of methyl 3-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)acrylate (6b)**




The title compound was prepared according to the general procedure **A** from methyl 3-(4-methoxyphenyl)propiolate (76.1 mg, 0.40 mmol) and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 8:1 to 5:1) as colorless oil (78.4 mg, 0.30 mmol, 75%, *E*/*Z* = 47:53). NMR data of the mixture of isomers: **$^{1}$H NMR (300 MHz, CDCl$_3$)**: δ = 7.69 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6,80 (s, 1H), 4.92 (t, *J* = 7.9 Hz, 1H), 4.73-4.66 (m, 1H), 4.10-4.01 (m, 2 H), 3.90-3.80 (m, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.80 (s, 3H), 3.69 (s, 3H), 2.35-1.88 (m, 8H). **$^{13}$C NMR (75 MHz, CDCl$_3$)**: δ = 169.2, 167.5, 160.0, 159.5, 141.5, 133.1, 131.6, 131.5, 131.0, 129.9, 127.9, 127.3, 113.8, 113.6, 79.8, 74.9, 69.0, 68.7, 55.3, 55.2, 51.6, 51.5, 31.8, 30.9, 27.2, 25.6. **IR (film):** 2951, 2875, 1713, 1605, 1510, 1440, 1384, 1302, 1248, 1176, 1126, 1032, 979, 928, 828, 753, 665, 522. **MS (EI):** *m*/*z* (%) = 262 ([M$^+$], 6), 230 (6), 203 (100), 161 (28). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{15}H_{18}O_4$+Na$^+$: 285.1097; found: 285.1095.

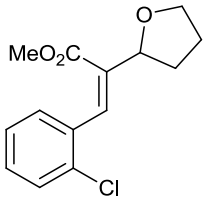
**Synthesis of methyl 3-(4-bromophenyl)-2-(tetrahydrofuran-2-yl)acrylate (6c)**




The title compound was prepared according to the general procedure **A** from methyl 3-(4-bromophenyl)propiolate (95.6 mg, 0.40 mmol) and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 11:1) as colorless oil (98.0 mg, 0.31 mmol, 79%, *E*/*Z* = 35:65). $^{1}$H NMR data of the *E*-isomer: **$^{1}$H NMR (300 MHz, CDCl$_3$)**: δ = 7.63 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 4.80 (t, *J* = 7.9 Hz, 1H), 4.05-3.94 (m, 1H), 3.80 (s, 3H), 3.83-3.75 (m, 1H), 2.31-1.85 (m, 4H). $^{1}$H NMR data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, CDCl$_3$)**: δ = 7.43 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.81 (s, 1H), 4.74-4.67 (m, 1H), 4.05-3.94 (m, 1H), 3.91-3.83 (m, 1H), 3.67 (s, 3H), 2.31-1.85 (m, 4H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, CDCl$_3$)**: δ = 168.5, 167.1, 140.1, 136.0, 134.6, 134.1, 133.7, 131.5, 131.3, 130.7, 130.6, 129.9, 122.8, 122.0, 79.3, 74.8,

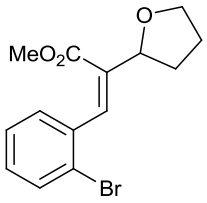
69.1, 68.7, 51.7 (2 C), 31.7, 31.1, 27.1, 25.6. **IR (film):** 2951, 2873, 1716, 1638, 1586, 1486, 1437, 1380, 1335, 1209, 1128, 1058, 1011, 977, 911, 816, 729, 648, 494. **MS (EI):** *m*/*z* (%) = 310 ([$M^+$], 5), 251 (100), 209 (39), 199 (32), 115 (35), 102 (37), 71 (30). **HR-MS (EI):** *m*/*z* (%) = calculated for $C_{14}H_{15}O_3Br$: 310.0205; found: 310.0196.

**Synthesis of methyl 3-(2-chlorophenyl)-2-(tetrahydrofuran-2-yl)acrylate** (**6d**)




The title compound was prepared according to the general procedure **A** from methyl 3-(2-chlorophenyl)propiolate (77.8 mg, 0.40 mmol) and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 10:1) as colorless oil (91.0 mg, 0.34 mmol, 85%, *E*/*Z* = 32:68). $^1$H NMR data of the *E*-isomer: **$^1$H NMR (300 MHz, CDCl$_3$)**: δ = 7.83 (s, 1H), 7.50-7.20 (m, 4H), 4.77 (t, *J* = 7.9 Hz, 1H), 4.15-3.91 (m, 1H), 3.88 (s, 3H), 3.87-3.79 (m, 1H), 2.37-1.88 (m, 4H). $^1$H NMR data of the *Z*-isomer: **$^1$H NMR (300 MHz, CDCl$_3$)**: δ = 7.50-7.20 (m, 4H), 7.15 (d, *J* = 1.5, 1H), 4.93-4.86 (m, 1H), 4.15-3.91 (m, 2H), 3.64 (s, 3H), 2.37-1.88 (m, 4H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, CDCl$_3$)**: δ = 167.8, 166.7, 138.7, 137.0, 134.9, 134.7, 133.8, 133.7, 133.1, 130.5, 130.4, 129.7, 129.5, 129.4, 129.1, 128.9, 126.4, 126.2, 78.7, 75.3, 69.0, 68.7, 51.8, 51.5, 31.9, 31.1, 27.0, 25.3. **IR (film):** 2951, 2875, 1717, 1642, 1436, 1376, 1330, 1236, 1207, 1126, 1055, 980, 913, 832, 737, 694, 647, 610, 544, 454. **MS (EI):** *m*/*z* (%) = 266 ([$M^+$], 1), 231 (67), 207 (100), 165 (39), 101 (18). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{14}H_{15}ClO_3$+$Na^+$: 289.0602; found: 289.0603.

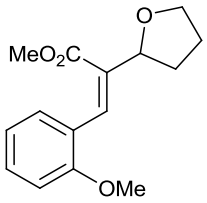
**Synthesis of methyl 3-(2-bromophenyl)-2-(tetrahydrofuran-2-yl)acrylate** (**6e**)




The title compound was prepared according to the general procedure **A** from methyl 3-(2-bromophenyl)propiolate (95.6 mg, 0.40 mmol) and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 11:1) as colorless oil (106 mg, 0.34 mmol, 85%, *E*/*Z* = 26:74). $^1$H NMR data of the *E*-isomer: **$^1$H NMR (300 MHz, CDCl$_3$)**: δ = 7.71 (s, 1H),

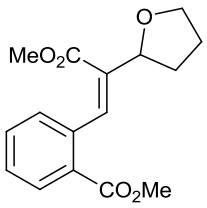
7.59 (d, *J* = 7.9 Hz, 1H), 7.24-7.09 (m, 3H), 4.69 (t, *J* = 7.9 Hz, 1H), 4.00-3.85 (m, 1H), 3.82 (s, 3H), 3.80-3.72 (m, 1H), 2.30-1.81 (m, 4H). $^{1}$H NMR data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 7.55 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.33-7.29 (m, 1H), 7.24-7.09 (m, 2H), 7.04 (d, *J* = 1.3, 1H), 4.84 (ddd, *J* = 6.7, 5.4, 1.4 Hz, 1H), 4.10-4.01 (m, 1H), 4.00-3.85 (m, 1H), 3.56 (s, 3H), 2.30-1.81 (m, 4H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 167.6, 166.7, 140.8, 136.9, 136.8, 135.6, 134.4, 132.7, 132.5, 132.3, 130.5, 129.8, 129.5, 129.1, 127.0, 126.8, 123.7, 123.2, 78.6, 75.3, 69.0, 68.7, 51.8, 51.5, 31.8, 31.1, 27.0, 25.3. **IR (film):** 2951, 2874, 1716, 1642, 1434, 1375, 1329, 1238, 1206, 1126, 1057, 1028, 980, 911, 832, 731, 665, 611, 445. **MS (EI):** *m*/*z* (%) = 310 ([$M^+$], 1), 251 (60), 231 (100), 209 (25), 115 (22), 102 (25). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{14}H_{15}BrO_3$+$Na^+$: 333.0097; found: 333.0095.

**Synthesis of methyl 3-(2-methoxyphenyl)-2-(tetrahydrofuran-2-yl)acrylate** (**6f**)



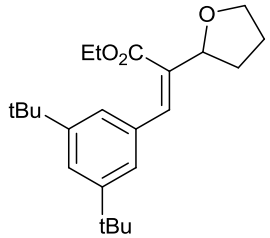

The title compound was prepared according to the general procedure **A** from methyl 3-(2-methoxyphenyl)propiolate (76.1 mg, 0.40 mmol) and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 8:1 to 5:1) as colorless oil (93.6 mg, 0.36 mmol, 890%, *E*/*Z* = 35:65). $^{1}$H NMR data of the *E*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 7.87 (s, 1H), 7.36-7.26 (m, 1H), 7.23 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.91-6.83 (m, 1H), 4.83 (t, *J* = 7.9 Hz, 1H), 4.08-3.96 (m, 1H), 3.91-3.76 (m, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.34-1.83 (m, 4H). $^{1}$H NMR data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 7.36-7.26 (m, 1H), 7.18 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.04 (s, 1H), 6.91-6.83 (m, 2H), 4.79-4.73 (m, 1H), 4.08-3.96 (m, 1H), 3.91-3.76 (m, 1H), 3.81 (s, 3H), 3.61 (s, 3H), 2.34-1.83 (m, 4H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 168.8, 167.1, 157.5, 156.9, 138.4, 135.0, 132.7, 130.3, 130.2, 129.3, 128.5, 124.9, 123.9, 120.1 (2 C), 110.4, 79.6, 75.3, 69.0, 68.6, 55.4, 55.3, 51.5, 51.3, 31.8, 30.8, 27.2, 25.6 (2 $C_{sp2}$ are overlapping and are not resolved). **IR (film):** 2950, 2875, 1714, 1637, 1595, 1441, 1383, 1296, 1242, 1123, 1053, 980, 918, 749, 491. **MS (EI):** *m*/*z* (%) = 262 ([$M^+$], 4), 230 (9), 203 (100), 161 (21), 131 (17), 115 (12). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{15}H_{18}O_4$+$Na^+$: 285.1097; found: 285.1096.

**Synthesis of methyl 2-(3-methoxy-3-oxo-2-(tetrahydrofuran-2-yl)prop-1-enyl)benzoate (6g)**




The title compound was prepared according to the general procedure **A** from methyl 2-(3-methoxy-3-oxoprop-1-ynyl)benzoate (87.3 mg, 0.40 mmol) and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 3:1) as slightly yellow oil (99.9 mg, 0.34 mmol, 86%, *E*/*Z* = 29:71). $^{1}$H NMR data of the *E*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 8.16 (s, 1H), 8.04 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.53 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.48-7.29 (m, 2H), 4.58 (dd, *J* = 8.0, 7.8 Hz, 1H), 3.96-3.87 (m, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.76-3.67 (m, 1H), 2.31-1.76 (m, 4H). $^{1}$H NMR data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 8.00 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.50 (s, 1H), 7.48-7.29 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 4.88 (ddd, *J* = 6.9, 5.6, 1.4 Hz, 1H), 4.13-4.04 (m, 1H), 3.96-3.87 (m, 1H), 3.87 (s, 3H), 3.48 (s, 3H), 2.31-1.76 (m, 4H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 167.8 (2 C), 167.0, 166.9, 142.7, 139.1, 137.2, 135.3, 134.3, 132.0, 131.9, 131.7, 130.6, 130.3, 130.2, 129.5, 128.8, 128.2, 128.1, 127.4, 78.5, 75.5, 68.9, 68.7, 52.2, 52.0, 51.7, 51.2, 31.9, 31.1, 27.0, 25.3. **IR (film):** 2952, 2875, 2252, 1714, 1642, 1599, 1569, 1436, 1374, 1257, 1203, 1127, 1057, 965, 913, 824, 727, 648, 614, 523. **MS (EI):** *m*/*z* (%) = 258 ([$M^+$-MeOH], 3), 219 (100), 199 (48), 174 (13), 157 (18), 115 (13), 71 (13). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{16}H_{18}O_5$+$Na^+$: 313.1046; found: 313.1042.

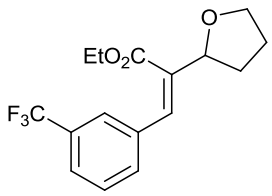
**Synthesis of ethyl 3-(3,5-di-tert-butylphenyl)-2-(tetrahydrofuran-2-yl)acrylate (6h)**




The title compound was prepared according to the general procedure **B** from ethyl ethyl 3-(3,5-di-tert-butylphenyl)propiolate (143 mg, 0.50 mmol), which was stirred for 32 h and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 15:1) as colorless oil (133 mg, 0.37 mmol, 74%, *E*/*Z* = 44:56). $^{1}$H NMR data of the *E*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 7.76 (s, 1H), 7.39 (t, *J* = 1.7 Hz, 1H), 7.18 (d, *J* = 1.4 Hz,

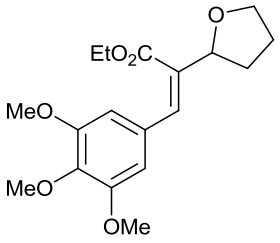
2H), 4.88 (dd, *J* = 8.2, 7.7 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.20-3.98 (m, 1H), 3.79 (ddd, *J* = 7.7, 7.6, 5.1 Hz, 1H), 2.43-2.31 (m, 1H), 2.26-1.85 (m, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.33 (s, 18H). $^{1}$H NMR data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, CDCl$_3$)**: δ = 7.32 (t, *J* = 1.8 Hz, 1H), 7.13 (d, *J* = 1.6 Hz, 2H), 6.85 (s, 1H), 4.75-4.69 (m, 1H), 4.20-3.98 (m, 3H), 3.93-3.84 (m, 1H), 2.26-1.85 (m, 4H), 1.30 (s, 18H), 1.11 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, CDCl$_3$)**: δ = 168.9, 167.2, 150.6, 150.4, 142.6, 135.0, 134.8, 134.1, 132.9, 132.1, 123.6, 122.6 (2 C), 122.1, 79.8, 75.2, 69.1, 68.7, 60.6, 60.5, 34.8 (2 C), 31.6, 31.4 (2 C), 31.2, 27.3, 25.6, 14.3, 13.9. **IR (film):** 2960, 2871, 2250, 1714, 1634, 1593, 1468, 1366, 1329, 1242, 1202, 1124, 1058, 911, 875, 769, 730, 647, 517. **MS (EI):** *m*/*z* (%) = 358 ([M$^+$], 1), 285 (100), 269 (15), 255 (30), 57 (54). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{23}H_{34}O_3$+Na$^+$: 381.2400; found: 381.2392.

**Synthesis of ethyl 2-(tetrahydrofuran-2-yl)-3-(3-(trifluoromethyl)phenyl)acrylate** (**6i**)



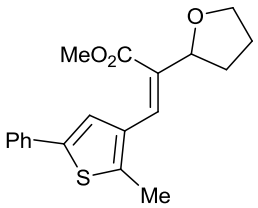

The title compound was prepared according to the general procedure **B** from ethyl ethyl 3-(3-(trifluoromethyl)phenyl)propiolate (121 mg, 0.50 mmol), which was stirred for 20 h and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 12:1) as colorless oil (107 mg, 0.34 mmol, 68%, *E*/*Z* = 35:65). $^{1}$H NMR data of the *E*-isomer: **$^{1}$H NMR (300 MHz, CDCl$_3$)**: δ = 7.70 (s, 1H), 7.61-7.38 (m, 4H), 4.81-4.73 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.05-3.96 (m, 1H), 3.83-3.75 (m, 1H), 2.34-1.88 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 3H). $^{1}$H NMR data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, CDCl$_3$)**: δ = 7.61-7.38 (m, 4H), 6.93 (d, *J* = 1.3 Hz, 1H), 4.81-4.73 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.05-3.96 (m, 1H), 3.93-3.85 (m, 1H), 2.34-1.88 (m, 4H), 1.10 (t, *J* = 7.1 Hz, 3H). **$^{19}$F NMR (300 MHz, CDCl$_3$)**: δ = −63.63 (s, *Z*-isomer), −63.68 (s, *E*-isomer). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, CDCl$_3$)**: δ = 167.7, 166.6, 139.1, 137.6, 136.7, 135.8, 135.5, 132.2, 131.6, 131.5, 131.1-130.3 (m, 2 C), 130.0, 128.7, 128.5, 125.9 (q, *J* = 4.0 Hz, 1 C), 125.2-124.9 (m, 2 C), 124.3 (q, *J* = 3.7 Hz, 1 C), 122.2, 79.1, 75.0, 69.1, 68.8, 60.9, 60.8, 31.8, 31.3, 27.0, 25.6, 14.2, 13.7. **IR (film):** 2980, 2876, 1715, 1644, 1444, 1378, 1328, 1289, 1206, 1166, 1123, 1061, 914, 866, 802, 733, 700, 659, 510, 450, 409. **MS (EI):** *m*/*z* (%) = 314 ([M$^+$], 1), 241 (100), 199 (43), 171 (13), 151 (14), 71 (14). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{16}H_{17}F_3O_3$+Na$^+$: 337.1022; found: 337.1015.

**Synthesis of ethyl 2-(tetrahydrofuran-2-yl)-3-(3,4,5-trimethoxyphenyl)acrylate (6j)**




The title compound was prepared according to the general procedure **B** from ethyl 3-(3,4,5-trimethoxyphenyl)propiolate (132 mg, 0.50 mmol), which was stirred for 48 h and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 3:1) as slightly yellow oil (97.8 mg, 0.29 mmol, 58%, *E*/*Z* = 54:46). $^{1}$H NMR data of the *E*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 7.65 (s, 1H), 6.61 (s, 2H), 4.88 (t, *J* = 7.9 Hz, 1H), 4.26 (dq, *J* = 7.1, 1.1 Hz, 2H), 4.10-3.75 (m, 2H), 3.86 (s, 3H), 3.85 (s, 6H), 2.37-1.86 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H). $^{1}$H NMR data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 6.77-6.75 (m, 1H), 6.55 (s, 2H), 4.73-4.67 (m, 1H), 4.16 (dq, *J* = 7.1, 1.4 Hz, 2H), 4.10-3.75 (m, 2H), 3.83 (s, 3H), 3.82 (s, 6H), 2.37-1.86 (m, 4H), 1.16 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 168.6, 167.0, 152.9, 152.8, 141.6, 138.4, 138.0, 135.5, 133.2, 131.2, 130.8, 130.3, 106.6, 105.6, 79.5, 75.0, 69.0, 68.7, 60.9, 60.8, 60.7, 60.6, 56.1, 56.0, 31.6, 30.9, 27.2, 25.6, 14.2, 13.9. **IR (film):** 2943, 2877, 2838, 2250, 1711, 1629, 1579, 1504, 1457, 1418, 1382, 1330, 1238, 1120, 1053, 1005, 916, 832, 778, 730, 642, 525, 436. **MS (EI):** *m*/*z* (%) = 336 ([$M^+$], 60), 275 (21), 262 (100), 207 (48), 115 (22). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{18}H_{24}O_6$+$Na^+$: 359.1465; found: 359.1464.

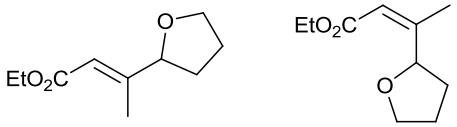
**Synthesis of methyl 3-(2-methyl-5-phenylthiophen-3-yl)-2-(tetrahydrofuran-2-yl) acrylate (6k)**




The title compound was prepared according to the general procedure **A** from methyl 3-(2-methyl-5-phenylthiophen-3-yl)propiolate (103 mg, 0.40 mmol) and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 10:1 to 8:1) as slightly yellow oil (97.5 mg, 0.30 mmol, 74%, *E*/*Z* = 42:58). $^{1}$H NMR data of the *E*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 7.59 (s, 1H), 7.56-7.48 (m, 2H), 7.41-7.24 (m, 3H), 7.22 (s, 1H), 4.98 (t, *J* = 7.8 Hz, 1H), 4.12-3.96 (m, 2H), 3.93-3.79 (m, 2H), 3.82 (s, 3H), 2.48 (s, 3H), 2.33-1.88

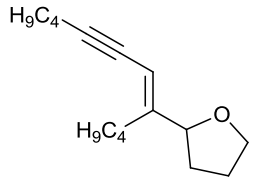
(m, 4H). $^{1}$H NMR data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 7.56-7.48 (m, 2H), 7.41-7.24 (m, 3H), 7.16 (s, 1H), 6.82 (d, *J* = 1.2 Hz, 1H) 4.79-4.72 (m, 1H), 4.12-3.96 (m, 2H), 3.93-3.79 (m, 2H), 3.76 (s, 3H), 2.45 (s, 3H), 2.33-1.88 (m, 4H). $^{13}$C NMR data of the mixture of isomers **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 168.7, 167.4, 140.2, 140.0, 139.6, 138.7, 134.8, 134.2, 134.0, 133.4, 133.3, 133.0, 132.1, 128.9, 128.8, 127.4, 127.2, 125.6, 125.4, 125.0, 124.3, 123.3, 79.5, 75.4, 69.0, 68.7, 51.7, 51.6, 32.0, 30.7, 27.1, 25.6, 14.0, 13.7. **IR (film):** 2949, 2869, 1713, 1602, 1496, 1438, 1383, 1333, 1242, 1126, 1054, 980, 920, 839, 755, 689, 554, 471. **MS (EI):** *m*/*z* (%) = 328 ([$M^+$], 37), 269 (46), 237 (100), 165 (27), 155 (50), 85 (39), 71 (71). **HR-MS (EI):** *m*/*z* (%) = calculated for $C_{19}H_{20}O_3S$: 328.1133; found: 328.1119.

**Synthesis of (*E*)- and (*Z*)-ethyl 3-(tetrahydrofuran-2-yl)but-2-enoate (6l)**



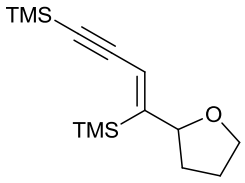

The title compounds were prepared according to the general procedure **B** from ethyl but-2-ynoate (112 mg, 1.0 mmol), which was stirred for 48 h and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 15:1) as colorless oils (30.4 mg, 0.17 mmol, 17%, *E*-isomer; and 42.8 mg, 0.23 mmol, 23%, *Z*-isomer). Analytical data of the *E*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 5.96-5.93 (m, 1H), 4.31 (t, *J* = 7.1 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.99-3.81 (m, 2H), 2.21-2.09 (m, 1H), 2.08 (d, *J* = 1.0 Hz, 3H), 1.95-1.85 (m, 2H), 1.71-1.59 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 167.0, 158.8, 113.5, 82.3, 68.9, 59.6, 31.2, 25.6, 15.3, 14.3. **IR (film):** 2976, 2871, 1711, 1654, 1448, 1371, 1315, 1272, 1222, 1144, 1074, 1042, 920, 872, 811, 732, 650, 576, 480. **MS (EI):** *m*/*z* (%) = 184 ([$M^+$], 6), 155 (26), 139 (26), 111 (100), 97 (18), 69 (35). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{10}H_{16}O_3$+$Na^+$: 207.0992; found: 207.0991. Analytical data of the *Z*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 5.67-5.65 (m, 1H), 5.46 (t, *J* = 7.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.95-3.79 (m, 2H), 2.39-2.28 (m, 1H), 1.98-1.89 (m, 2H), 1.80 (d, *J* = 1.3 Hz, 3H), 1.59-1.45 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$):** δ = 165.8, 161.3, 116.2, 77.5, 69.0, 59.7, 31.3, 26.4, 19.0, 14.2. **IR (film):** 2978, 2868, 1710, 1643, 1444, 1378, 1233, 1149, 1047, 926, 857, 797, 732, 653, 563, 455, 409. **MS (EI):** *m*/*z* (%) = 184 ([$M^+$], 12), 155 (100), 139 (26), 113 (60), 97 (19), 85 (18), 69 (24). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{10}H_{16}O_3$+$Na^+$: 207.0992; found: 207.0991.

**Synthesis of 2-(dodec-5-en-7-yn-5-yl)tetrahydrofuran** (**6m**)



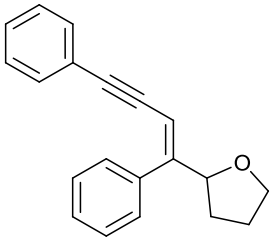

The title compound was prepared according to the general procedure **B** from dodeca-5,7-diyne (162 mg, 1.0 mmol), which was stirred for 56 h and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 50:1 to 25:1) as colorless oil (60.9 mg, 0.26 mmol, 26%, *E*/*Z* = >99:1; recovered starting material: 81.2 mg, 0.50 mmol). **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 5.55 (dd, *J* = 3.7, 2.1 Hz, 1H), 4.34 (t, *J* = 7.1 Hz, 1H), 3.95-3.87 (m, 1H), 3.84-3.76 (m, 1H), 2.43-2.31 (m, 3H), 2.15-1.99 (m, 2H), 1.94-1.83 (m, 2H), 1.69-1.30 (m, 9H), 0.91 (t, *J* = 7.1 Hz, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 154.1, 104.2, 94.2, 80.8, 77.9, 68.4, 31.4, 31.0, 30.7, 30.5, 25.7, 22.9, 21.9, 19.3, 13.9, 13.6. **IR (film):** 2932, 2865, 2213, 1715, 1670, 1458, 1375, 1321, 1252, 1180, 1056, 925, 854, 732, 641, 457, 411. **MS (EI):** *m*/*z* (%) = 234 ([$M^+$], 8), 191 (8), 177 (100), 91 (12). **HR-MS (EI):** *m*/*z* (%) = calculated for $C_{16}H_{26}O$: 234.1984; found: 234.1984.

**Synthesis of (1-(tetrahydrofuran-2-yl)but-1-en-3-yne-1,4-diyl)bis(trimethylsilane)** (**6n**)



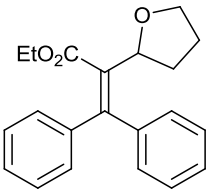

The title compound was prepared according to the general procedure **B** from 1,4-bis(trimethylsilyl)buta-1,3-diyne (194 mg, 1.0 mmol), which was stirred for 24 h and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 50:1) as colorless oil (75.4 mg, 0.28 mmol, 28%, *Z*/*E* = >99:1; recovered starting material: 82.3 mg, 0.42 mmol). **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 6.33 (d, *J* = 1.8 Hz, 1H), 4.51 (dt, *J* = 7.1, 1.7 Hz, 1H), 3.92 (dt, *J* = 8.1, 6.5 Hz, 1H), 3.79 (dt, *J* = 7.6, 7.1 Hz, 1H), 2.14-2.02 (m, 1H), 1.92-1.81 (m, 2H), 1.57-1.45 (m, 1H), 0.24 (s, 9H), 0.18 (s, 9H). **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 159.0, 116.3, 105.2, 99.7, 81.6, 68.4, 32.8, 25.4, −0.3, −1.0. **IR (film):** 2959, 2896, 2133, 1567, 1453, 1409, 1348, 1248, 1179, 1089, 1053, 957, 833, 757, 696, 648, 522, 436. **MS (EI):** *m*/*z* (%) = 266 ([$M^+$], 14), 223 (19), 193 (16), 150 (28), 135 (15), 73 (100). **HR-MS (EI):** *m*/*z* (%) = calculated for $C_{14}H_{26}OSi_2$: 266.1522; found: 266.1530.

**Synthesis of 2-(1,4-diphenylbut-1-en-3-ynyl)tetrahydrofuran** (**6o**)




The title compound was prepared according to the general procedure **B** from 1,4-diphenylbutadiyne (202 mg, 1.0 mmol), which was stirred for 48 h and obtained after usual workup and column chromatography (*n*-pentane:diethyl ether = 25:1) as slightly yellow oil (112 mg, 0.41 mmol, 41%, *E*/*Z* = >20:1; recovered starting material: 94.8 mg, 0.47 mmol). NMR data of the major isomer: **$^{1}$H NMR (300 MHz, CDCl$_3$)**: δ = 7.58-7.53 (m, 2H), 7.44-7.33 (m, 3H), 7.25 (s, 5H), 6.13 (d, *J* = 1.6 Hz, 1H), 4.90 (ddd, *J* = 7.3, 7.2, 1.5 Hz, 1H), 4.04 (dt, *J* = 8.1, 6.5 Hz, 1H), 3.96-3.87 (m, 1H), 2.11-1.99 (m, 1H), 1.96-1.85 (m, 2H), 1.70-1.59 (m, 1H). **$^{13}$C NMR (75 MHz, CDCl$_3$)**: δ = 153.6, 137.9, 131.3, 128.4, 128.1, 128.0, 127.9, 127.8, 123.8, 105.1, 92.8, 88.0, 81.0, 68.8, 32.0, 25.5. **IR (film):** 3058, 2973, 2868, 2247, 2195, 1954, 1886, 1679, 1594, 1490, 1443, 1377, 1323, 1271, 1179, 1066, 911, 856, 753, 732, 691, 576, 524, 480. **MS (EI):** *m*/*z* (%) = 274 ([M$^+$], 100), 246 (38), 231 (30), 217 (55), 202 (91), 102 (20). **HR-MS (EI):** *m*/*z* (%) = calculated for $C_{20}H_{18}O$: 274.1358; found: 274.1359.

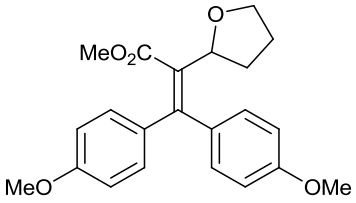
**Synthesis of ethyl 3,3-diphenyl-2-(tetrahydrofuran-2-yl)acrylate** (**9a**)




The title compound was prepared from ethyl 3-phenylpropiolate (69.7 mg, 0.40 mmol) according to the general procedure **A**. After 6 h at 40 °C the reaction mixture was cooled to room temperature and iodobenzene (81.6 mg, 0.40 mmol) was added, followed by the addition of tetrakis(triphenylphosphine)palladium(0) (11.6 mg, 0.01 mmol) and the mixture was again stirred at 40 °C under argon atmosphere for additional 17 h. The product was obtained after filtration through a short pad of silica and column chromatography (*n*-pentane:diethyl ether = 10:1) as pale yellow solid (115 mg, 0.36 mmol, 89%). **$^{1}$H NMR (300 MHz, CDCl$_3$)**: δ = 7.38-7.18 (m, 10H), 4.59 (dd, *J* = 8.6, 6.8 Hz, 1H), 3.97 (dq, *J* = 7.1, 2.4 Hz, 2H), 3.92-3.83 (m, 1 H), 3.73 (ddd, *J* = 8.1, 8.0, 5.0 Hz, 1H), 2.41-2.27 (m, 1H), 2.03-1.90 (m, 2H), 1.86-1.71 (m, 1H), 0.89 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (75 MHz, CDCl$_3$)**: δ =

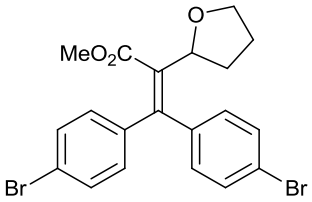
169.0, 145.1, 141.4, 139.9, 134.5, 129.0, 128.5, 128.3, 127.9, 127.6 (2 C), 78.0, 68.9, 60.5, 31.4, 26.5, 13.6. **IR (neat):** 3053, 2980, 2929, 2873, 1707, 1625, 1490, 1445, 1367, 1307, 1257, 1146, 1106, 1041, 935, 864, 811, 768, 735, 700, 632, 587, 519, 460, 406. **MS (EI):** *m*/*z* (%) = 322 ([$M^+$], 3), 276 (90), 249 (100), 207 (25), 178 (52). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{21}H_{22}O_3$+$Na^+$: 345.1461; found: 345.1454.

**Synthesis of methyl 3,3-bis(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)acrylate** (**9b**)



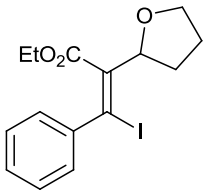

The title compound was prepared from methyl 3-(4-methoxyphenyl)propiolate (76.1 mg, 0.40 mmol) according to the general procedure **A**. After 20 h at 40 °C the reaction mixture was cooled to room temperature and 4-iodoanisole (93.6 mg, 0.40 mmol) was added, followed by the addition of tetrakis(triphenylphosphine)palladium(0) (11.6 mg, 0.01 mmol) and the mixture was again stirred at 40 °C under argon atmosphere for additional 20 h. The product was obtained after filtration through a short pad of silica and column chromatography (*n*-pentane:diethyl ether = 4:1) as pale yellow solid (113 mg, 0.31 mmol, 76%). **$^1$H NMR (300 MHz, $CDCl_3$)**: δ = 7.14 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 4.61 (dd, *J* = 8.5, 6.8 Hz, 1H), 3.91-3.83 (m, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.72 (ddd, *J* = 8.1, 8.0, 5.1 Hz, 1H), 3.51 (s, 3H), 2.35-2.21 (m, 1H), 2.03-1.73 (m, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 170.1, 159.2 (2C), 145.0, 134.1, 132.6, 132.4, 130.6, 129.9, 113.6, 113.3, 78.3, 68.8, 55.2, 55.1, 51.6, 31.3, 26.5. **IR (neat):** 2950, 2869, 1715, 1605, 1508, 1457, 1322, 1286, 1244, 1176, 1131, 1033, 981, 922, 830, 734, 590, 560, 517, 420. **MS (EI):** *m*/*z* (%) = 368 ([$M^+$], 14), 336 (100), 309 (94), 291 (21), 277 (28), 265 (26), 207 (35). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{22}H_{24}O_5$+$H^+$: 369.1697; found: 369.1707.

**Synthesis of methyl 3,3-bis(4-bromophenyl)-2-(tetrahydrofuran-2-yl)acrylate** (**9c**)




The title compound was prepared from methyl 3-(4-bromophenyl)propiolate (95.6 mg, 0.40 mmol) according to the general procedure **A**. After 9 h at 40 °C the reaction mixture was cooled to room temperature and 1-bromo-4-iodobenzene (113 mg, 0.40 mmol) was added, followed by the addition of tetrakis(triphenylphosphine)palladium(0) (11.6 mg, 0.01 mmol) and the mixture was stirred at room temperature under argon atmosphere for additional 15 h. The product was obtained after filtration through a short pad of silica and column chromatography (*n*-pentane:diethyl ether = 10:1) as pale yellow solid (143 mg, 0.31 mmol, 77%). **$^{1}$H NMR (300 MHz, $CDCl_3$)**: $\delta$ = 7.48 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 4.51 (dd, *J* = 8.5, 6.8 Hz, 1H), 3.86 (dt, *J* = 7.3, 7.2 Hz, 1H), 3.77-3.68 (m, 1H), 3.52 (s, 3H), 2.34-2.20 (m, 1H), 2.02-1.88 (m, 2H), 1.88-1.73 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$)**: $\delta$ = 169.0, 142.6, 139.5, 138.1, 135.3, 131.7, 131.3, 130.8, 130.1, 122.3, 77.8, 69.0, 51.8, 31.4, 26.4. (2 $C_{sp2}$ are overlapping). **IR (neat):** 2951, 2879, 1723, 1628, 1584, 1484, 1432, 1393, 1313, 1256, 1185, 1135, 1056, 1009, 946, 816, 744, 691, 655, 606, 509. **MS (EI):** *m*/*z* (%) = 466 ([$M^+$], 1), 434 (71), 407 (100), 365 (18), 284 (19), 256 (19), 189 (18), 176 (29). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{20}H_{18}Br_2O_3$+$Na^+$: 488.9496; found: 488.9494.

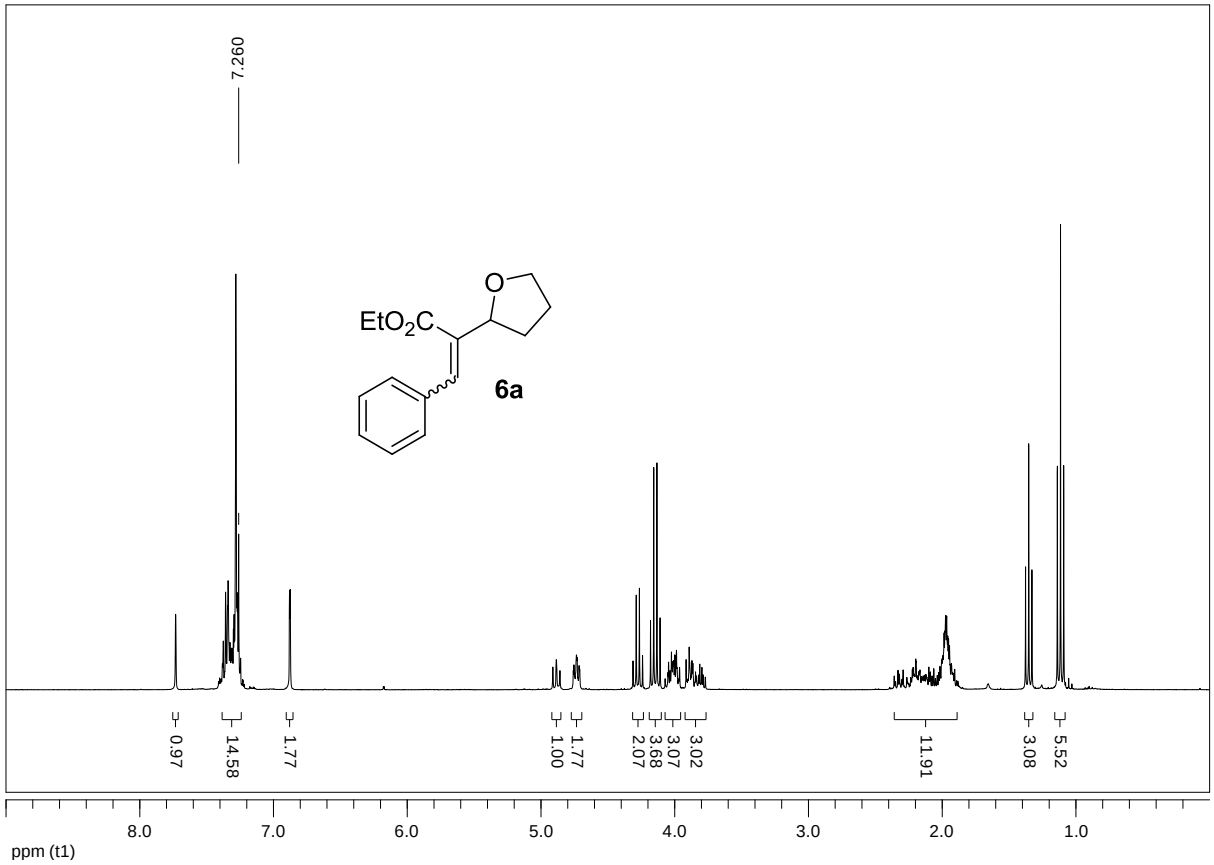
**Synthesis of (*E*)-ethyl 3-iodo-3-phenyl-2-(tetrahydrofuran-2-yl)acrylate**

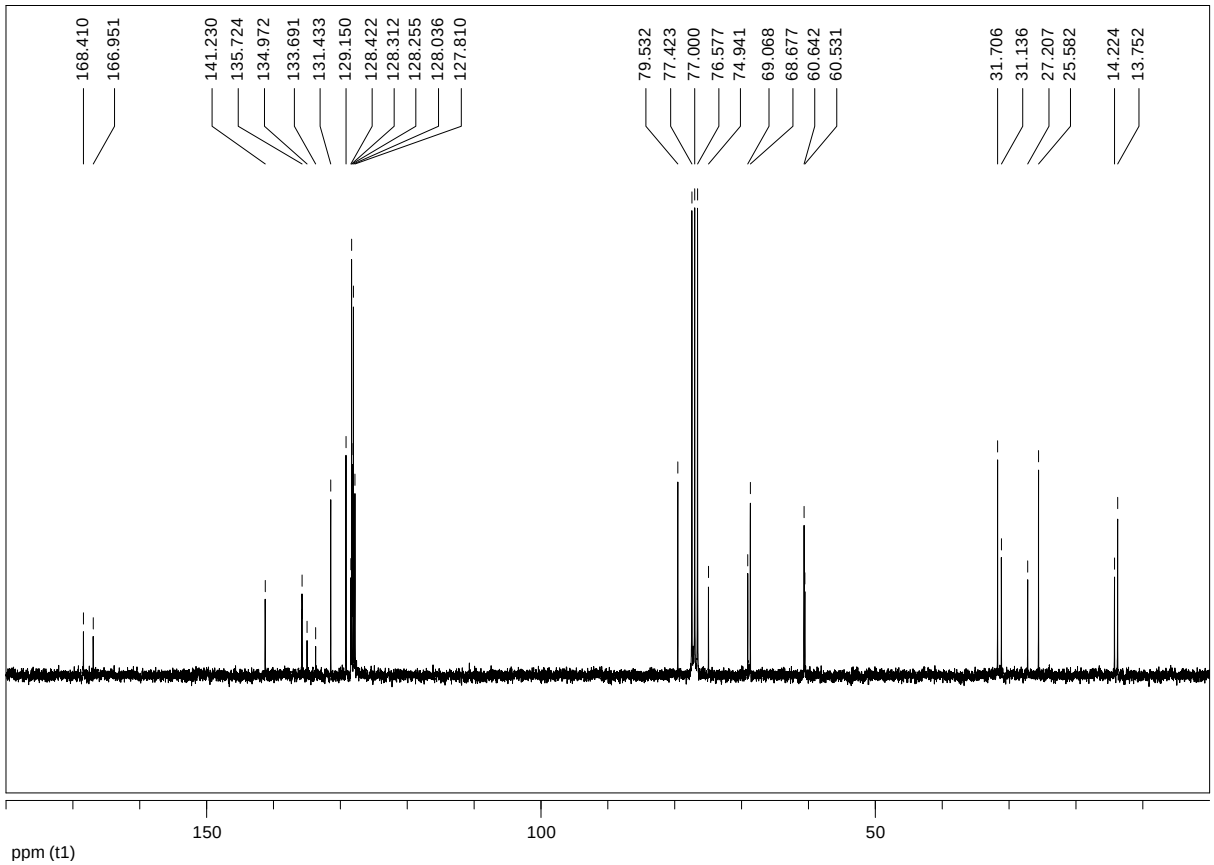


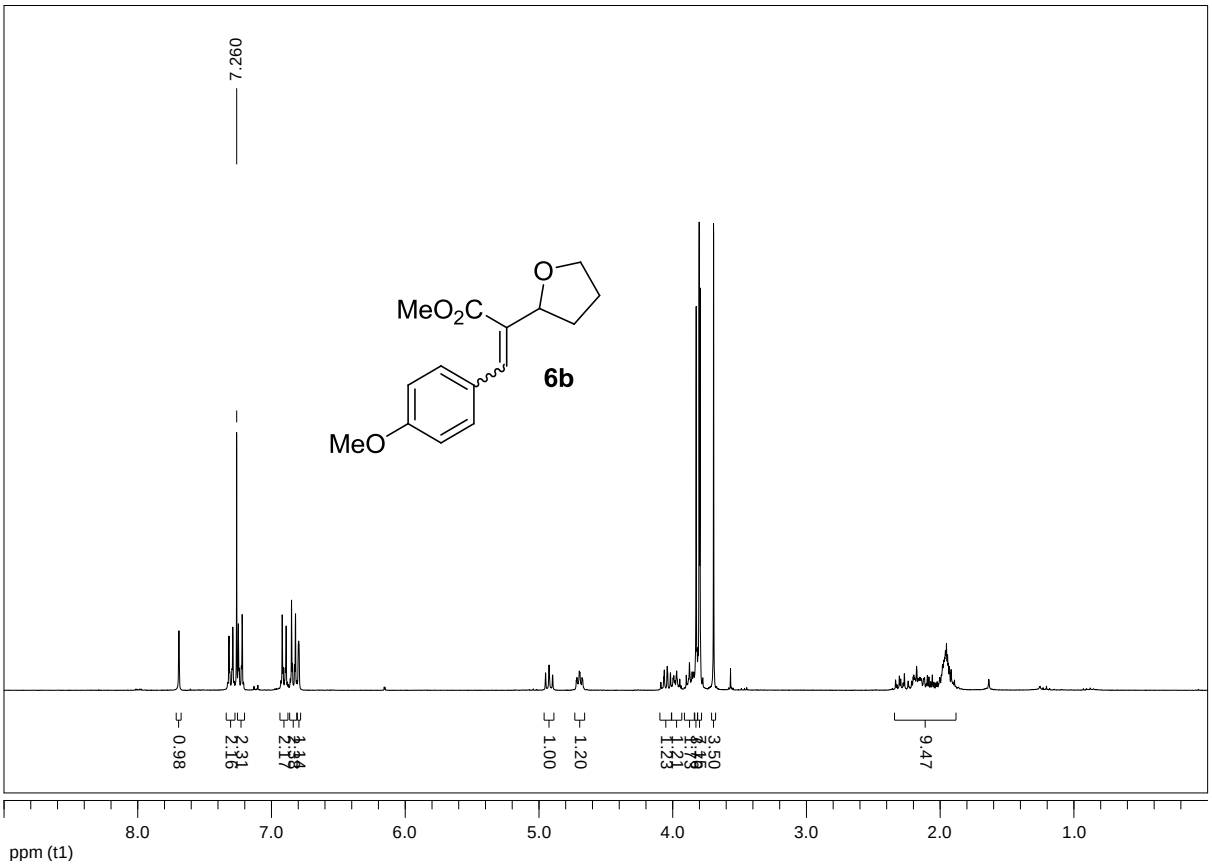

The title compound was prepared according to the general procedure **A** from ethyl 3-phenylpropiolate (69.7 mg, 0.40 mmol). After 16 h at 40 °C the reaction mixture was cooled to 0 °C and iodine (355 mg, 1.4 mmol) was added and the mixture was stirred at room temperature under argon atmosphere for additional 1.5 h. The mixture was quenched with sodium thiosulphate solution and extracted with diethyl ether. The organic layers were combined, dried over magnesium sulphate, the solvent was evaporated and the crude product was purified by column chromatography (*n*-pentane:diethyl ether = 12:1). The *E*-isomer was

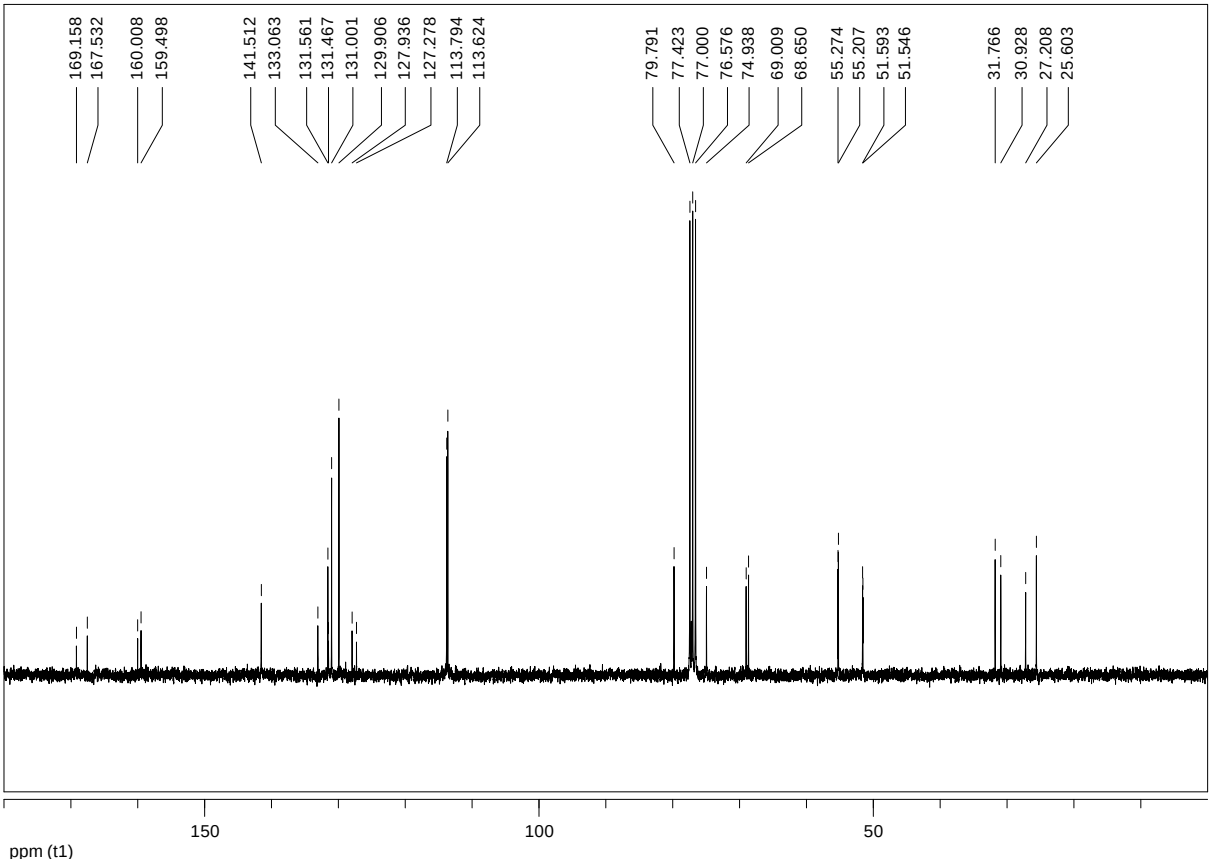
isolated as slightly yellow oil (58.7 mg, 0.16 mmol, 39%). The *Z*-isomere (~25-30%) was contaminated with small amounts of inseparable **6a** and could not be obtained in pure form. Analytical data are given for the purified *E*-isomer: **$^{1}$H NMR (300 MHz, $CDCl_3$)**: δ = 7.34-7.20 (m, 5H), 4.81 (t, *J* = 7.6 Hz, 1H), 3.95-3.83 (m, 4H), 2.54-2.42 (m, 1H), 2.24-1.89 (m, 3H), 0.82 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)**: δ = 165.1, 144.5, 143.1, 128.5, 128.0 (2C), 103.1, 86.1, 69.6, 60.9, 31.0, 26.1, 13.5. **IR (film):** 2969, 2872, 1716, 1620, 1448, 1368, 1264, 1140, 1059, 1017, 920, 868, 797, 761, 731, 693, 623, 516. **MS (EI):** *m*/*z* (%) = 326 ([$M^+$-EtOH], 12), 299 (24), 245 (62), 129 (31), 115 (17), 102 (17), 71 (100). **HR-MS (ESI):** *m*/*z* (%) = calculated for $C_{15}H_{17}IO_3$+$Na^+$: 395.0115; found: 395.0115.

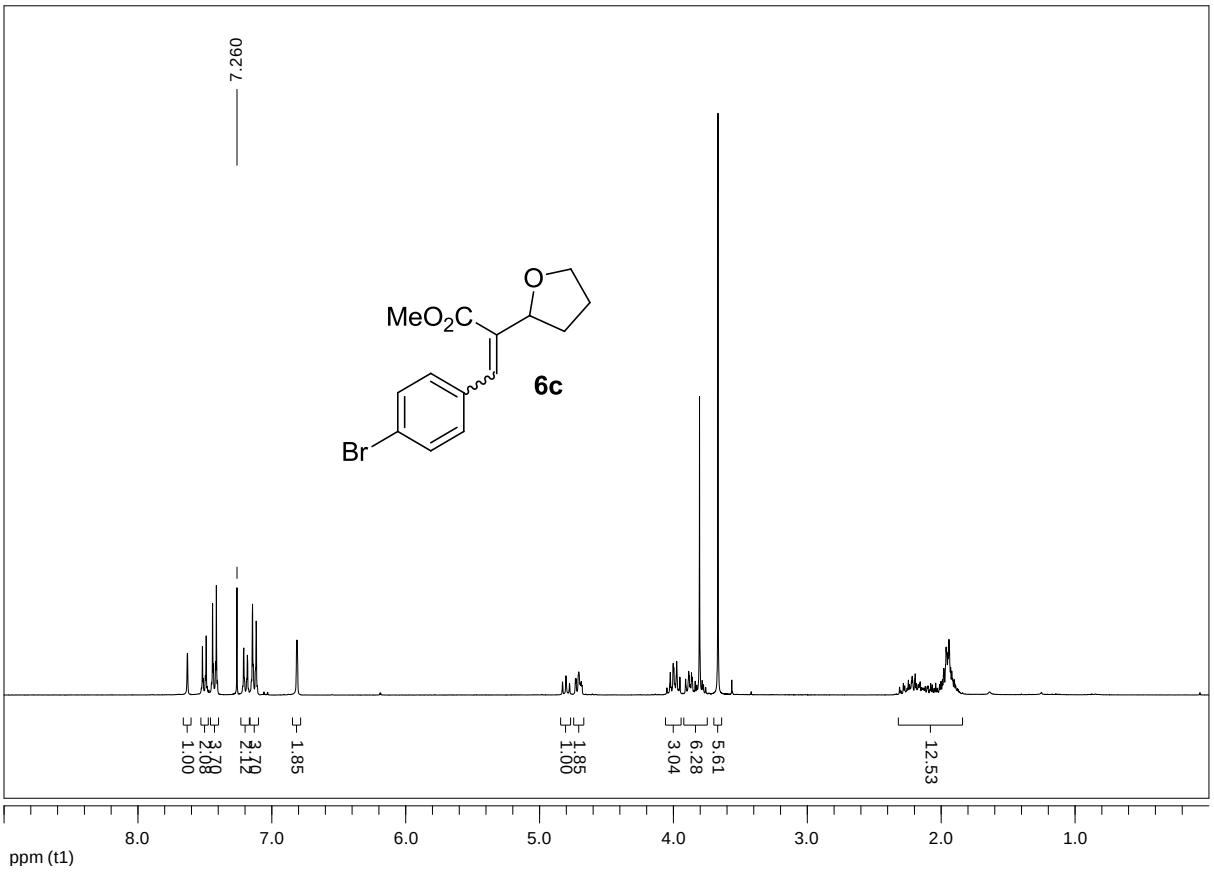
NMR spectra of the products:

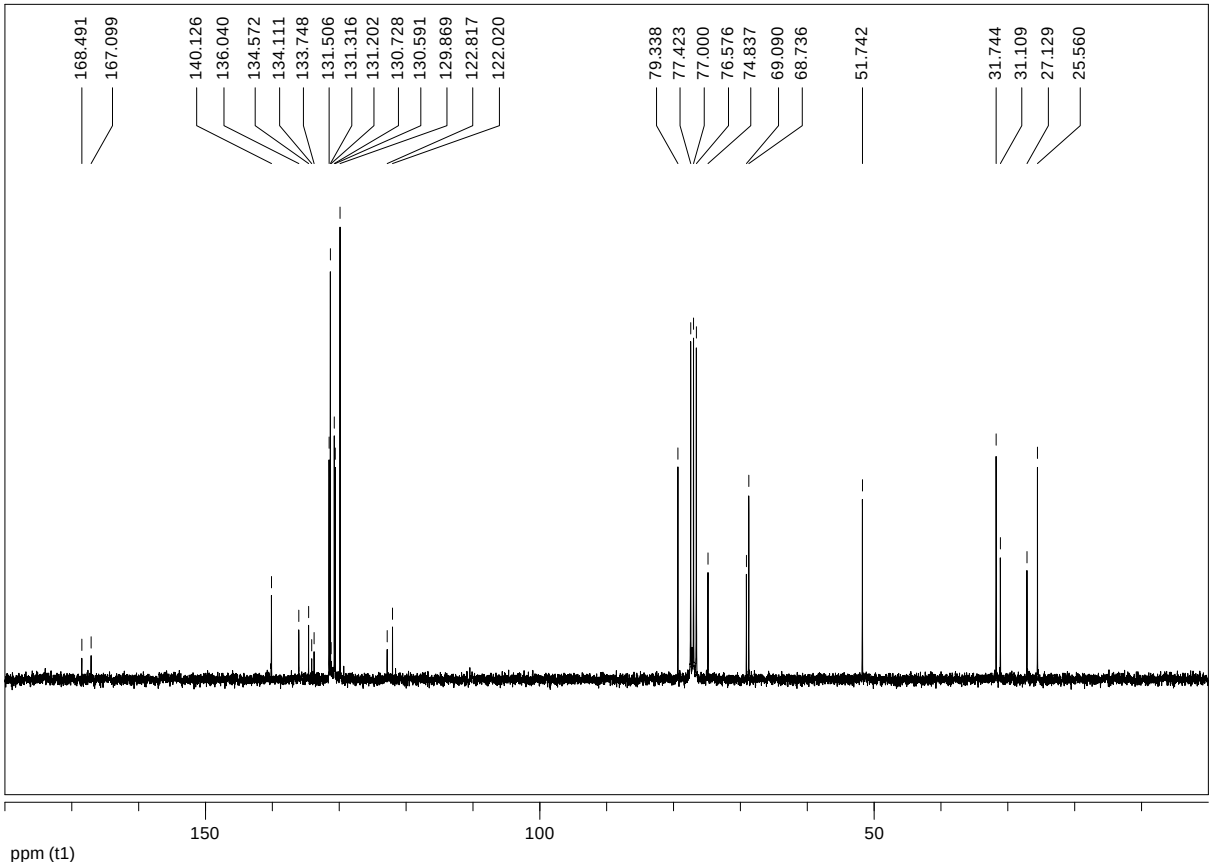


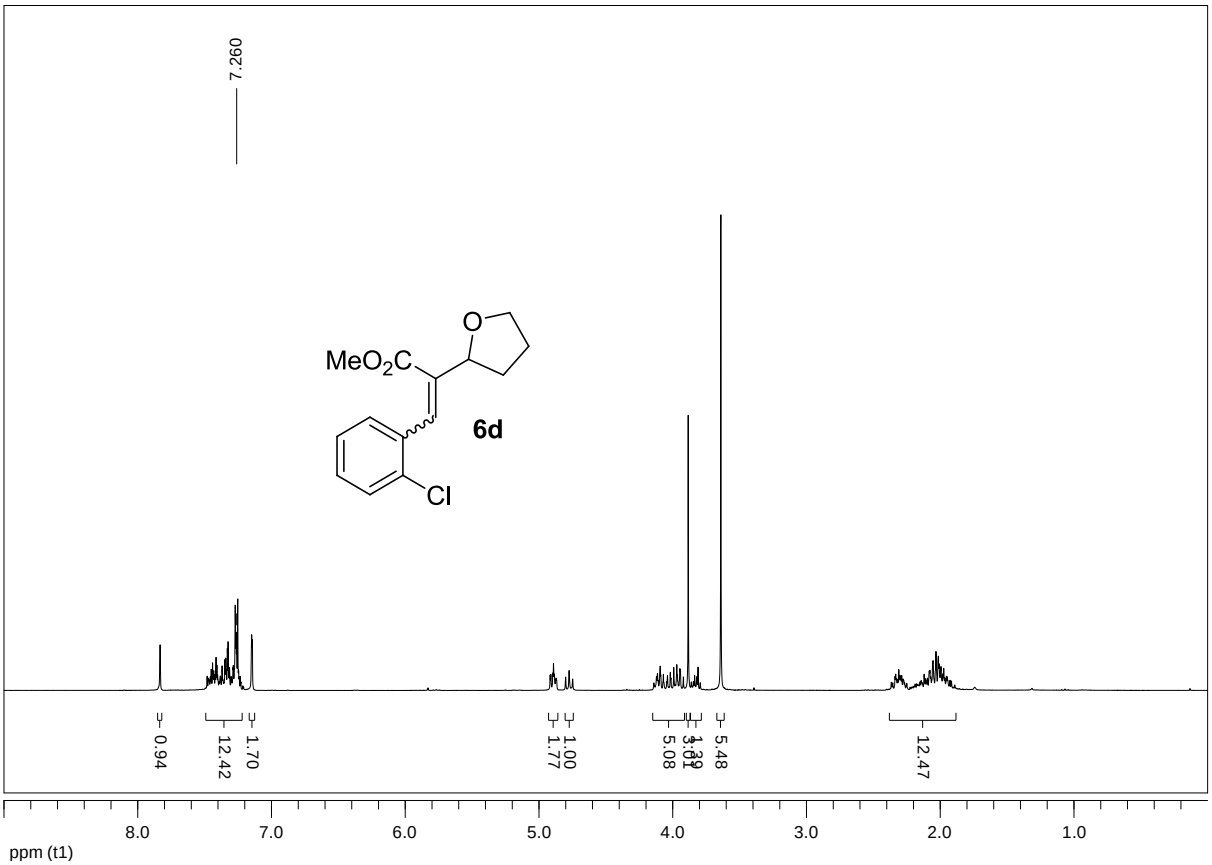



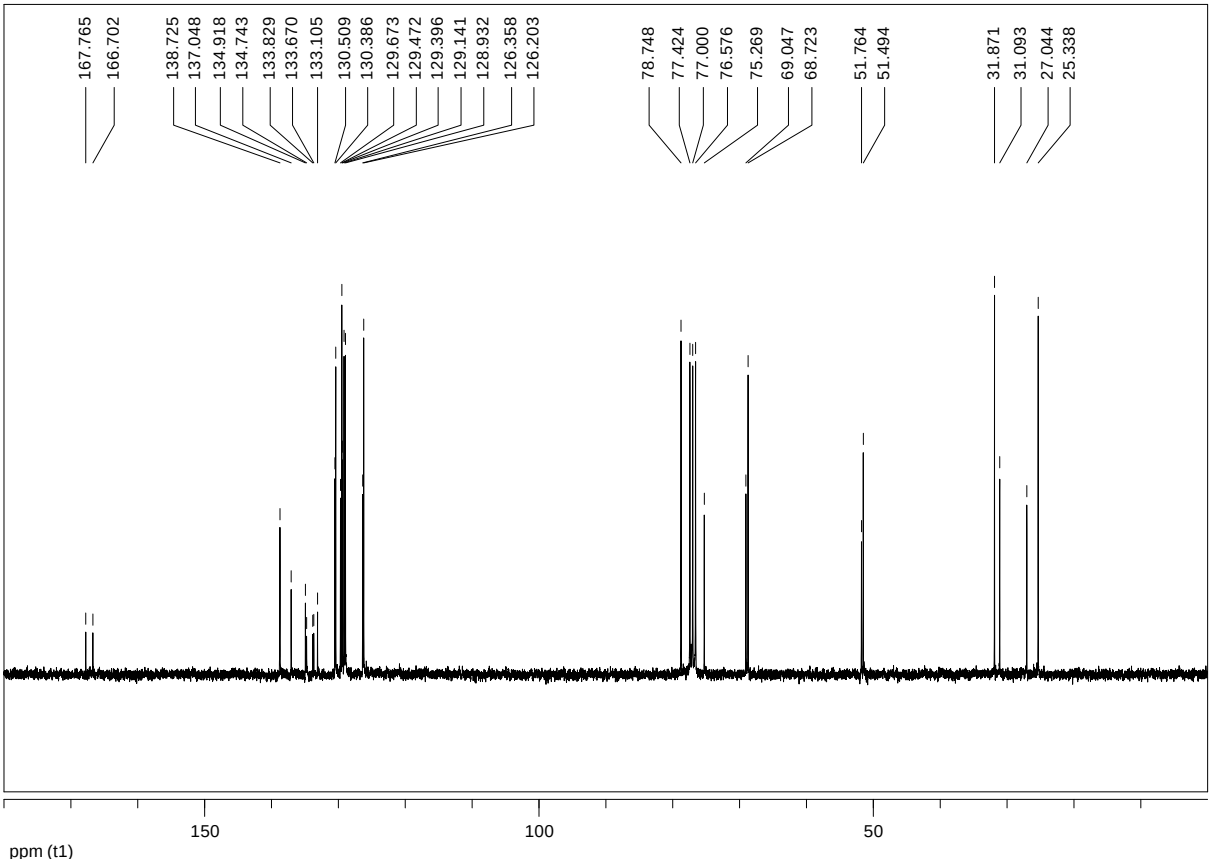

7.26
MeO2C
O
MeO
6b
0.98
2.31
2.16
2.17
1.00
1.20
1.23
3.50
9.47
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

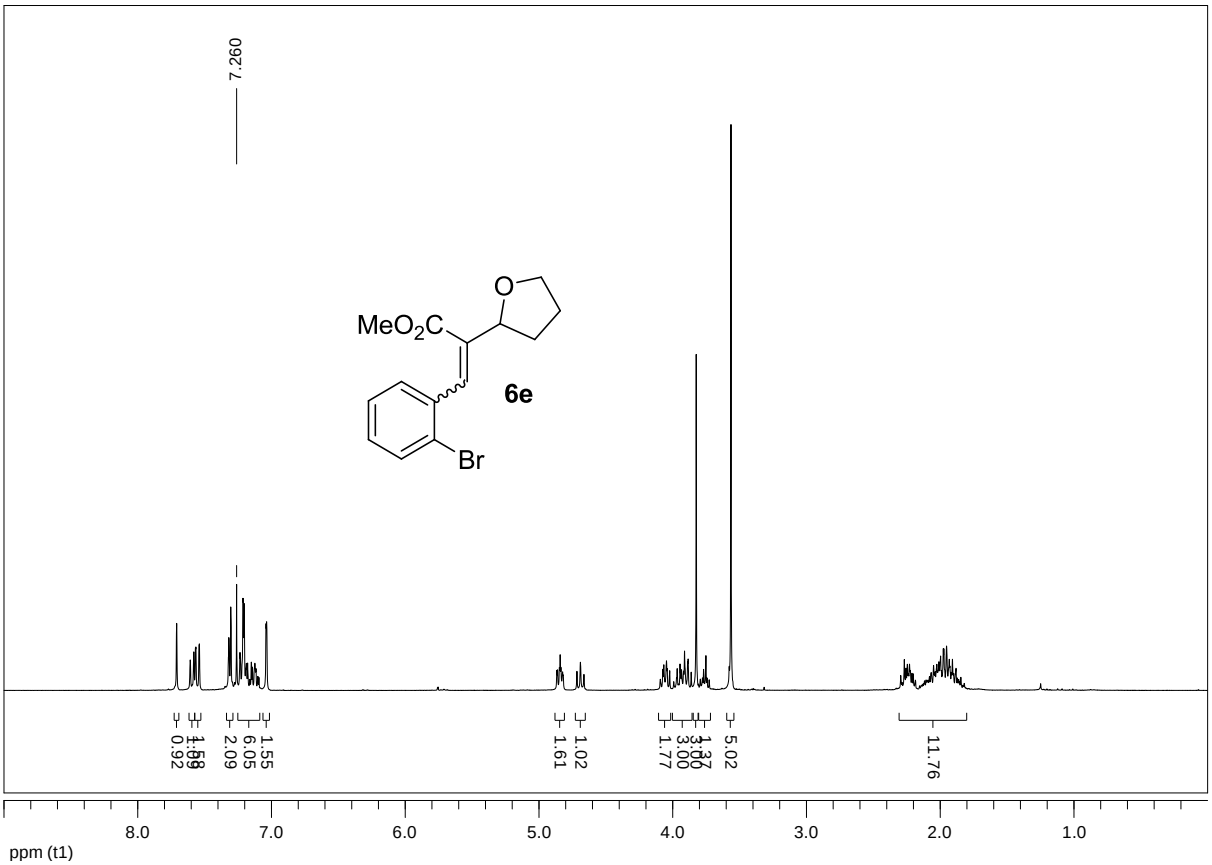

169.158
167.532
160.008
159.498
141.512
133.063
131.561
131.467
131.001
129.906
127.936
127.278
113.794
113.624
79.791
77.423
77.000
76.576
74.938
69.009
68.650
55.274
55.207
51.593
51.546
31.766
30.928
27.208
25.603
150
100
50
ppm (t1)

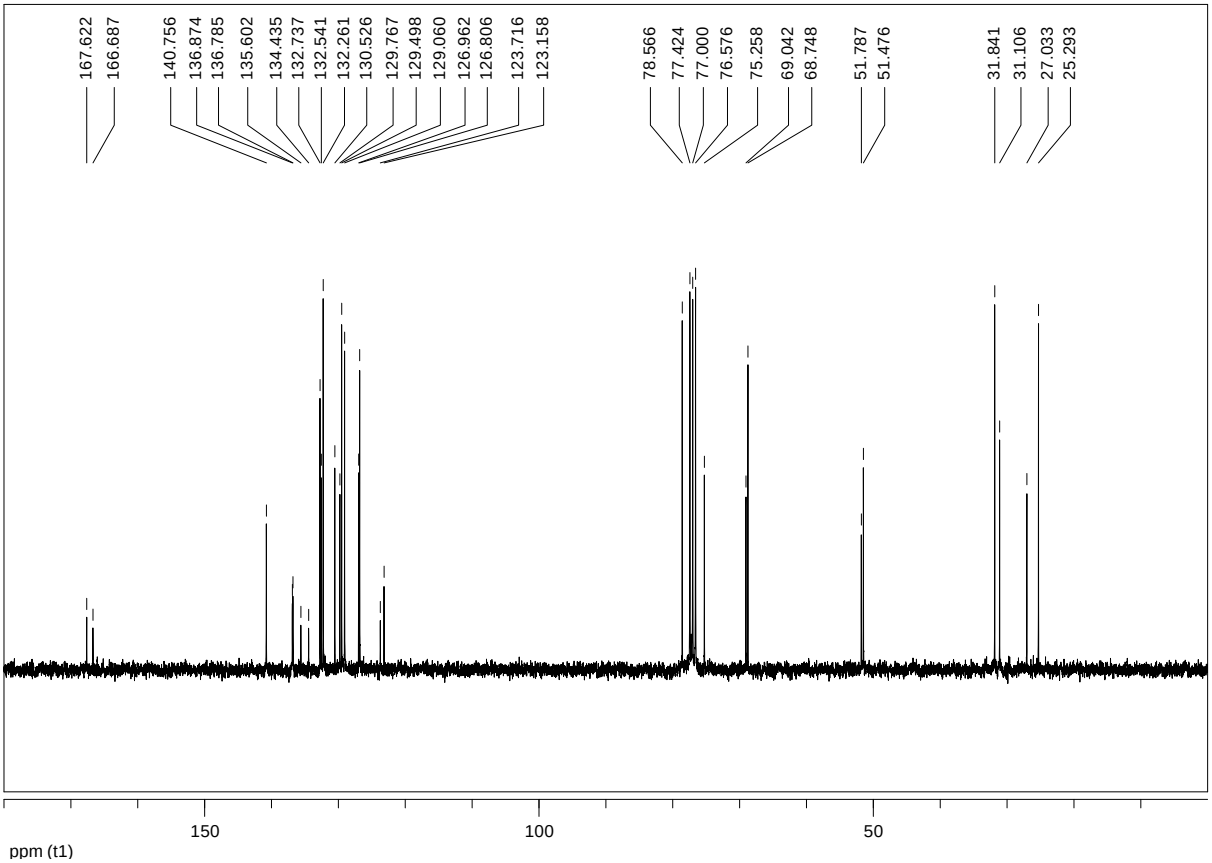

7.260
O
MeO2C
6c
Br
1.00
0.78
0.78
3.12
3.12
1.85
1.00
1.85
3.04
9.28
5.91
12.53
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

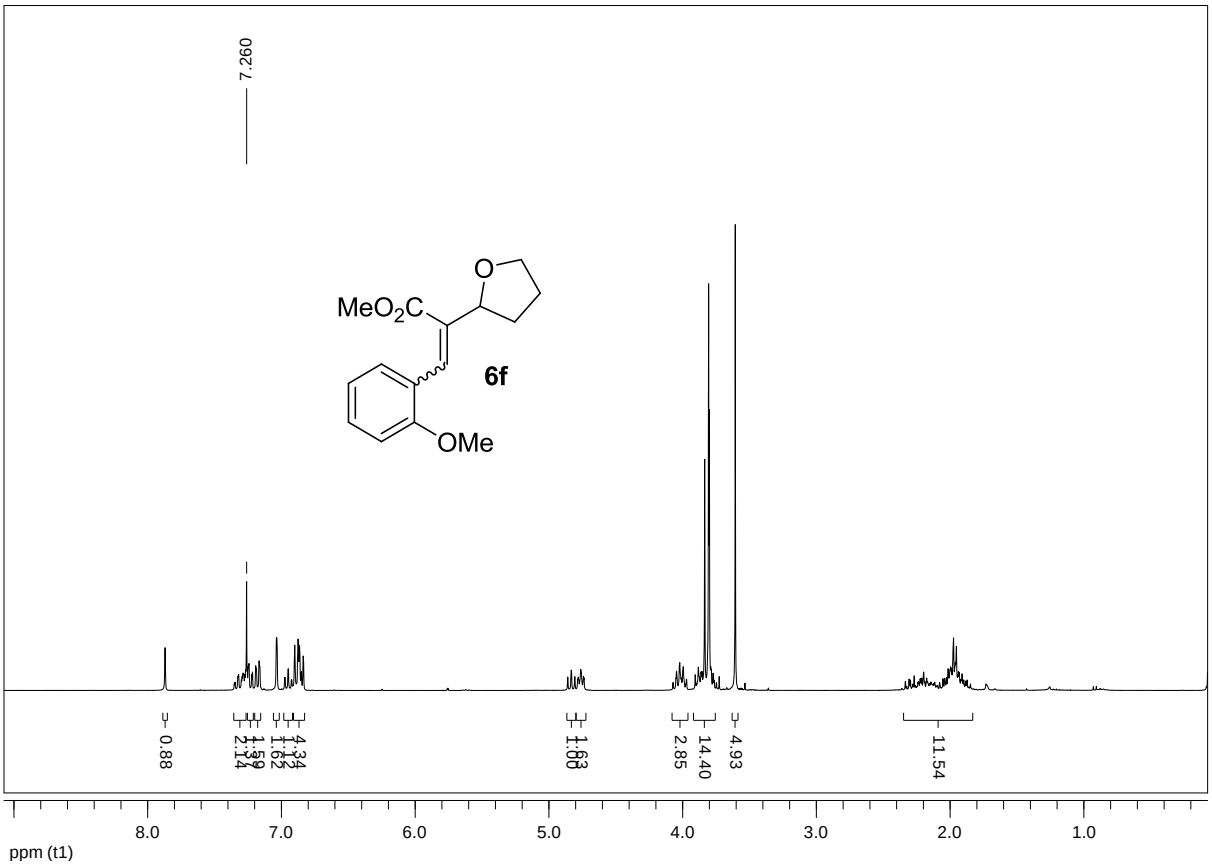

168.491
167.099
140.126
136.040
134.572
134.111
133.748
131.506
131.316
131.202
130.728
130.591
129.869
122.817
122.020
79.338
77.423
77.000
76.576
74.837
69.090
68.736
51.742
31.744
31.109
27.129
25.560
150
100
50
ppm (t1)

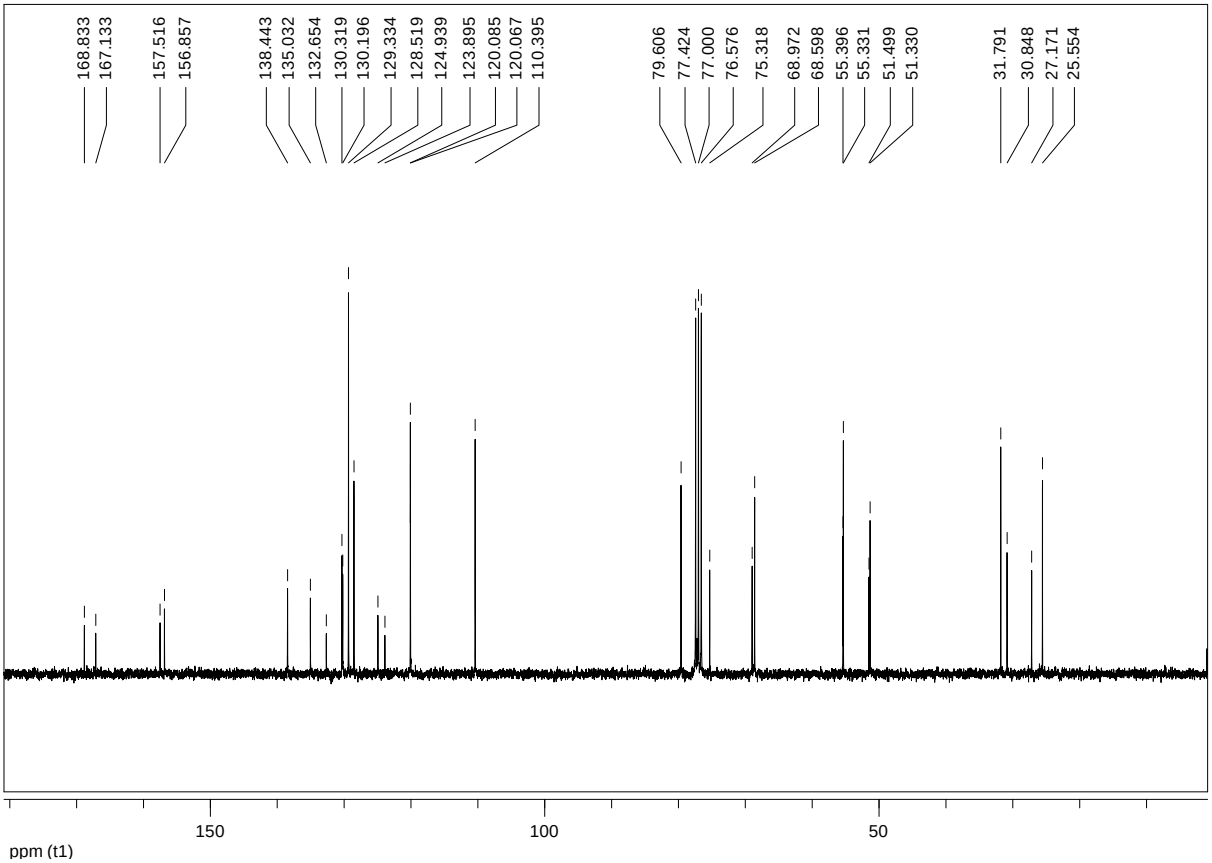

7.260
O
MeO2C
6d
Cl
0.94
12.42
1.70
1.77
1.00
5.08
3.01
3.00
5.48
12.47
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


167.765
166.702
138.725
137.048
134.918
134.743
133.829
133.670
133.105
130.509
130.386
129.673
129.472
129.396
129.141
128.932
126.358
126.203
78.748
77.424
77.000
76.576
75.269
69.047
68.723
51.764
51.494
31.871
31.093
27.044
25.338
150
100
50
ppm (t1)


7.260
O
MeO2C
6e
Br
0.92
1.68
2.09
6.05
1.55
1.91
1.02
1.77
3.00
1.37
5.02
11.79
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


167.622
166.687
140.756
136.874
136.785
135.602
134.435
132.737
132.541
132.261
130.526
129.767
129.498
129.060
126.962
126.806
123.716
123.158
78.566
77.424
77.000
76.576
75.258
69.042
68.748
51.787
51.476
31.841
31.106
27.033
25.293
150
100
50
ppm (t1)


7.260
MeO2C
O
6f
OMe
0.88
2.14
1.63
2.85
14.40
4.93
11.54
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


168.833
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157.516
156.857
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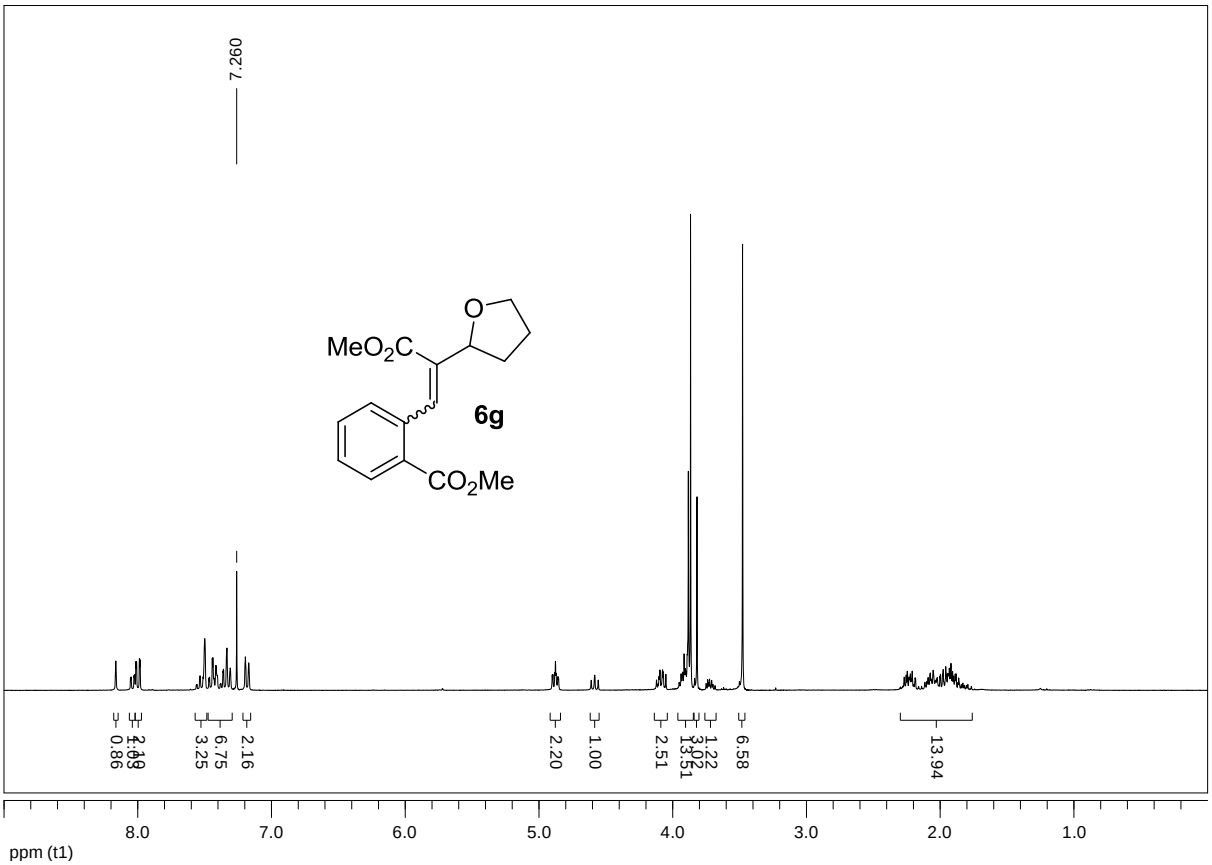
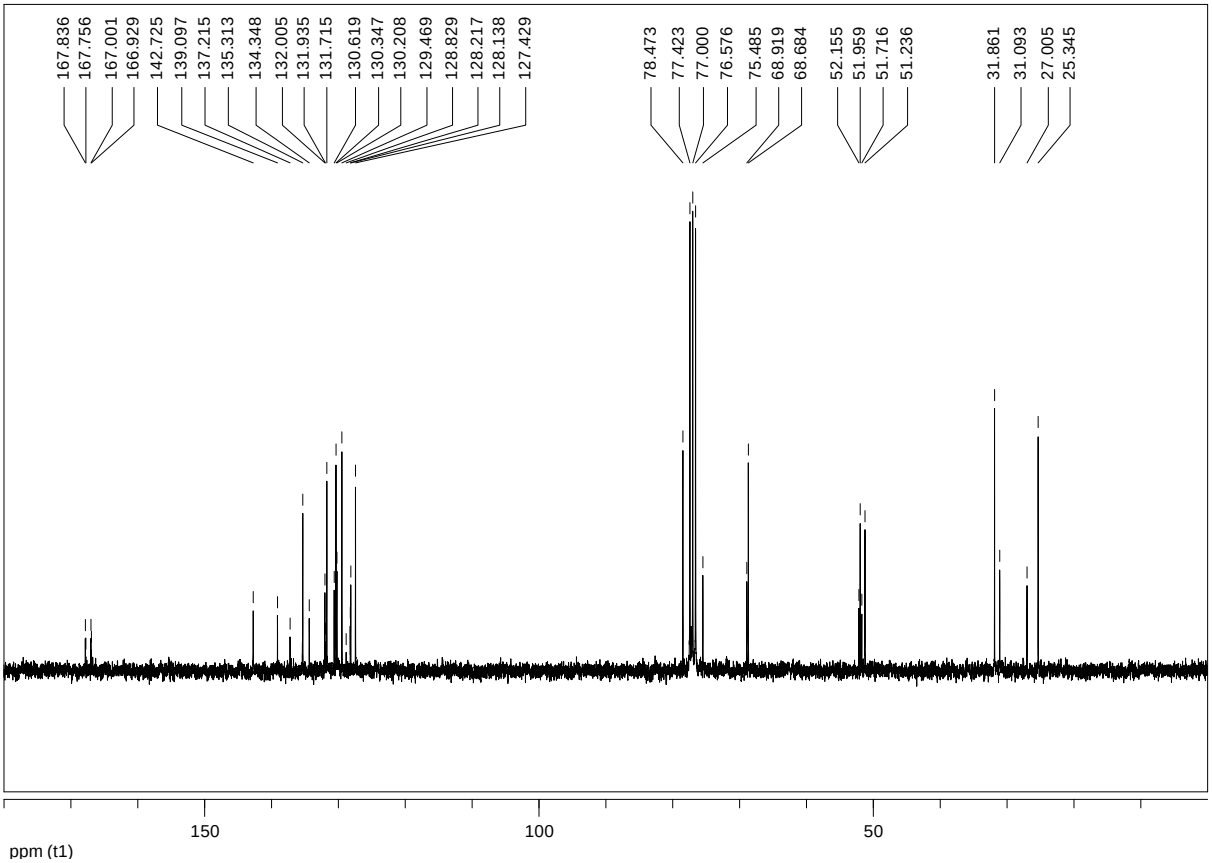
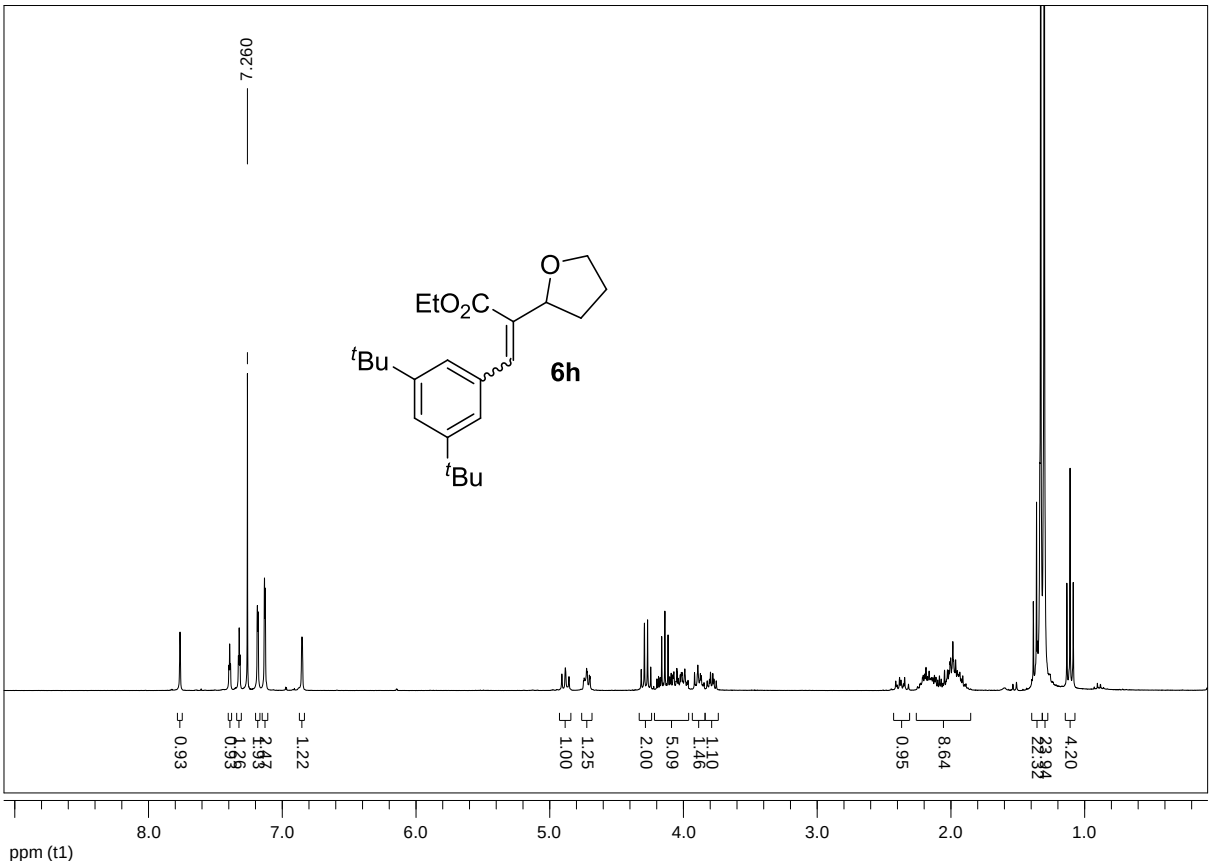
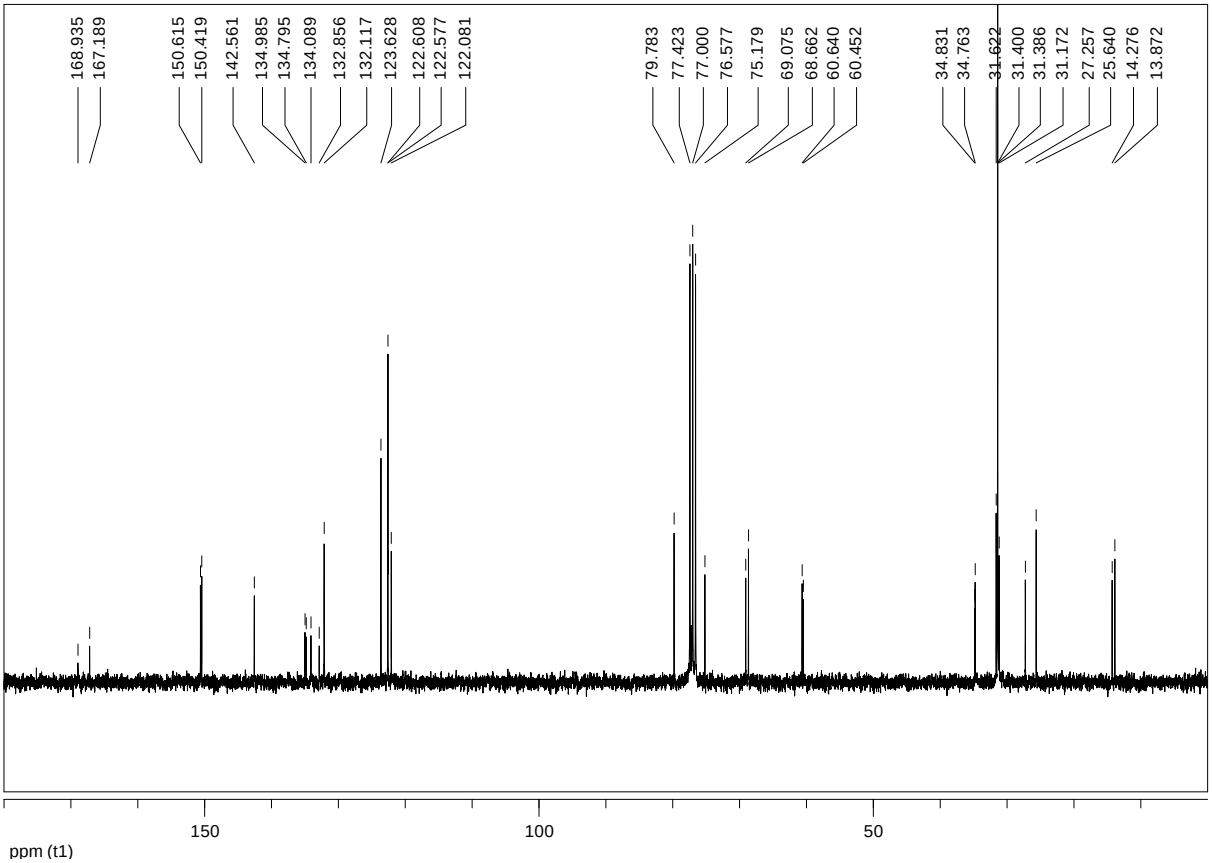
135.032
132.654
130.319
130.196
129.334
128.519
124.939
123.895
120.085
120.067
110.395
79.606
77.424
77.000
76.576
75.318
68.972
68.598
55.396
55.331
51.499
51.330
31.791
30.848
27.171
25.554
150
100
50
ppm (t1)


7.260
O
MeO2C
6g
CO2Me
0.86
2.09
2.25
9.75
2.16
2.20
1.00
2.51
3.05
1.22
6.58
13.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


167.836
167.756
167.001
166.929
142.725
139.097
137.215
135.313
134.348
132.005
131.935
131.715
130.619
130.347
130.208
129.469
128.829
128.217
128.138
127.429
78.473
77.423
77.000
76.576
75.485
68.919
68.684
52.155
51.959
51.716
51.236
31.861
31.093
27.005
25.345
150
100
50
ppm (t1)


7.260
O
EtO2C
tBu
tBu
6h
0.93
1.00
1.25
2.00
5.09
1.10
1.46
0.95
8.64
4.20
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


168.935
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150.419
142.561
134.985
134.795
134.089
132.856
132.117
123.628
122.608
122.577
122.081
79.783
77.423
77.000
76.577
75.179
69.075
68.662
60.640
60.452
34.831
34.763
31.622
31.400
31.386
31.172
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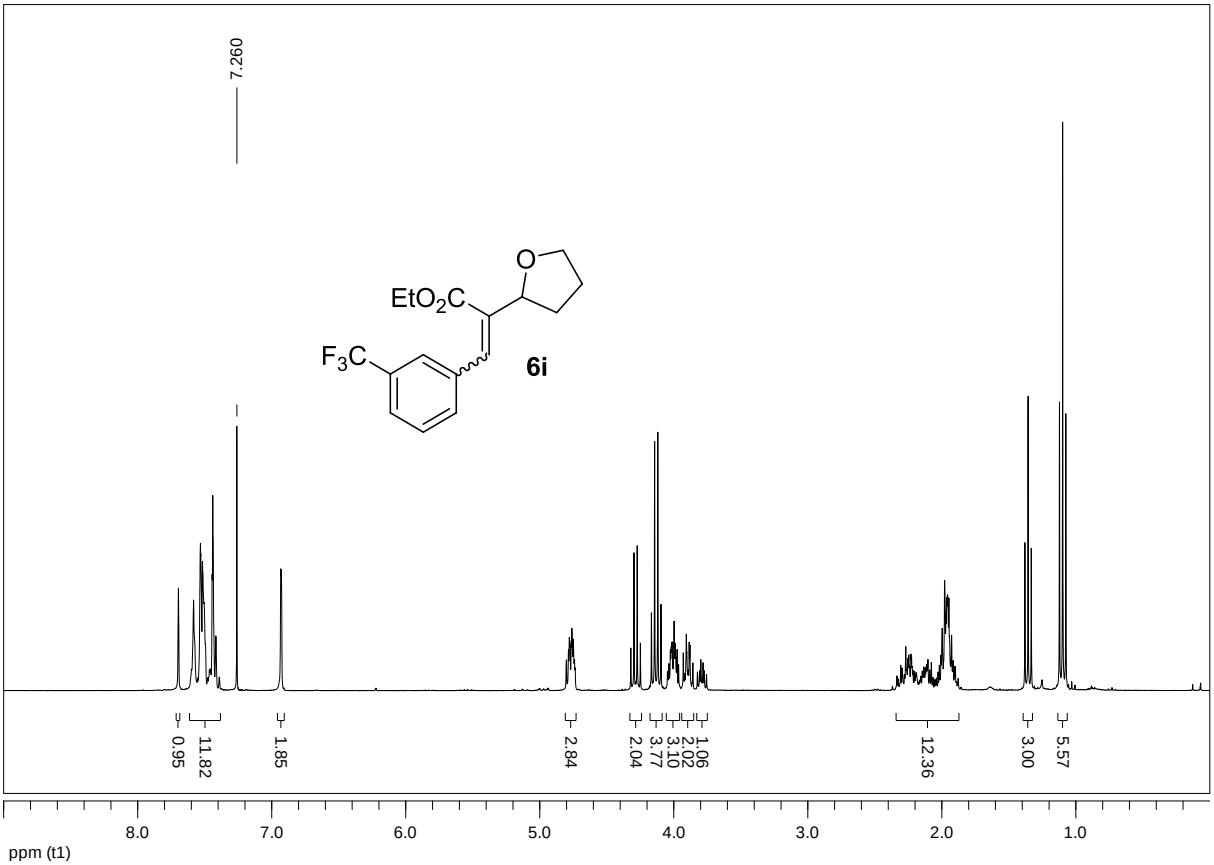
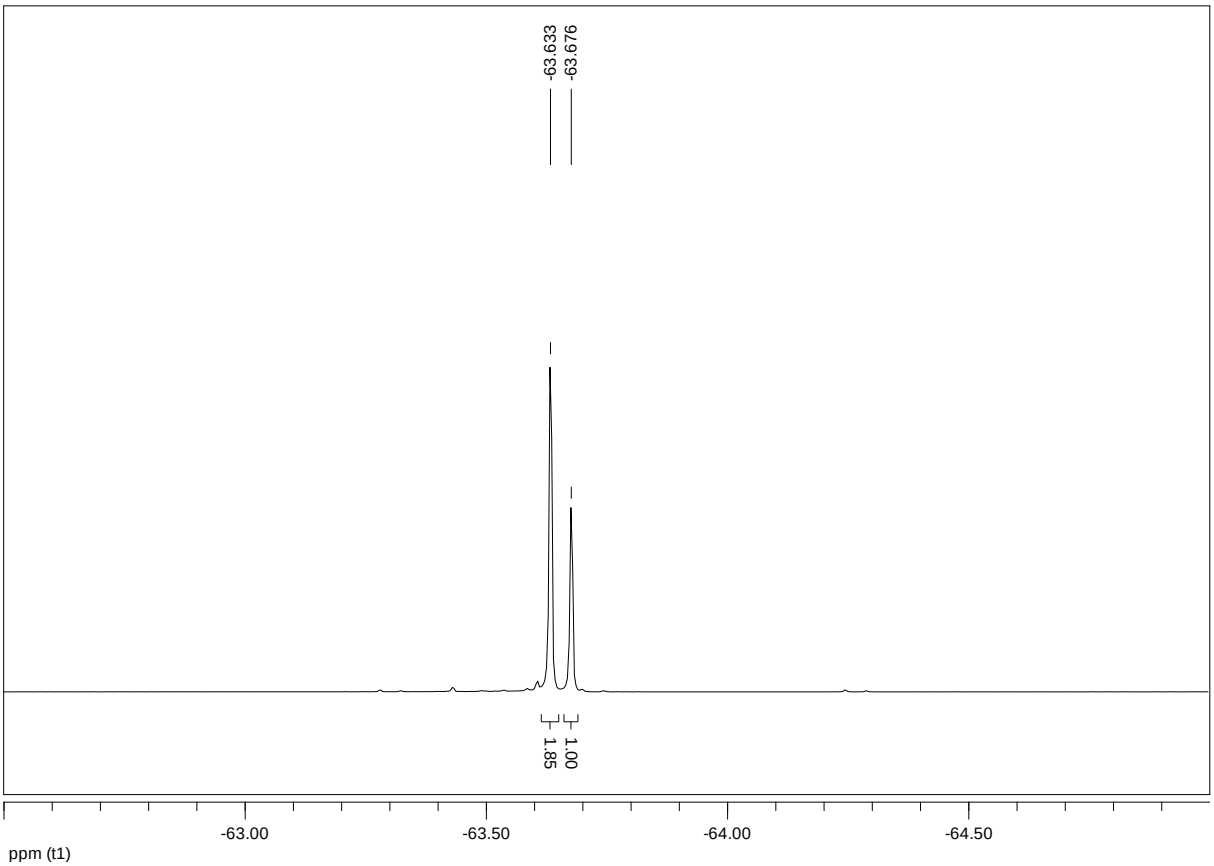
14.276
13.872
150
100
50
ppm (t1)


7.260
O
EtO2C
F3C
6i
0.95
11.82
1.85
2.84
2.04
3.77
3.10
2.02
1.06
12.36
3.00
5.57
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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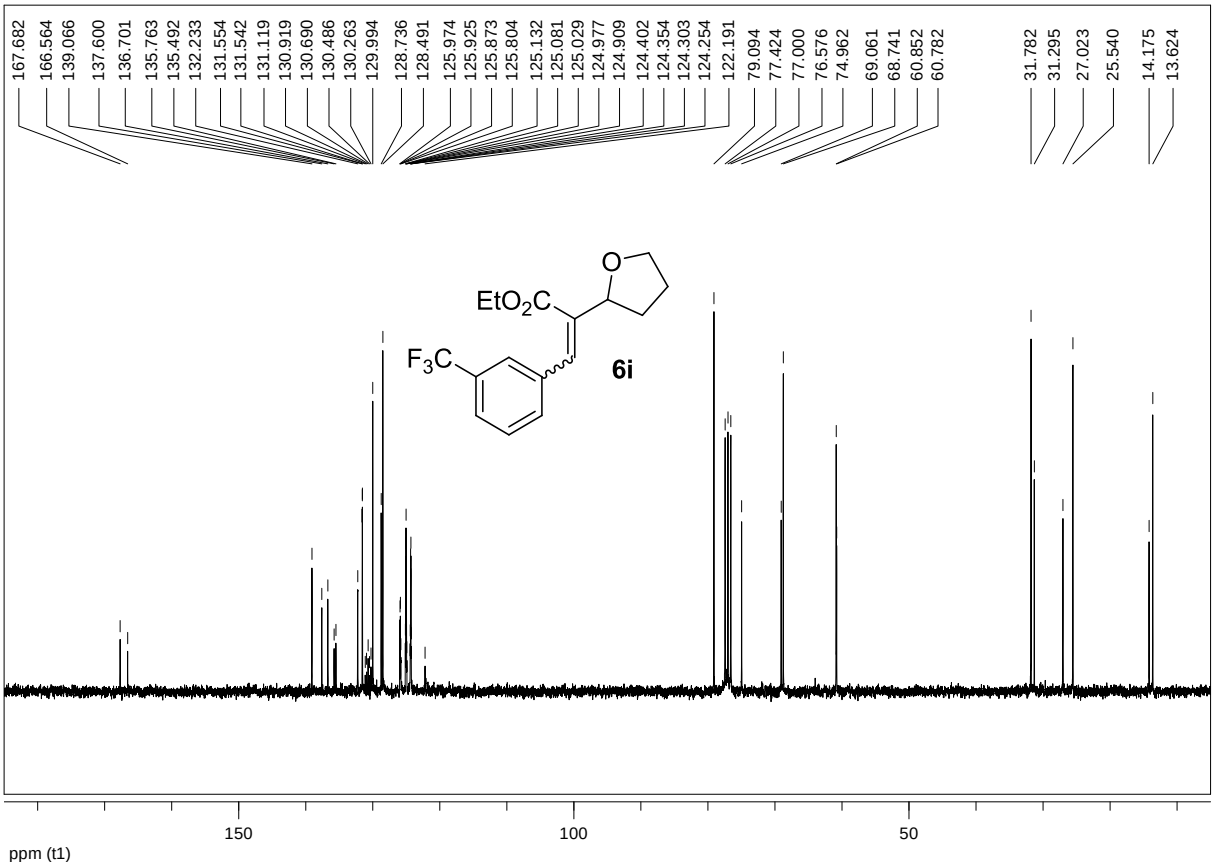
-63.676
1.85
1.00
-63.00
-63.50
-64.00
-64.50
ppm (t1)


167.682
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139.066
137.600
136.701
135.763
135.492
132.233
131.554
131.542
131.119
130.919
130.690
130.486
130.263
129.994
128.736
128.491
125.974
125.925
125.873
125.804
125.132
125.081
125.029
124.977
124.909
124.402
124.354
124.303
124.254
122.191
79.094
77.424
77.000
76.576
74.962
69.061
68.741
60.852
60.782
31.782
31.295
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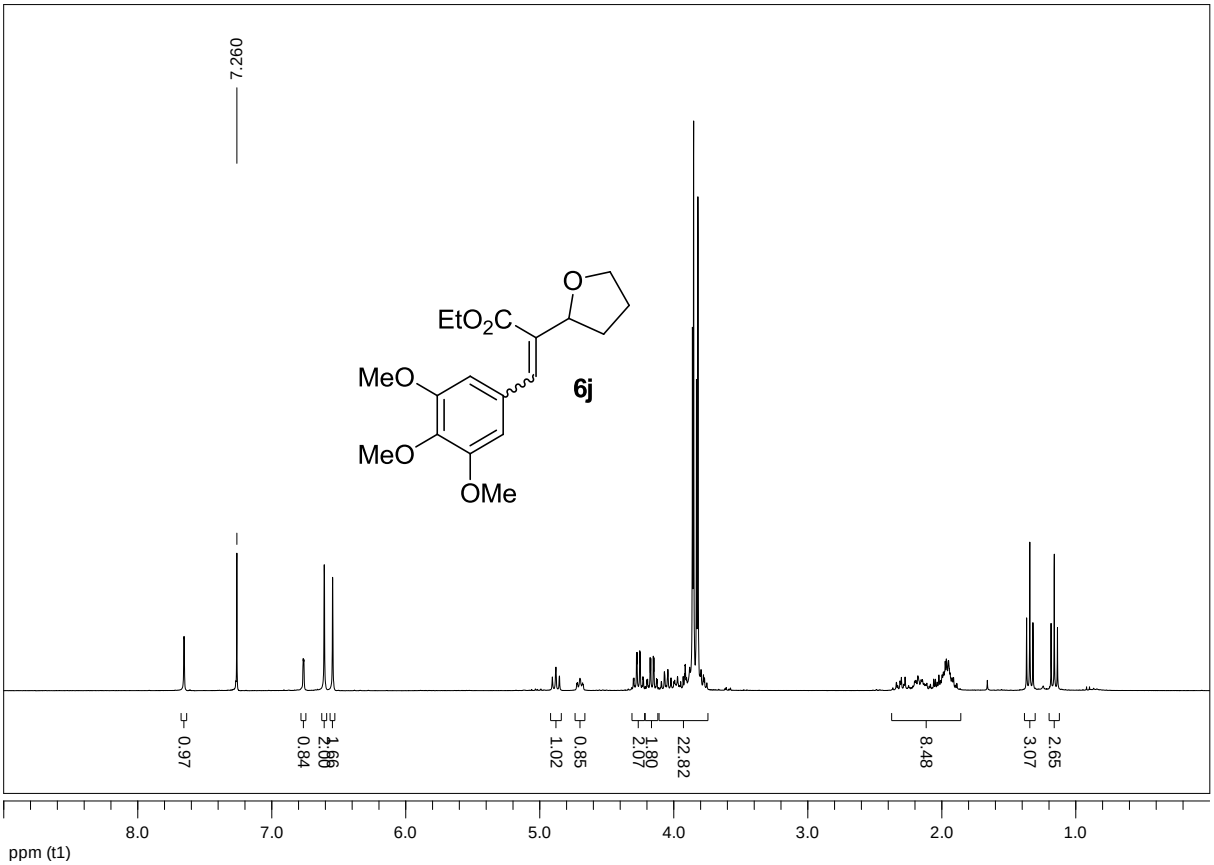
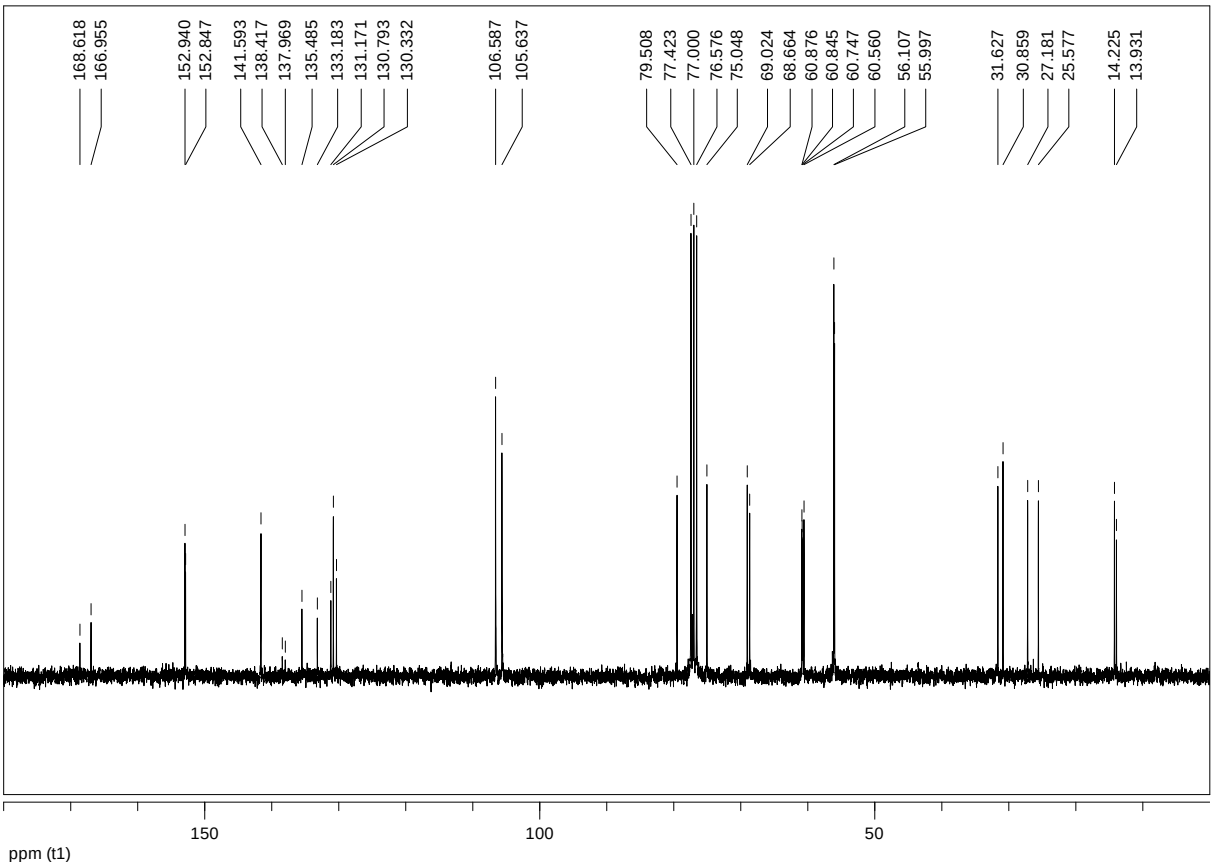
F3C
6i
150
100
50
ppm (t1)


7.260
EtO2C
O
MeO
MeO
OMe
6j
0.97
0.84
2.00
2.00
1.02
0.85
2.07
1.80
22.82
8.48
3.07
2.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


168.618
166.955
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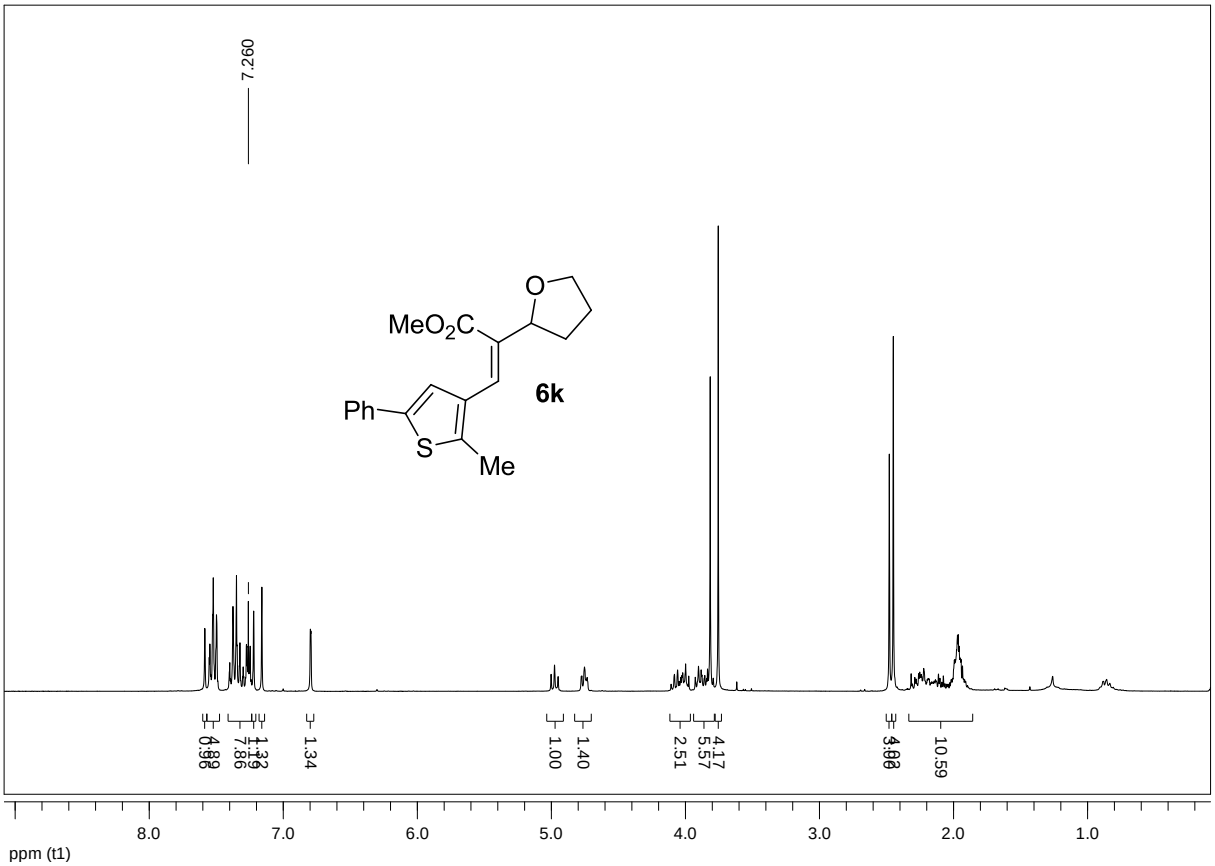
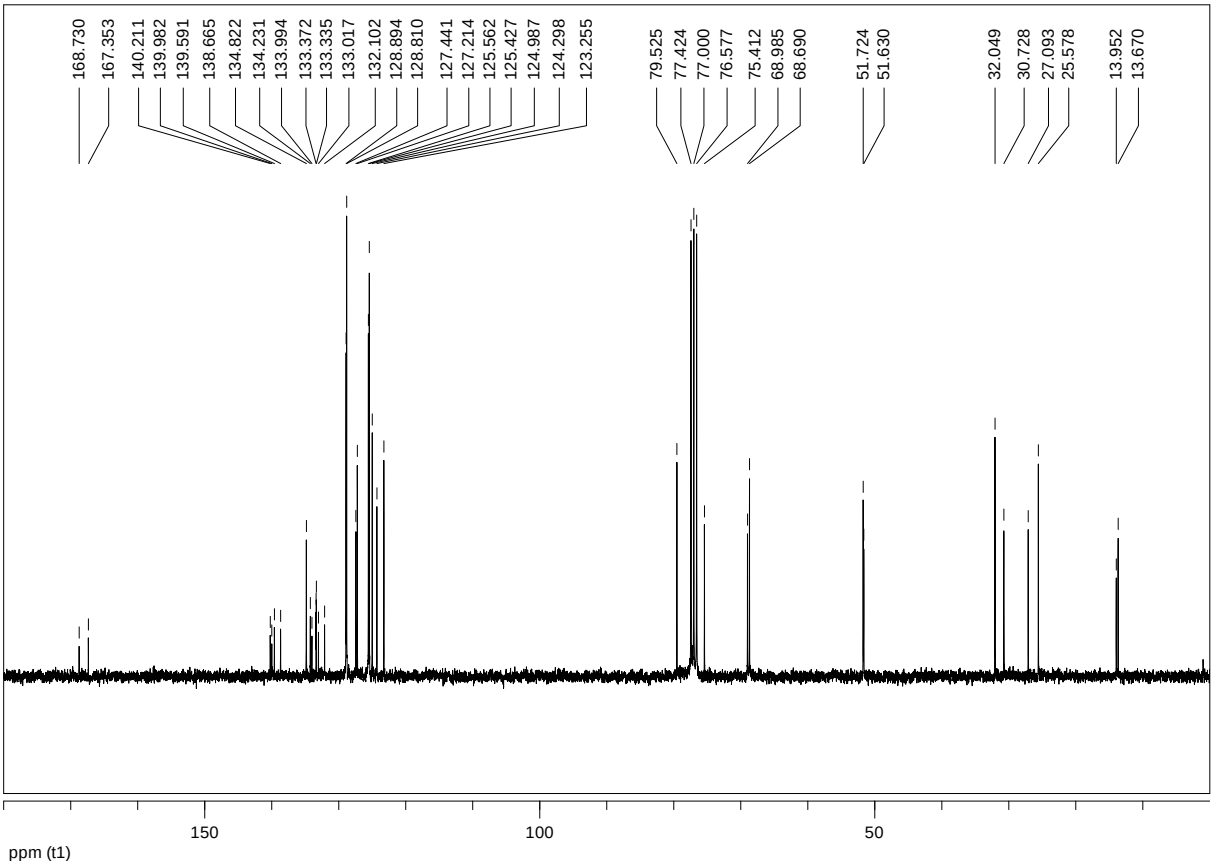
152.847
141.593
138.417
137.969
135.485
133.183
131.171
130.793
130.332
106.587
105.637
79.508
77.423
77.000
76.576
75.048
69.024
68.664
60.876
60.845
60.747
60.560
56.107
55.997
31.627
30.859
27.181
25.577
14.225
13.931
150
100
50
ppm (t1)


7.260
O
MeO2C
Ph
S
Me
6k
0.96
0.89
7.86
1.34
1.00
1.40
2.51
5.57
4.17
3.00
10.59
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


168.730
167.353
140.211
139.982
139.591
138.665
134.822
134.231
133.994
133.372
133.335
133.017
132.102
128.894
128.810
127.441
127.214
125.562
125.427
124.987
124.298
123.255
79.525
77.424
77.000
76.577
75.412
68.985
68.690
51.724
51.630
32.049
30.728
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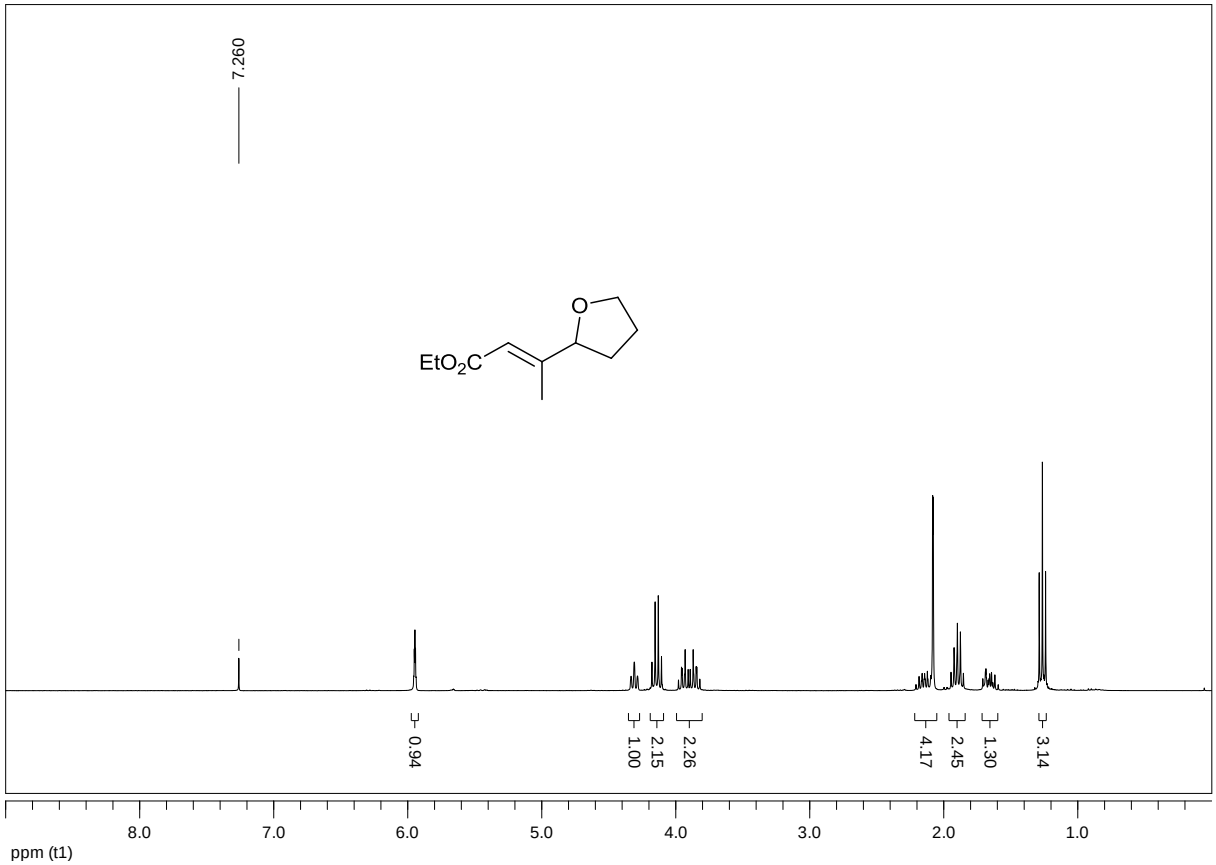
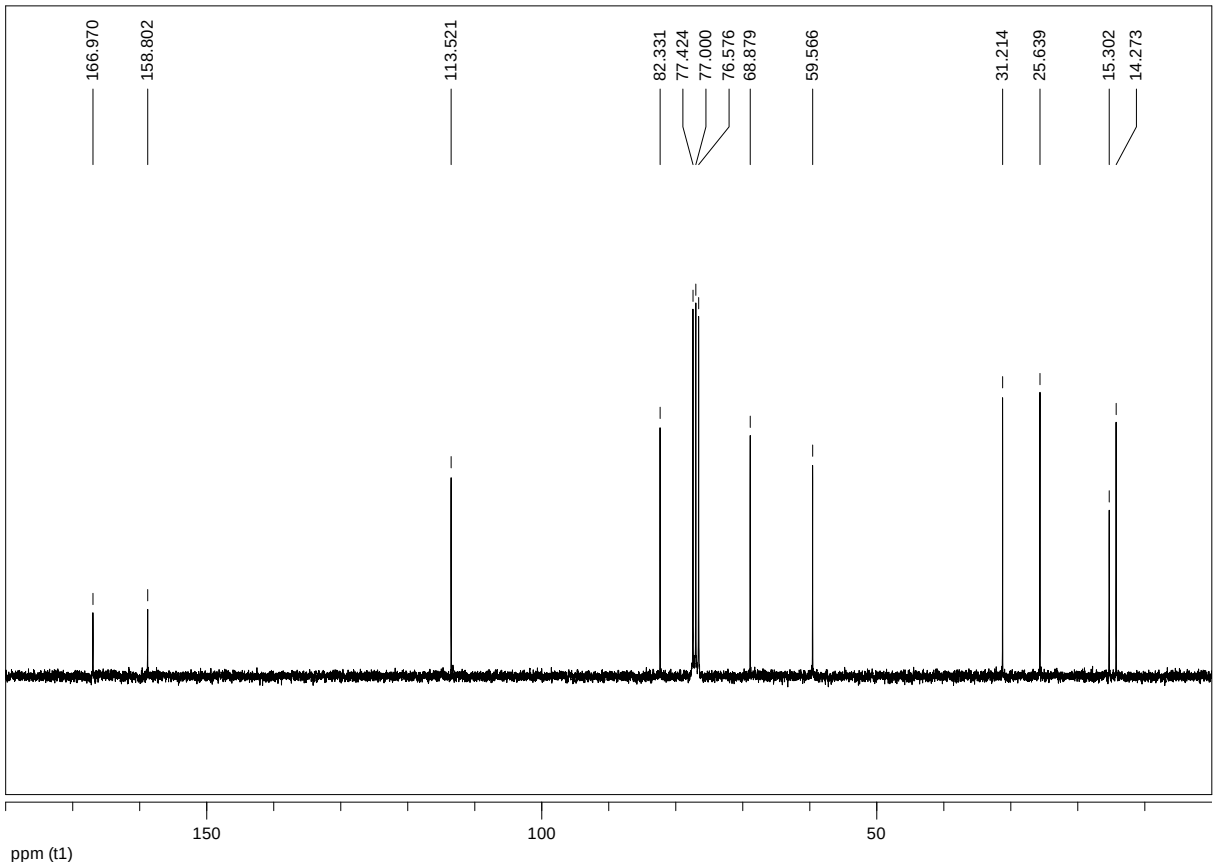
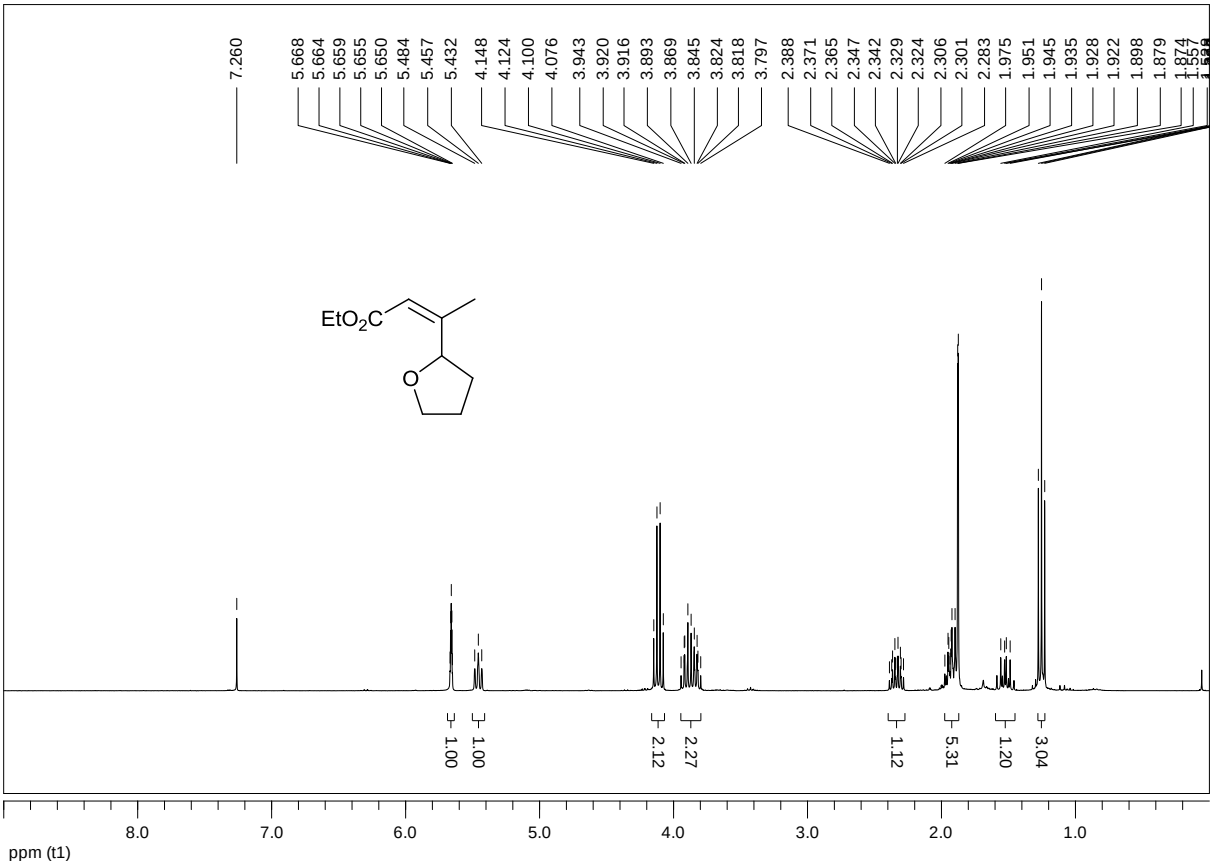
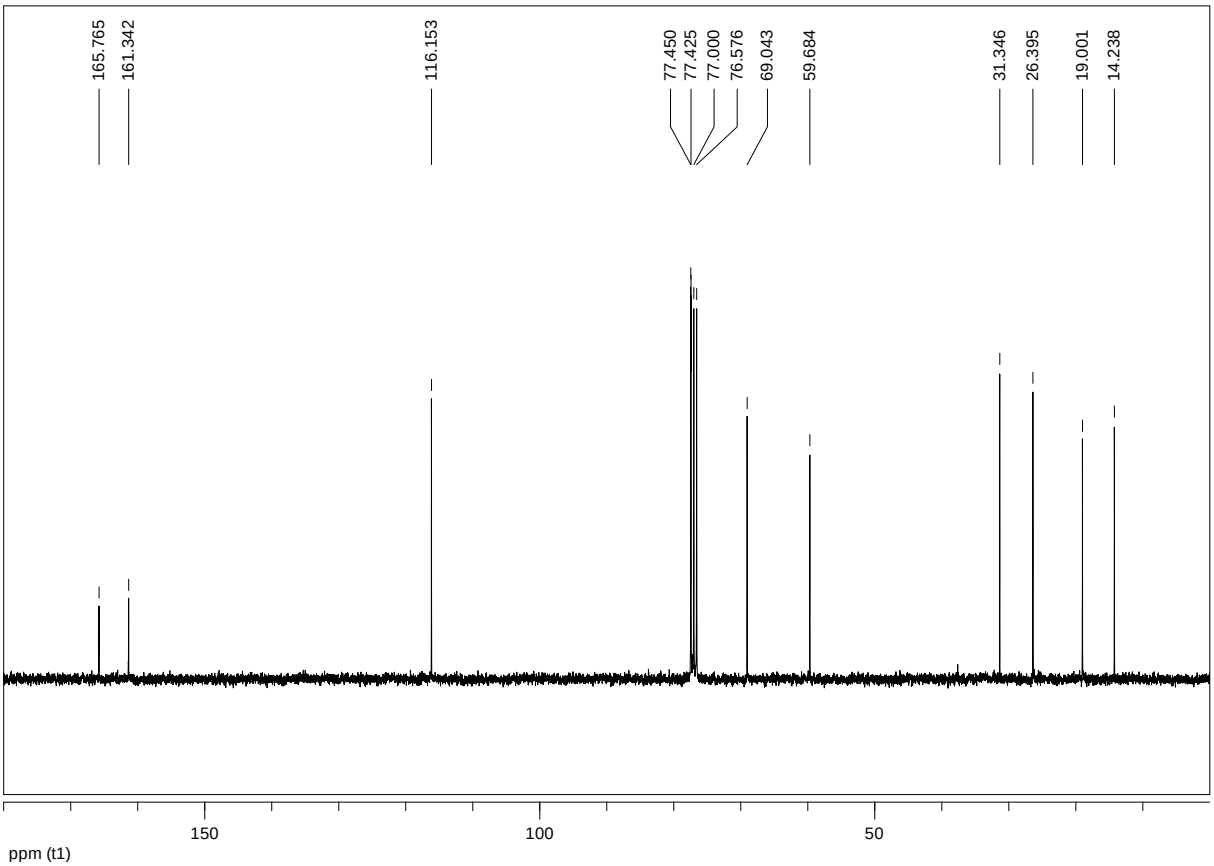
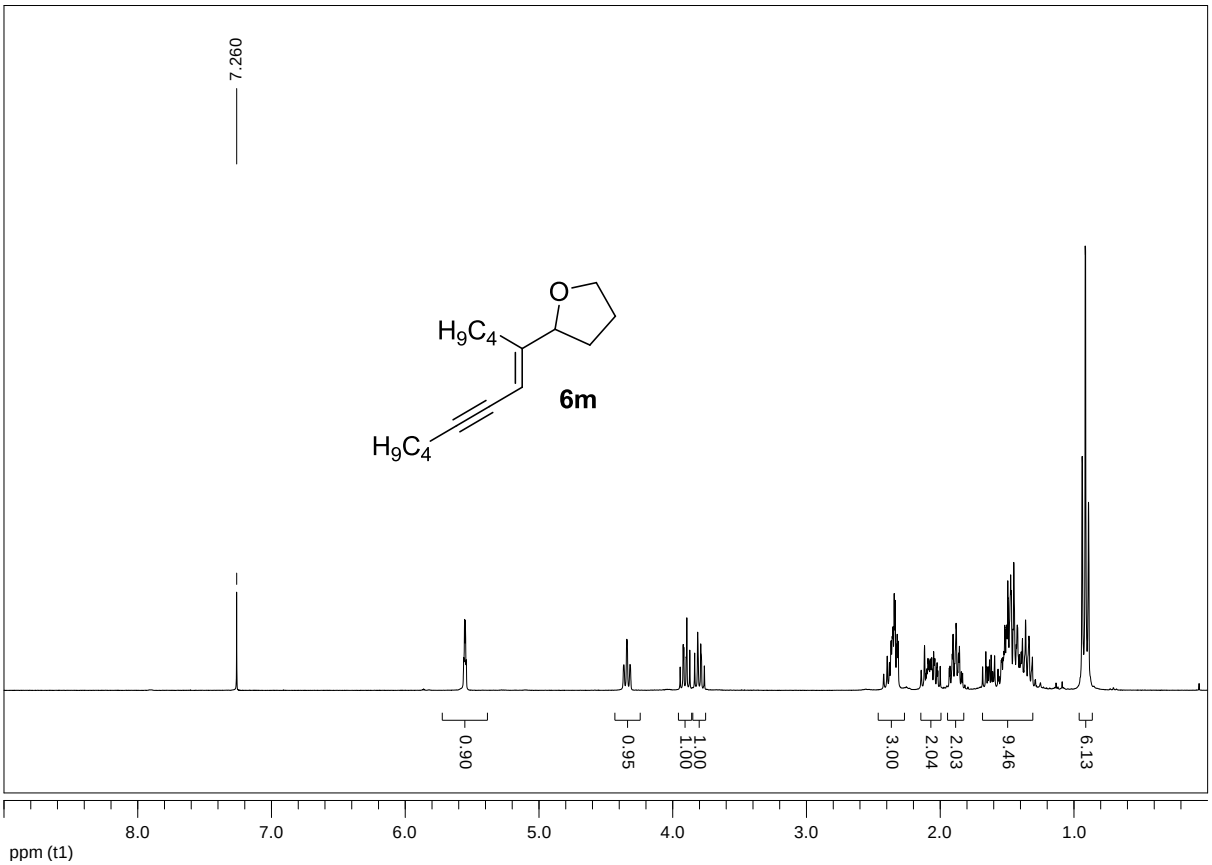
13.952
13.670
150
100
50
ppm (t1)

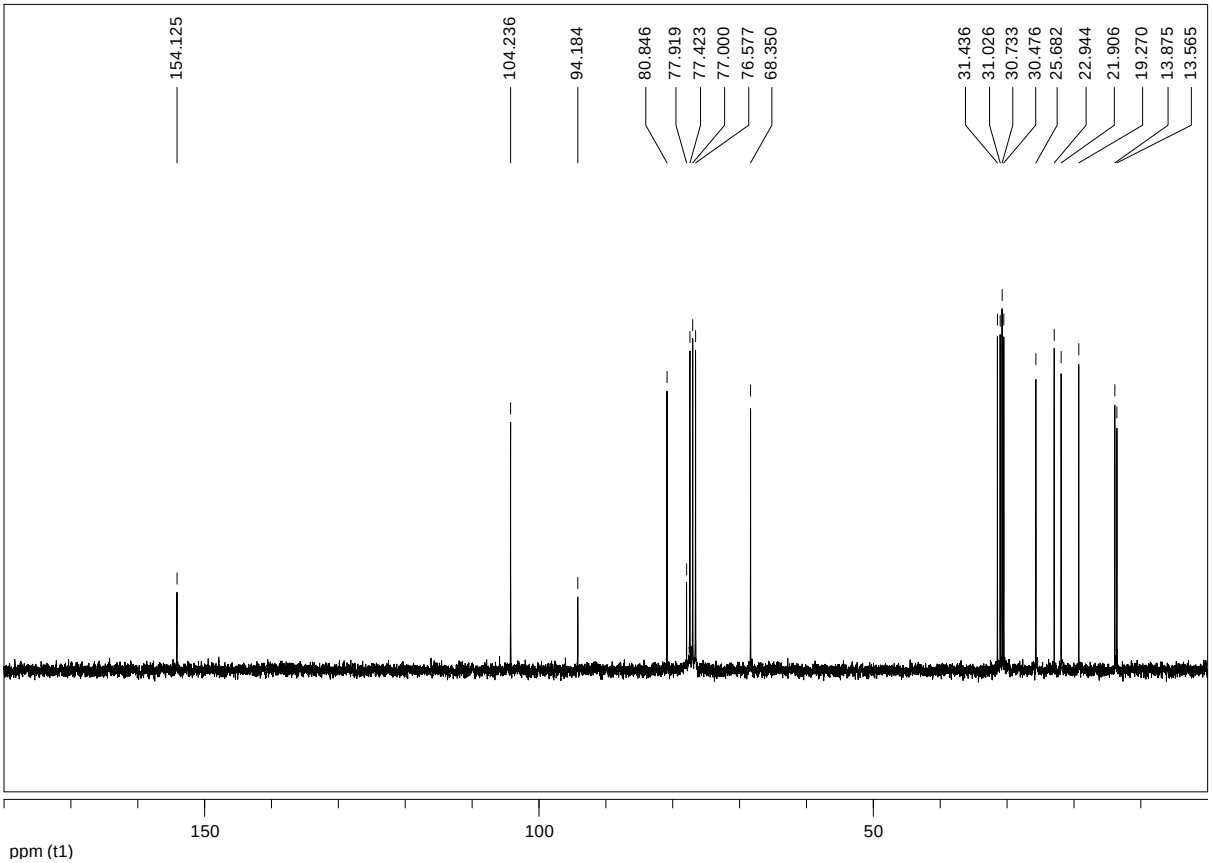

7.260
O
EtO2C
0.94
1.00
2.15
2.26
4.17
2.45
1.30
3.14
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

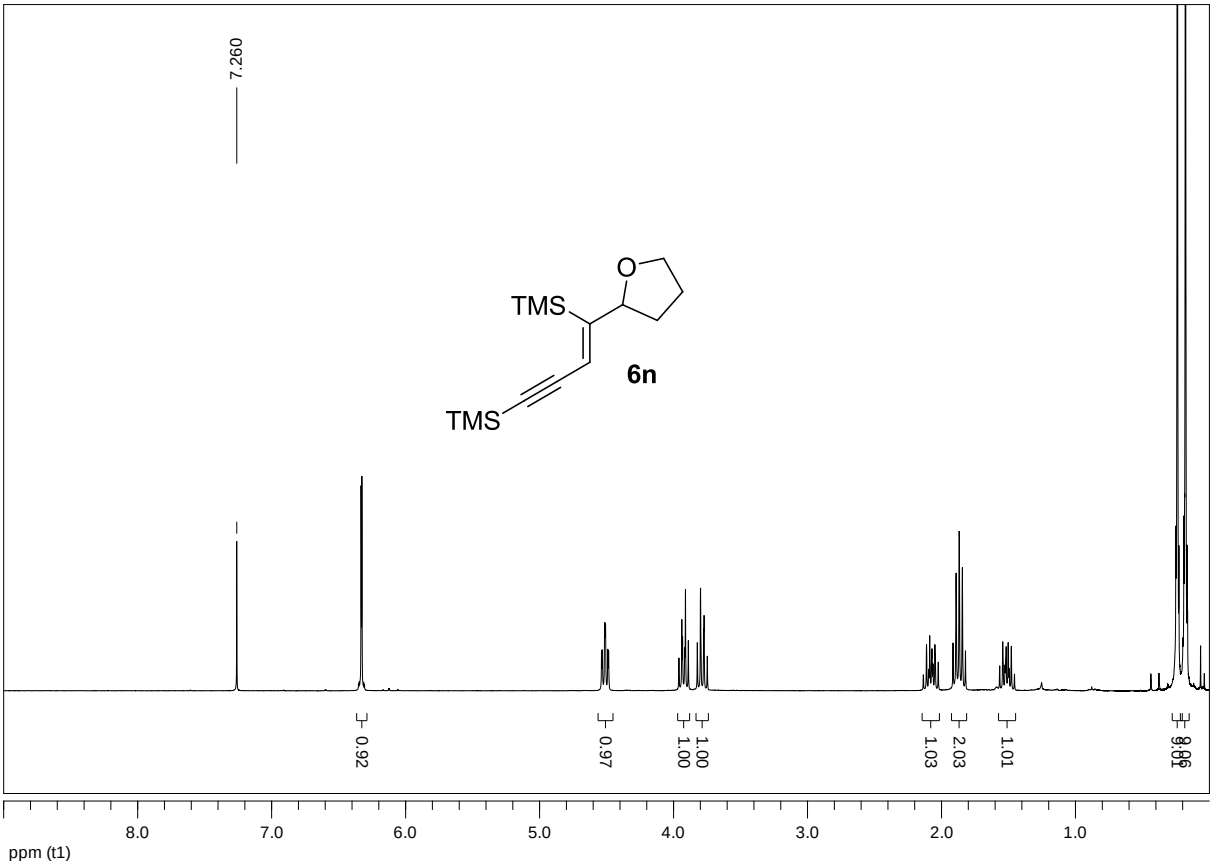

166.970
158.802
113.521
82.331
77.424
77.000
76.576
68.879
59.566
31.214
25.639
15.302
14.273
150
100
50
ppm (t1)

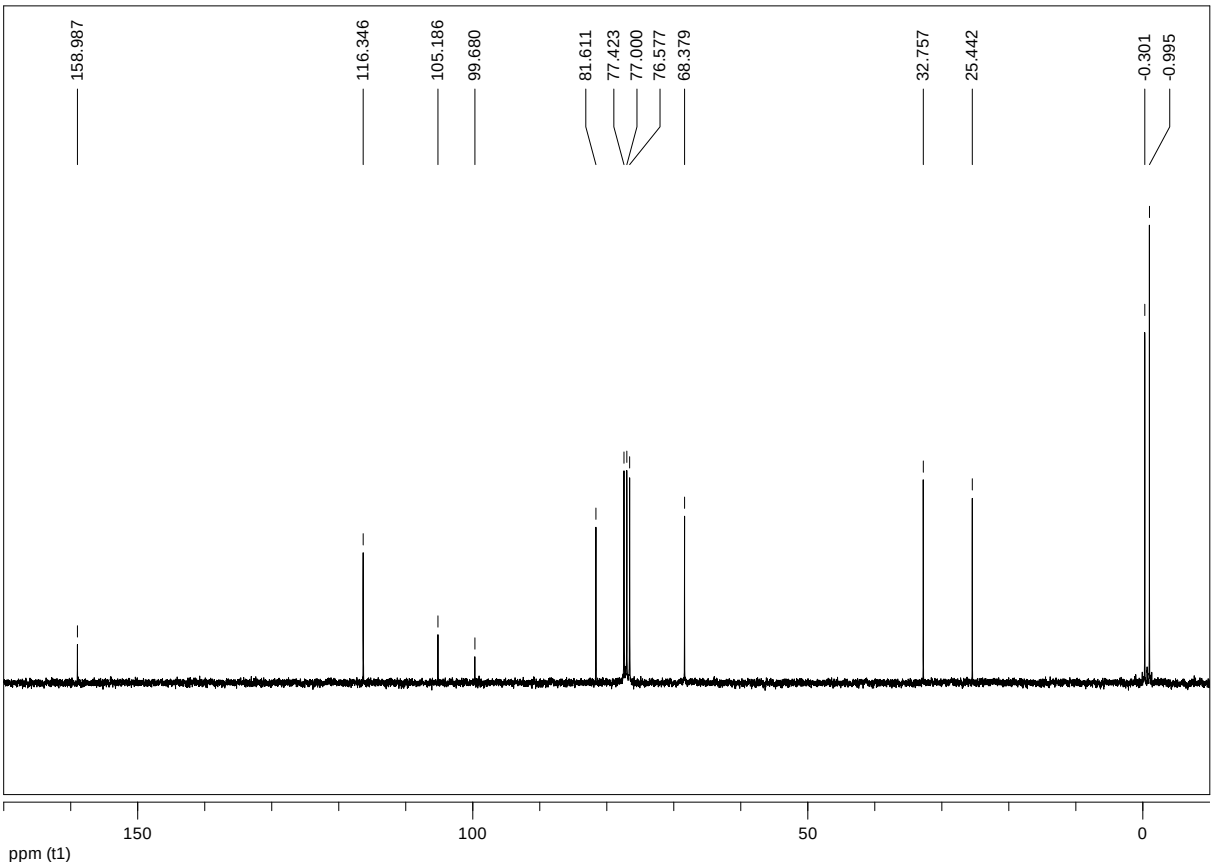

7.260
5.668
5.664
5.659
5.655
5.650
5.484
5.457
5.432
4.148
4.124
4.100
4.076
3.943
3.920
3.916
3.893
3.869
3.845
3.824
3.818
3.797
2.388
2.371
2.365
2.347
2.342
2.329
2.324
2.306
2.301
2.283
1.975
1.951
1.945
1.935
1.928
1.922
1.898
1.879
EtO2C
O
1.00
1.00
2.12
2.27
1.12
5.31
1.20
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

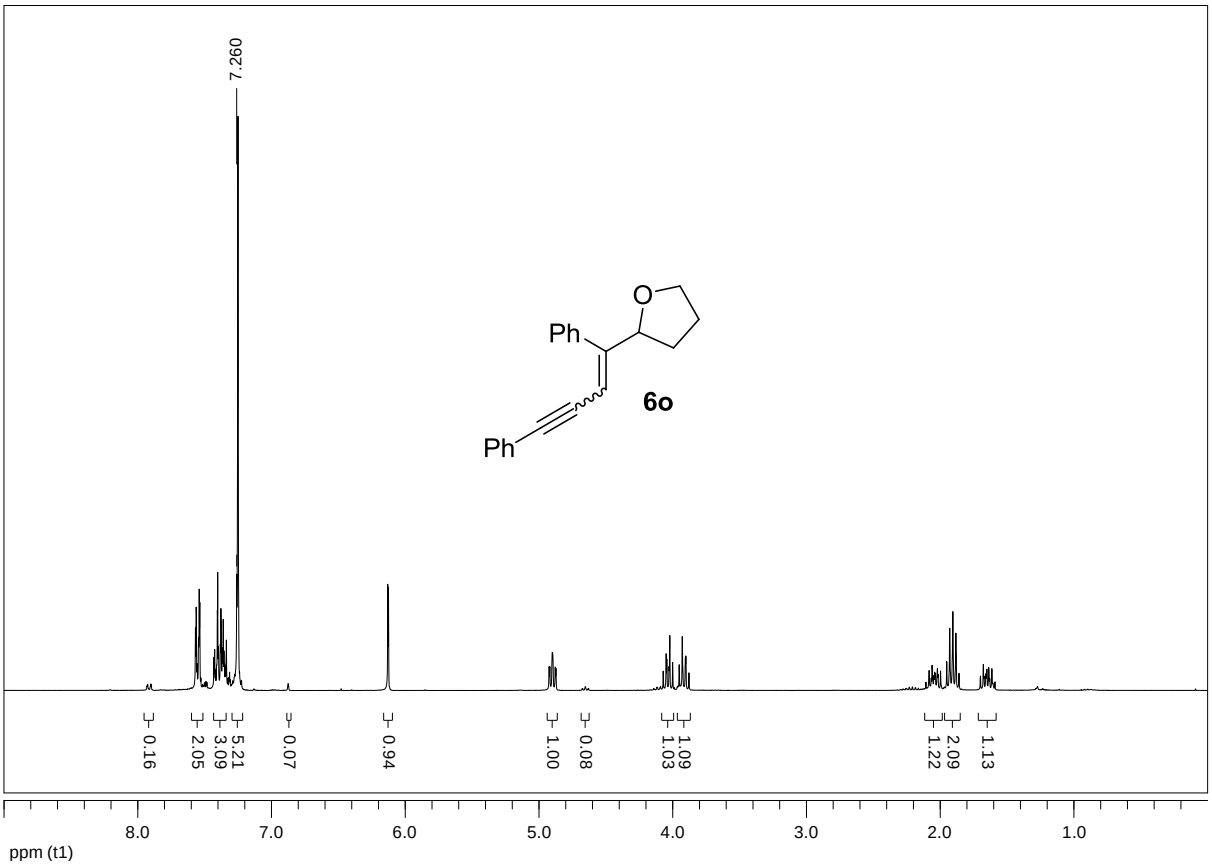

165.765
161.342
116.153
77.450
77.425
77.000
76.576
69.043
59.684
31.346
26.395
19.001
14.238
150
100
50
ppm (t1)

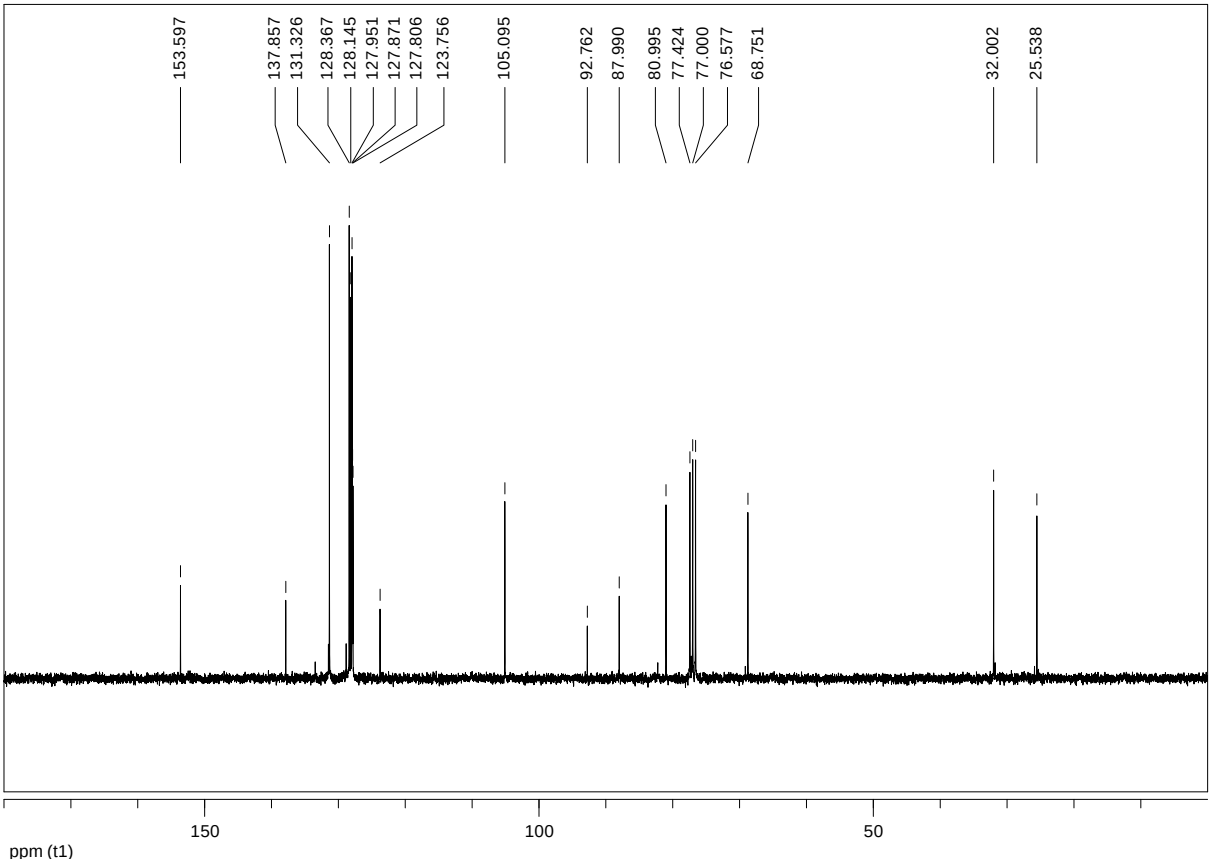

7.260
O
$H_9C_4$
$H_9C_4$
6m
0.90
0.95
1.00
3.00
2.04
2.03
6.46
9.13
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

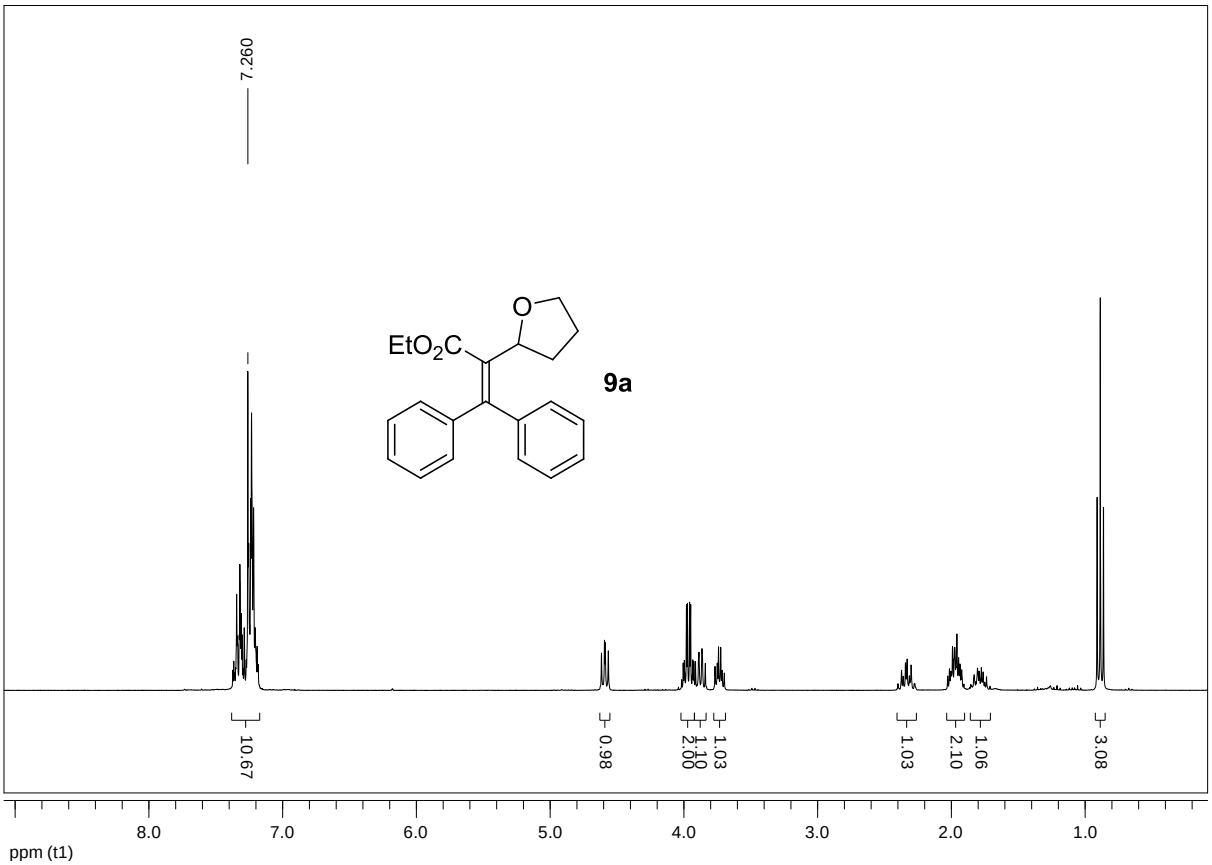

154.125
104.236
94.184
80.846
77.919
77.423
77.000
76.577
68.350
31.436
31.026
30.733
30.476
25.682
22.944
21.906
19.270
13.875
13.565
150
100
50
ppm (t1)

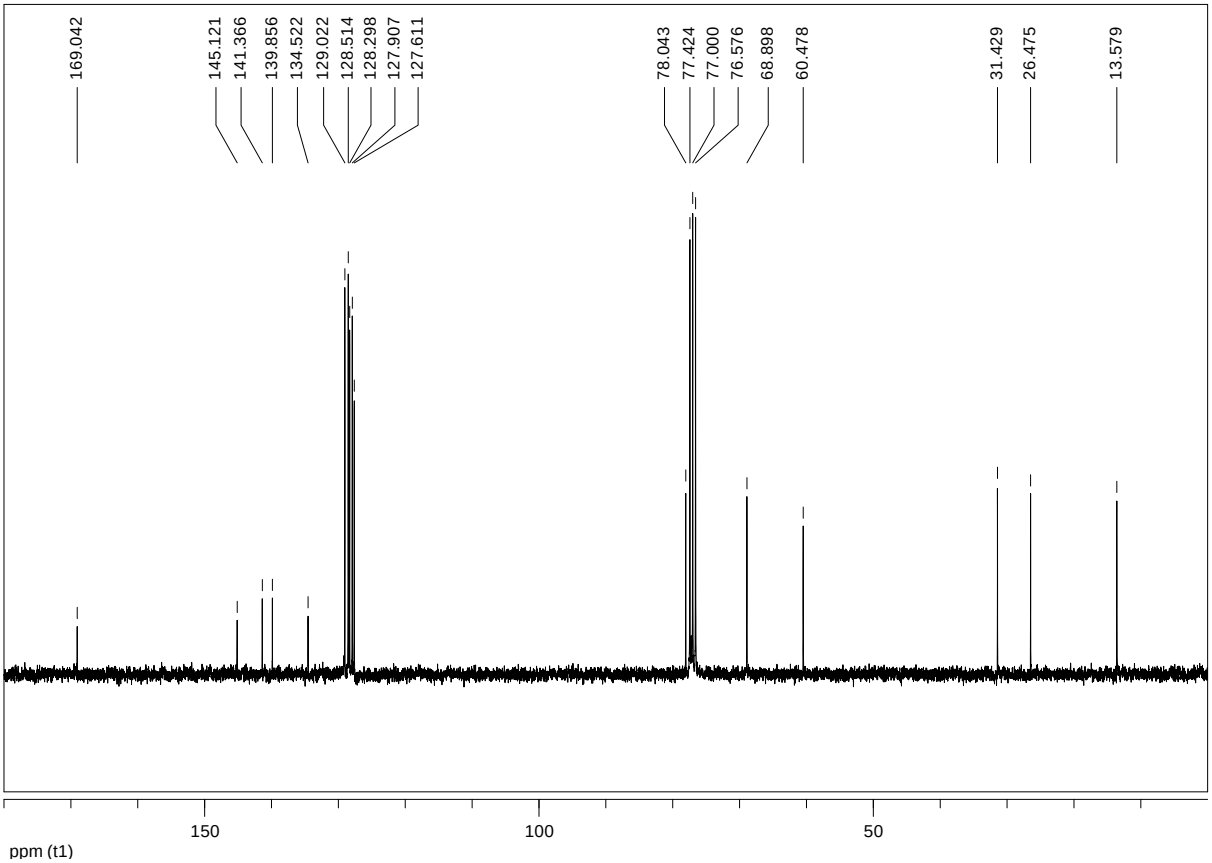

7.260
O
TMS
TMS
6n
0.92
0.97
1.00
1.00
1.03
2.03
1.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

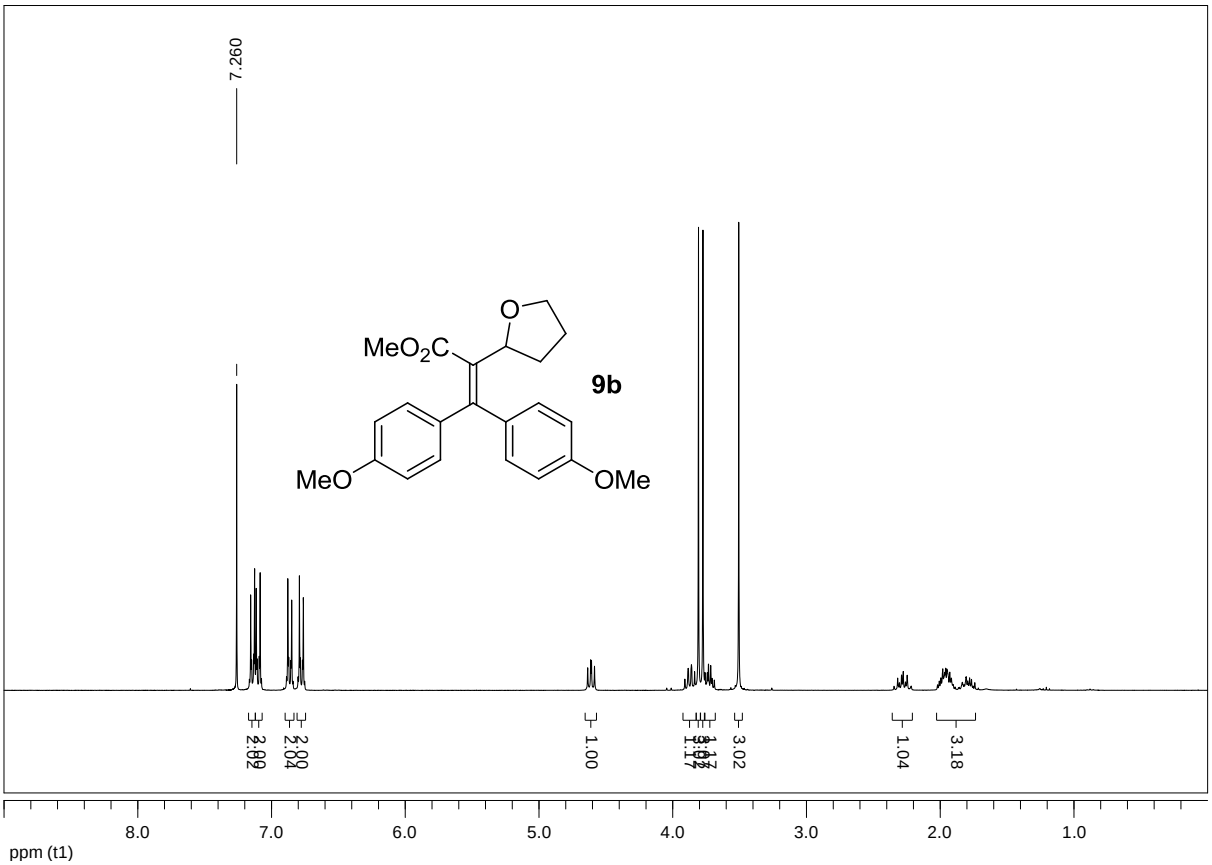

158.987
116.346
105.186
99.680
81.611
77.423
77.000
76.577
68.379
32.757
25.442
-0.301
-0.995
150
100
50
0
ppm (t1)

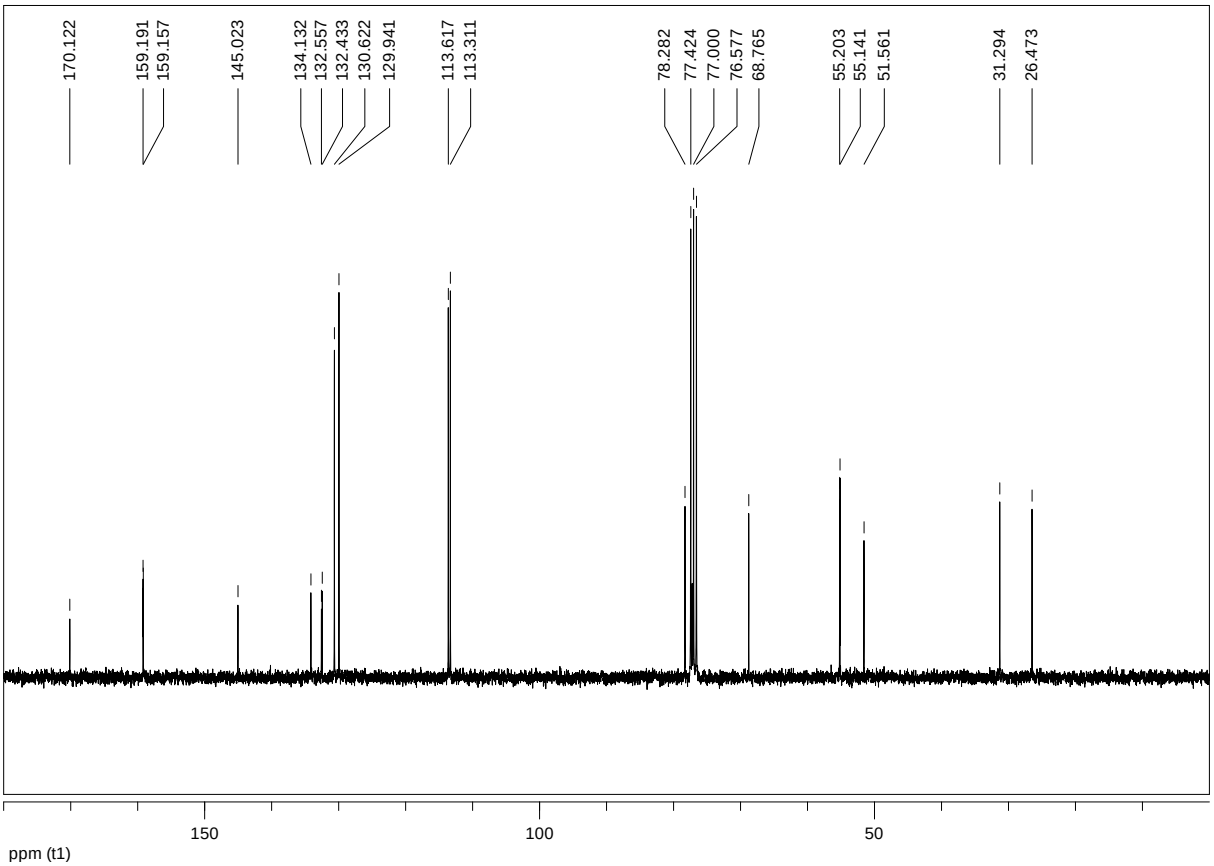

7.260
O
Ph
Ph
6o
0.16
2.05
3.09
5.21
0.07
0.94
1.00
0.08
1.03
1.09
1.22
2.09
1.13
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

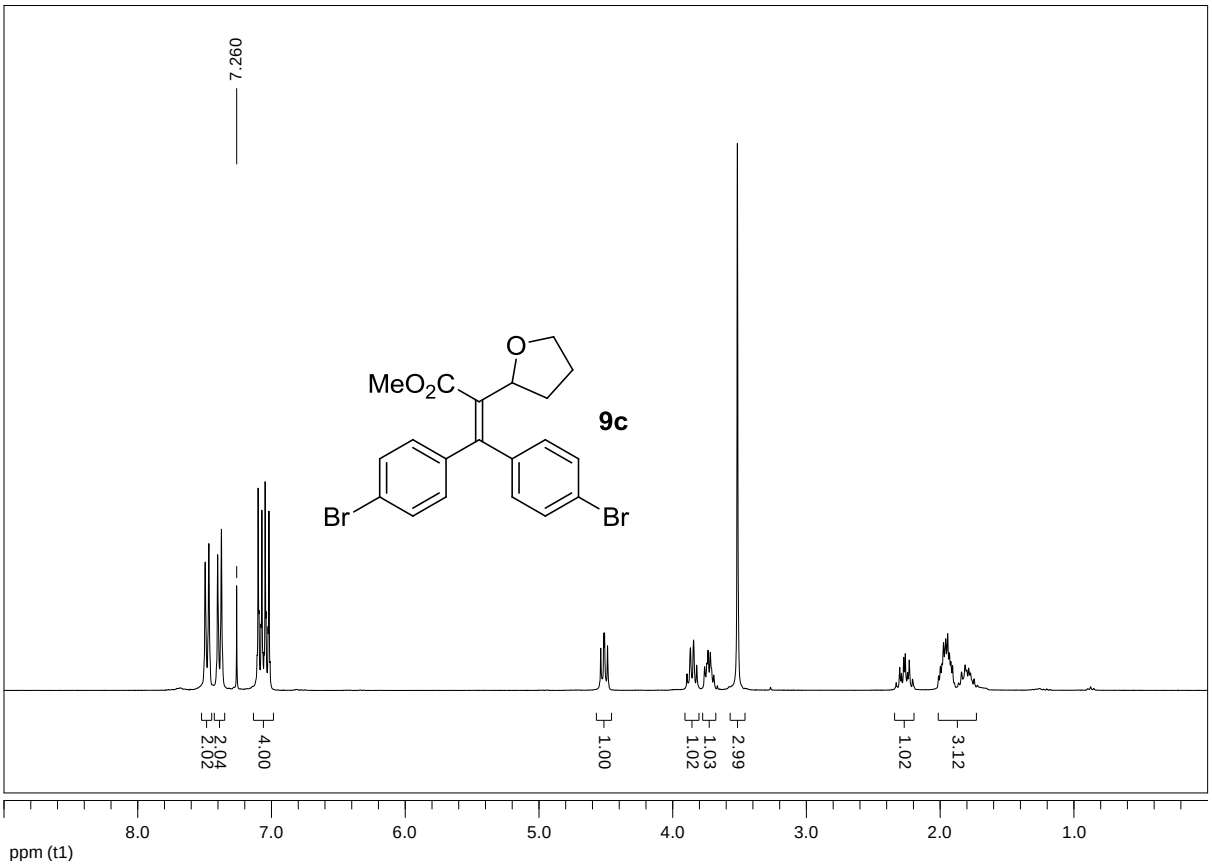

153.597
137.857
131.326
128.367
128.145
127.951
127.871
127.806
123.756
105.095
92.762
87.990
80.995
77.424
77.000
76.577
68.751
32.002
25.538
150
100
50
ppm (t1)

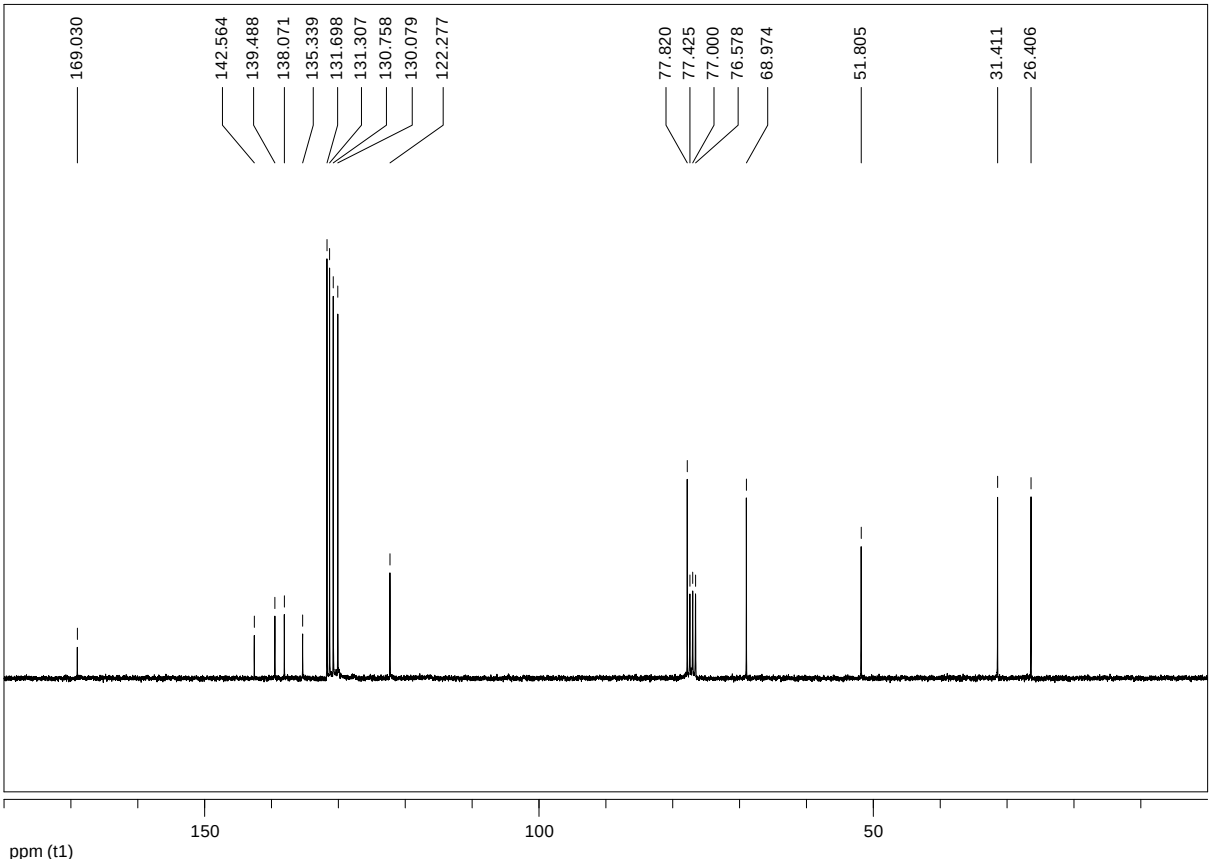

7.260
O
EtO2C
9a
10.67
0.98
2.00
1.10
1.03
1.03
2.10
1.09
3.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

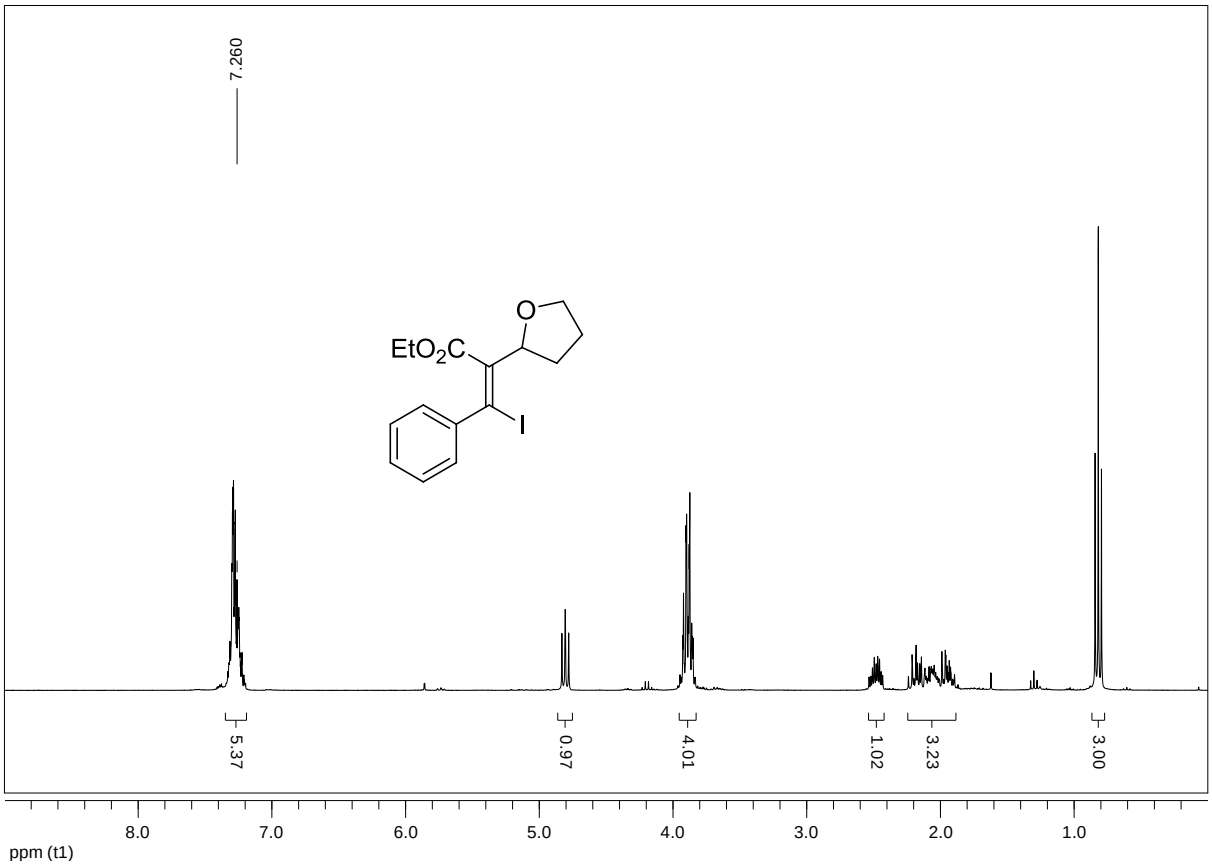

169.042
145.121
141.366
139.856
134.522
129.022
128.514
128.298
127.907
127.611
78.043
77.424
77.000
76.576
68.898
60.478
31.429
26.475
13.579
150
100
50
ppm (t1)

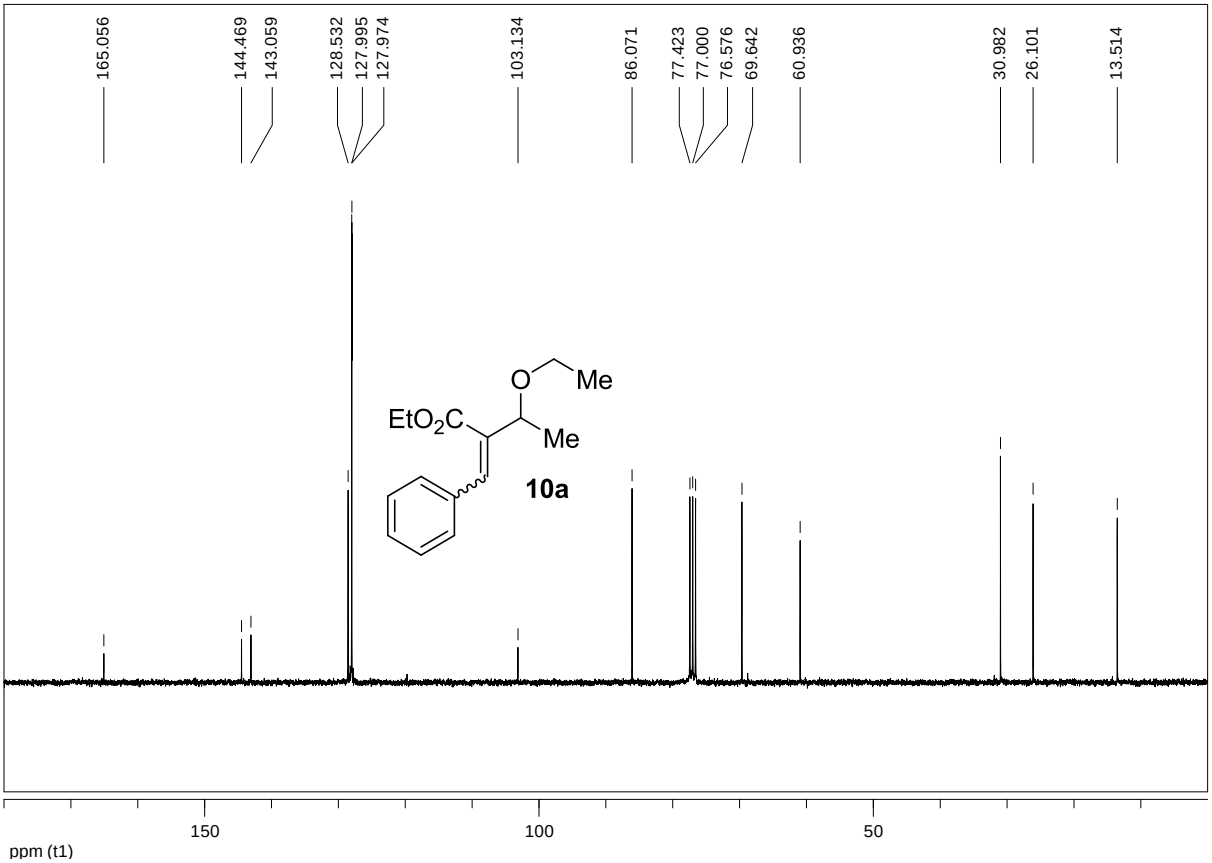

7.260
MeO2C
O
9b
MeO
OMe
2.00
2.04
2.00
1.00
1.17
3.02
1.04
3.18
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


170.122
159.191
159.157
145.023
134.132
132.557
132.433
130.622
129.941
113.617
113.311
78.282
77.424
77.000
76.577
68.765
55.203
55.141
51.561
31.294
26.473
150
100
50
ppm (t1)


7.260
O
MeO2C
9c
Br
Br
2.02
2.04
4.00
1.00
1.02
1.03
2.99
1.02
3.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


169.030
142.564
139.488
138.071
135.339
131.698
131.307
130.758
130.079
122.277
77.820
77.425
77.000
76.578
68.974
51.805
31.411
26.406
150
100
50
ppm (t1)


7.260
O
EtO2C
I
5.37
0.97
4.01
1.02
3.23
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


165.056
144.469
143.059
128.532
127.995
127.974
103.134
86.071
77.423
77.000
76.576
69.642
60.936
30.982
26.101
13.514
O
Me
EtO2C
Me
10a
150
100
50
ppm (t1)