Electronic Supplementary Material (ESI) for Green Chemistry.

Alkoxide-Catalyzed Addition of Alkyl Carbonates across Alkynes – Stereoselective Synthesis of (*E*)-β-Alkoxyacrylates

Timo Wendling, Eugen Risto, Benjamin Erb and Lukas J. Gooßen*

Fakultät für Chemie und Biochemie, Ruhr Universität Bochum, Universitätsstr. 150, 44801 Bochum (Germany).

(Germany), Fax: (+49)234 32 14675, E-mail: lukas.goossen@rub.de

Supporting Information

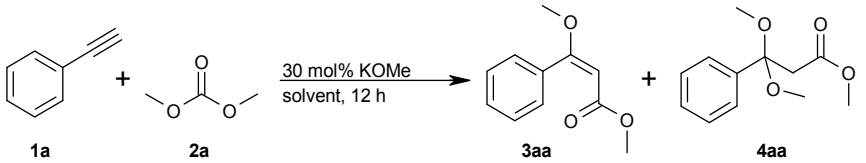
Experimental procedures and data

General Methods. All reactions were performed in oven-dried glassware containing a Teflon-coated stirring bar and dry septum. Solvents were purified and dried by standard procedures prior to use. All reactions were monitored by GC using *n*-dodecane as an internal standard. Response factors of the products with regard to *n*-dodecane were obtained experimentally by analyzing known quantities of the substances. GC analyses were carried out using a HP6890 with HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25, 100/2.3-30-300/3) and a time program beginning with 2 min at 60 °C followed by 30 °C/min ramp to 300 °C, then 3 min at this temp. NMR spectra were obtained on Bruker AMX 400 system using $CDCl_3$ as solvent, with proton and carbon resonances at 400 MHz and 101 MHz, respectively. Mass spectrometric data were acquired on a GC-MS Saturn 2100 T (Varian). Infrared spectra were recorded on Perkin Elmer Spectrum 100 FT-IR Spectrometer with Universal ATR Sampling Accessory. Melting points were measured on a Mettler FP 61. CHN-elemental analyses were performed with a Hanau Elemental Analyzer vario Micro cube and HRMS with a Waters GCT Premier. Commercial substrates were used as received unless otherwise stated.

Starting materials 2-Ethynylnaphthalene (**1j**) and phenylacetylene-d_1 (**1a-*d*$_1$**) were synthesized following known procedures.[1,2]

Additional Screening Experiments

Table S1.

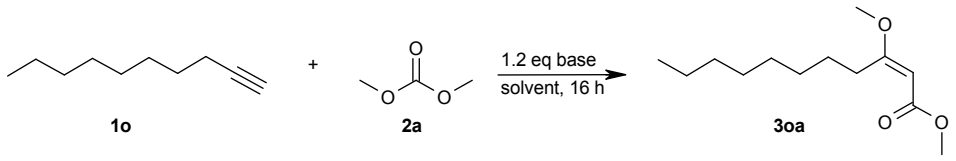


1a **2a** **3aa** **4aa**

Entry	DMC (eq)	Solvent (mL)	Temp. (°C)	Conversion[b] (%)	Yield[b] (%)		
					3aa	**4aa**	**E/Z**
1	5	DMSO (2)	rt	100	83	5	15 : 1
2	1.2	"	50	100	82	3	10 : 1
3	"	Anisol (2)	rt	-	-	-	-
4	"	MeCN (2)	"	-	-	-	-
5	"	MeOH (2)	"	-	-	-	-
6	"	DMSO (1)	"	100	82	6	15 : 1
7[c]	"	DMSO (2)	"	-	-	-	-
8[d]	"	"	"	87	70	3	17 : 1

[a] Reaction conditions: 0.50 mmol of **1a**, 0.60 mmol of **2a**, 0.15 mmol of KOMe, 12 h, rt. [b] Conversions, yields and E/Z ratios were determined by GC using *n*-dodecane as internal standard. [c] H_2O (50 µl) was added. [d] Under air.

Table S2.



1o + 2a → 3oa

Entry	DMC (eq)	Solvent (mL)	Base	Temp. (°C)	Conversion[b] (%)	Yield[b] (%)
1	3	Bu_2O	KOMe	90	-	-
2	**“**	**“**	**KO^{t}Bu**	**“**	**97**	**49**
3[c]	“	“	Potassium *tert*-Amylate	“	100	20
4	“	“	Me_4NF	“	8	-
5	“	“	Cs_2CO_3	“	-	-
6	“	“	K_3PO_4	“	-	-
7[d]	“	“	KO^{t}Bu	“	100	18
8	10	“	“	“	85	40
9	1.2	“	“	“	100	20
10	3	“	“	110	100	41
11	“	“	“	70	96	44
12	“	DMSO	“	90	71	21
13	“	Anisole	“	“	100	34
14	“	DMC	“	“	90	36
15	“	1,4-Dioxane	“	“	100	35
16	“	DMF	“	“	97	28
17	“	Toluene	“	“	100	37
18[e]	“	Bu_2O	“	“	70	38

[a] Reaction conditions: 0.50 mmol of **1o**, 1.50 mmol of **2a**, 0.60 mmol of base, 0.5 mL solvent, 16 h. [b] Conversions and yields were determined by GC using *n*-dodecane as internal standard. No (*Z*)-product was observed. [c] Potassium *tert*-Amylate (25% (w/v) in toluene). [d] 1.00 mmol of KO^{t}Bu. [e] 1 mL Bu_2O.

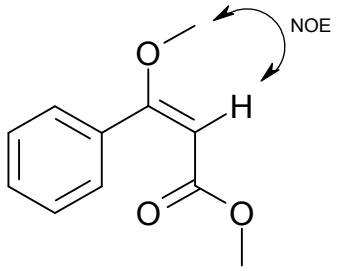
GP1: General procedure for the synthesis of aromatic β-methoxyacrylates

An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with potassium methoxide (21.0 mg, 0.30 mmol) and closed with a septum cap. The atmosphere was changed three times with nitrogen; afterwards DMSO (1 mL) and alkyl carbonate (1.20 mmol) were added *via* syringe. A stock solution of the liquid alkyne (1.00 mmol) dissolved in DMSO (0.5 mL) was added over 45 min *via* syringe pump. In case of solid alkynes, those were added directly together with the base. The resulting mixture was stirred (500 rpm) at room temperature for 12 h, diluted with 20 mL of ethyl acetate and washed with 20 mL of water. The aqueous phase was extracted with ethyl acetate (2 x 15 mL), the combined organic layers were washed with brine (15 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (SiO_2). The stereochemistry was confirmed by NOE experiments of selected examples.

GP 2: General procedure for the synthesis of aliphatic β-methoxyacrylates

An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with potassium *tert*-butoxide (135 mg, 1.20 mmol) and closed with a septum cap. The atmosphere was changed three times with nitrogen; afterwards di-*n*-butyl ether (1 mL), dimethyl carbonate (255 μL, 3.00 mmol) and the liquid alkyne (1.00 mmol) were added *via* syringe. The resulting mixture was stirred (500 rpm) at 90 °C for 16 h and then cooled to room temperature. Ethyl acetate (20 mL) was added and the mixture was washed with 20 mL water. The aqueous phase was separated and extracted with ethyl acetate (2 x 15 mL), the combined organic layers were washed with brine (15 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, ethyl acetate/cyclohexane gradient). The stereochemistry was confirmed by NOE experiments of selected examples.

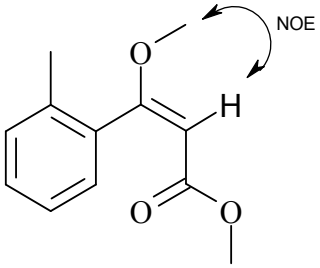
Synthesis of (*E*)-methyl 3-methoxy-3-phenylprop-2-enoate (3aa) [CAS: 60456-20-4]



Compound **3aa** was prepared following the general procedure GP1 from phenylacetylene (**1a**) (102 mg, 110 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, toluene/dichloromethane gradient) yielded **3aa** as a colorless oil (144 mg, 75 %).

Elemental analysis found: C, 68.5; H, 6.3. $C_{11}H_{12}O_3$ requires C, 68.7; H, 6.3%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3062, 2988, 2948, 2840, 1717, 1696, 1619, 1597, 1577, 1495, 1434, 1380, 1262, 1219, 1194, 1154, 1112, 1025, 985, 919, 820, 765, 695. ^{1}H-NMR (400 MHz, $CDCl_3$) 7.35-7.49 (5 H, m), 5.29 (1 H, s), 3.82 (3 H, s), 3.60 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 171.6, 167.1, 135.0, 129.7, 128.6, 128.6, 127.7, 127.7, 91.9, 56.3, 50.9. MS (Ion trap, EI) *m/z* 193.0 (24%), 192.0 (M^+, 30), 191.0 (81), 161.0 (100), 131.0 (22), 115.1 (30), 105.0 (25). HRMS-EI (TOF) found: 192.0783 $[M]^+$. $C_{11}H_{12}O_3$ requires 192.0786.

Synthesis of (*E*)-methyl 3-methoxy-3-(2-methylphenyl)prop-2-enoate (3ba) [CAS:147498-91-7]

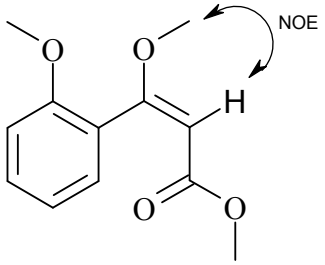


Compound **3ba** was prepared following the general procedure GP1 from 2-(methyl)phenylacetylene (**1b**) (120 mg, 130 µl, 1.00 mmol)) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3ba** as a yellow oil (188 mg, 91 %).

Elemental analysis found: C, 69.8; H, 6.9. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.8%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3071, 3021, 2950, 1721, 1621, 1599, 1436, 1373, 1264, 1192, 1153, 1122, 1098,

1031, 921, 823, 758, 727. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.32—7.28 (1 H, m), 7.24—7.16 (3 H, m), 5.37 (1 H, s), 3.80 (3 H, s), 3.55 (3 H, s), 2.26 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 171.9, 166.7, 135.5, 135.4, 129.8, 129.1, 128.2, 125.3, 93.1, 56.2, 50.9, 19.0. MS (Ion trap, EI) *m/z* 190.9 (23), 174.9 (100), 149.0 (17), 130.8 (25), 115.0 (24), 102.8 (20), 90.9 (19). HRMS-EI (TOF) found: 206.0948. $[M]^+$. $C_{12}H_{14}O_3$ requires 206.0943.

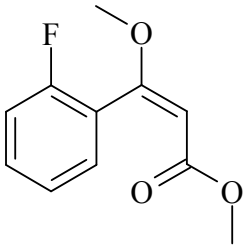
Synthesis of (*E*)-methyl 3-methoxy-3-(2-methoxyphenyl)prop-2-enoate (3ca) [CAS:82700-88-7]



Compound **3ca** was prepared following the general procedure GP1 from 2-ethynylanisole (**1c**) (136 mg, 134 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3ca** as a yellow oil (196 mg, 88 %).

Elemental analysis found: C, 64.9; H, 6.4. $C_{12}H_{14}O_4$ requires C, 64.8; H, 6.4%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3012, 2947, 2840, 1720, 1698, 1625, 1595, 1495, 1460, 1435, 1374, 1246, 1216, 1151, 1123, 1099, 1024, 920, 809, 751. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.35—7.39 (1 H, m), 7.20 (1 H, dd, *J* = 7.5, 1.8 Hz), 6.93—7.00 (2 H, m), 5.36 (1 H, s), 3.81 (3 H, s), 3.79 (3 H, s), 3.55 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 168.7, 166.9, 156.5, 130.6, 129.6, 124.7, 120.2, 110.9, 93.7, 56.2, 55.7, 50.8. MS (Ion trap, EI) *m/z* 192.0 (13), 190.8 (100), 148.9 (17), 130.9 (23), 120.9 (20), 90.9 (15), 76.9 (14). HRMS-EI (TOF) found: 222.0890. $[M]^+$. $C_{12}H_{14}O_4$ requires 222.0892.

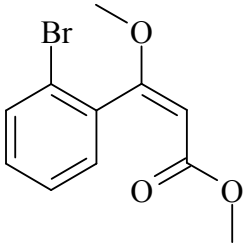
Synthesis of (*E*)-methyl 3-(2-fluorophenyl)-3-methoxyprop-2-enoate (3da)



Compound **3da** was prepared following the general procedure GP1 from 1-ethynyl-2-fluoro-benzene (**1d**) (124 mg, 117 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3da** as a yellow oil (182 mg, 87 %).

Elemental analysis found: C, 62.8; H, 5.4. $C_{11}H_{11}FO_3$ requires C, 62.9; H, 5.3%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3015, 2950, 2840, 1719, 1633, 1607, 1490, 1452, 1437, 1374, 1267, 1225, 1194, 1149, 1121, 1095, 1028, 987, 922, 826, 758. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.37—7.43 (1 H, m), 7.32 (1 H, td, *J* = 7.4, 1.8 Hz), 7.18 (1 H, td, *J* = 7.4, 1.8 Hz), 7.08—7.13 (1 H, m), 5.41 (1 H, s), 3.83 (3 H, s), 3.60 (3 H, s). ^{19}F–NMR (400 MHz, $CDCl_3$) -114.7. ^{13}C–NMR (101 MHz, $CDCl_3$) 166.6 (d, *J* = 111Hz), 160.7, 158.2, 131.2 (d, *J* = 9.1 Hz), 129.9 (d, *J* = 2.7 Hz), 123.7 (d, *J* = 3.6 Hz), 123.5, 115.4 (d, *J* = 21.8 Hz), 94.5, 56.5, 51.0. MS (Ion trap, EI) *m/z* 211.0 (M+, 16%), 210.0 (35), 209.1 (46), 179.1 (100), 149.0 (17), 123.0 (16), 115.0 (22).

Synthesis of (*E*)-methyl 3-(2-bromophenyl)-3-methoxyprop-2-enoate (3ea) [CAS: 147498-95-1]



Compound **3ea** was prepared following the general procedure GP1 from 1-bromo-2-ethynylbenzene (**1e**) (185 mg, 127 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3ea** as an orange oil (250 mg, 92 %).

Gram scale synthesis:

An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with potassium methoxide (332 mg, 4.50 mmol) and closed with a septum cap. The atmosphere was changed three times with argon; afterwards DMSO (9.90 g, 9 mL) and dimethyl carbonate (**2a**) (1.64 g, 1.53 mL, 18.0 mmol) were added *via* syringe. A stock solution of 1-bromo-2-ethynylbenzene (**1e**) (2.77 g, 1.90 ml, 15.0 mmol) dissolved in DMSO (2.20 g, 2 mL) was added over 120 min *via* syringe pump. The resulting mixture was stirred (500 rpm) at room temperature for 12 h. Purification by Kugelrohr distillation (210°C, 1x10^{-2} mbar) yielded **3ea** as an orange oil (3.24 g, 80 %).

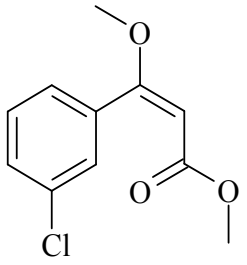
Calculation of E-factors:

$$E\ (with\ DMSO) = \frac{0.332\ g\ +\ 1.64\ g\ +\ 2.77\ g + 12.1\ g}{3.24\ g} = 5.2$$

$$E\ (without\ DMSO) = \frac{0.332\ g\ +\ 1.64\ g\ +\ 2.77\ g}{3.24\ g} = 1.5$$

Elemental analysis found: C, 48.7; H, 4.2. $C_{11}H_{11}BrO_3$ requires C, 48.8, H, 4.1%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3062, 2991, 2948, 2837, 1718, 1698, 1627, 1588, 1475, 1435, 1372, 1280, 1220, 1194, 1156, 1117, 1047, 1025, 984, 921, 825, 757, 721, 658. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.58—7.64 (1 H, m), 7.32—7.38 (1 H, m), 7.23—7.30 (2 H, m), 5.39 (1 H, s), 3.83 (3 H, s), 3.57 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 170.0, 166.4, 137.0, 132.5, 130.3, 129.8, 127.0, 121.7, 94.0, 56.6, 51.0. MS (Ion trap, EI) *m/z* 241.0 (9), 238.9 (10), 192.1 (12), 191.1 (100), 148.1 (9), 89.1 (9), 75.0 (7).

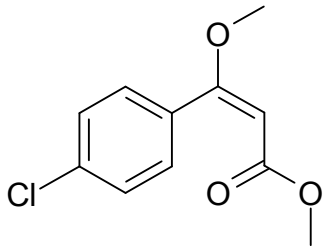
Synthesis of (*E*)-methyl 3-(3-chlorophenyl)-3-methoxprop-2-enoate (3fa)



Compound **3fa** was prepared following the general procedure GP1 from 3-chloro-1-ethynylbenzene (**1f**) (141 mg, 127 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, toluene/dichloromethane gradient) yielded **3fa** as a colourless oil (163 mg, 72 %).

Elemental analysis found: C, 58.3; H, 5.0. $C_{11}H_{11}ClO_3$ requires C, 58.3; H, 4.9%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3018, 2982, 2950, 2840, 1716, 1620, 1593, 1567, 1435, 1374, 1258, 1159, 1117, 1034, 990, 924, 816, 787, 698. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.42—7.43 (1 H, m), 7.38—7.41 (1 H, m), 7.32—7.33 (2 H, m), 5.29 (1 H, s), 3.81 (3 H, s), 3.61 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 169.8, 166.8, 136.6, 133.6, 129.7, 128.9, 128.7, 127.1, 92.5, 56.4, 51.0. MS (Ion trap, EI) *m/z* 226.9 (M^+, 33%), 225.9 (26), 225.0 (60), 197.0 (25), 195.0 (100), 44.0 (28), 40.0 (29). HRMS-EI (TOF) found: 226.0385. $[M]^+$. $C_{11}H_{11}ClO_3$ requires 226.0397.

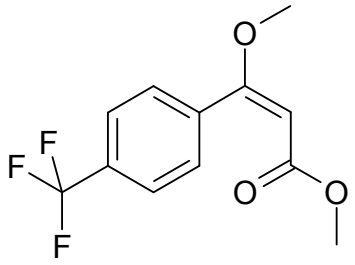
Synthesis of (*E*)-methyl 3-(4-chlorophenyl)-3-methoxyprop-2-enoate (3ga)



Compound **3ga** was prepared following the general procedure GP1 from 1-chloro-4-ethynylbenzene (**1g**) (137 mg, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, toluene/ dichloromethane gradient) yielded **3ga** as colorless needles (163 mg, 72 %).

mp 67.5—68.0 °C. Elemental analysis found: C, 58.5; H, 5.0. $C_{11}H_{11}ClO_3$ requires C, 58.3; H, 4.9%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3012, 2991, 2954, 2839, 1718, 1616, 1591, 1568, 1494, 1459, 1431, 1401, 1385, 1259, 1196, 1156, 1116, 1107, 1085, 1016, 984, 922, 831, 819, 783, 739, 722, 665. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.32—7.44 (4 H, m), 5.28 (1 H, s), 3.81 (3 H, s), 3.61 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 170.2, 166.9, 135.7, 133.3, 130.2, 130.2, 127.9, 127.9, 92.2, 56.4, 51.0. MS (Ion trap, EI) *m/z* 227.0 (27%), 226.0 (M^+, 32), 225.1 (76), 197.0 (37), 195.0 (100), 139.0 (27), 115.1 (27). HRMS-EI (TOF) found: 226.0398 $[M]^+$. $C_{11}H_{11}ClO_3$ requires 226.0397.

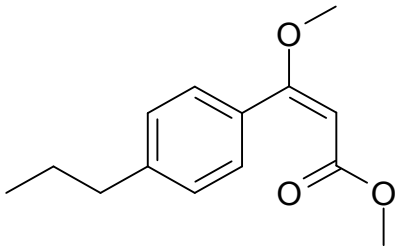
Synthesis of (*E*)-methyl 3-methoxy-3-[4-(trifluoromethyl)phenyl]prop-2-enoate (3ha)



Compound **3ha** was prepared following the general procedure GP1 from 4-(trifluoromethyl)phenylacetylene (**1h** (170 mg, 164 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ dichloromethane gradient) yielded **3ha** as an orange solid (198 mg, 76 %).

mp 37.5—38.0 °C. Elemental analysis found: C, 55.5; H, 4.5. $C_{12}H_{11}F_3O_3$ requires C, 55.4; H, 4.3%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3080, 3036, 3012, 2985, 2948, 2845, 1713, 1664,1631, 1608, 1520, 1458, 1437, 1408, 1382, 1325, 1277, 1196, 1153, 1104, 1061, 1034, 1019, 983, 922, 841, 830, 748, 721. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.66 (2 H, d, *J* = 8.3 Hz), 7.55 (2 H, d, *J* = 8.3 Hz), 5.35 (1 H, s), 3.84 (3 H, s), 3.61 (3 H, s). ^{19}F–NMR (400 MHz, $CDCl_3$) -62.8. ^{13}C–NMR (101 MHz, $CDCl_3$) 169.9, 166.8, 138.5, 131.4 (q, ^2J(C,F) = 32.7 Hz), 129.2, 129.2, 124.7 (q, ^3J(C,F) = 3.6 Hz), 124.7 (q, ^3J(C,F) = 3.6 Hz), 124.3 (q, ^1J(C,F) = 271.6 Hz), 92.8, 56.5, 51.1. MS (Ion trap, EI) *m/z* 260.0 (M^+ ,26%), 259.0 (58), 240.9 (19), 229.0 (100), 145.0 (17), 68.8 (18), 58.8 (20). HRMS-EI (TOF) found: 260.0654. $[M]^+$. $C_{12}H_{11}F_3O_3$ requires 260.0660.

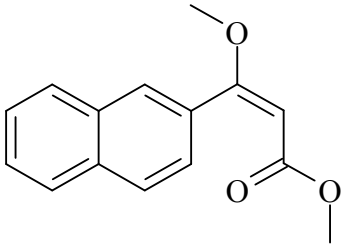
Synthesis of (*E*)-methyl 3-methoxy-3-(4-propylphenyl)prop-2-enoate (3ia)



Compound **3ia** was prepared following the general procedure GP1 from 1-ethynyl-4-propylbenzene (**1i**) (147 mg, 162 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, toluene/ dichloromethane gradient) yielded **3ia** as a colorless oil (210 mg, 90 %).

Elemental analysis found: C, 71.9; H, 7.5. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.7%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3012, 2958, 2875, 1720, 1698, 1605, 1513, 1435, 1380, 1260, 1218, 1154, 1111, 1035, 921, 816. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.37 (2 H, d, *J* = 8.3 Hz), 7.21 (2 H, d, *J* = 8.3 Hz), 5.26 (1 H, s), 3.81 (3 H, s), 3.61 (3 H, s), 2.60 (1 H, t, *J* = 7.5 Hz), 1.66 (2 H, sxt, *J* = 7.4 Hz), 0.96 (3 H, t, *J* = 7.3 Hz). ^{13}C–NMR (101 MHz, $CDCl_3$) 171.7, 167.3, 144.6, 132.2, 128.6, 128.6, 127.8, 127.8, 91.5, 56.3, 50.9, 38.0, 24.3, 13.9. MS (Ion trap, EI) *m/z* 235.0 (100), 234.1 (M^+, 47), 233.2 (70), 203.2 (71), 191.0 (96), 149.2 (45), 131.0 (38). HRMS-EI (TOF) found: 234.1250 $[M]^+$. $C_{14}H_{18}O_3$ requires 234.1256.

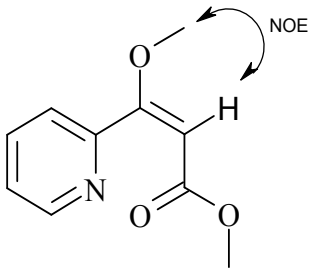
Synthesis of (*E*)-methyl 3-methoxy-3-(naphthalen-2-yl)prop-2-enoate (3ja)



Compound **3ja** was prepared following the general procedure GP1 from 2-ethynyl-naphthalene (**1j**) (152 mg, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ dichloromethane gradient) yielded **3ja** as a yellow oil (161 mg, 67 %).

Elemental analysis found: C, 74.2; H, 6.0. $C_{15}H_{14}O_3$ requires C, 74.4; H, 5.8%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3059, 3024, 2947, 2831, 1715, 1696, 1613, 1594, 1575, 1502, 1472, 1434, 1383, 1358, 1264, 1215, 1190, 1148, 1129, 1102, 1033, 995, 946, 921, 857, 815, 748. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.97 (1 H, s), 7.85—7.89 (3 H, m), 7.48—7.55 (3 H, m), 5.37 (1 H, s), 3.88 (3 H, s), 3.60 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 171.4, 167.2, 133.8, 132.6, 132.4, 128.6, 128.5, 127.7, 127.1, 126,8, 126.2, 126.1, 92.2, 56.5, 51.0. MS (Ion trap, EI) *m/z* 241.9 (M^+, 100%), 241.1 (52), 211.0 (51), 169.0 (19), 168.1 (19), 155.1 (26), 152.2 (18).

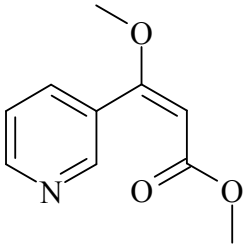
Synthesis of (*E*)-methyl 3-methoxy-3-(pyridin-2-yl)prop-2-enoate (3ka)



Compound **3ka** was prepared following the general procedure GP1 from 2-ethynylpiridine (**1k**) (105 mg, 103 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate/trimethylamine (10%) gradient) yielded **3ka** as a yellow oil (139 mg, 72 %).

Elemental analysis found: N, 7.2, C, 62.0; H, 5.9. $C_{10}H_{11}NO_3$ requires N, 7.3, C, 62.2; H, 5.7%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3068; 3015; 2991; 2948; 2843; 1714; 1625; 1584; 1568; 1474; 1434; 1375; 1283; 1222; 1194; 1165; 1124; 1031; 986; 922; 825; 798; 777; 746. ^{1}H—NMR (400 MHz, $CDCl_3$) 8.65 (1 H, d, ^3J = 4.2 Hz), 7.73 (1 H, td, *J* = 7.8 Hz), 7.43 (1 H, td, *J* = 7.8 Hz), 7.32 (1 H, dd, *J* = 8.8 Hz), 5.36 (1 H, s), 3.84 (3 H, s), 3.57 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 169.1, 166.9, 153.5, 149.2, 136.0, 124.0, 123.9, 93.4, 56.6, 51.1. MS (Ion trap, EI) *m/z* 193.8 (M^+, 50%), 177.8 (43), 161.9 (60), 147.8 (56), 133.9 (46), 103.9 (100), 77.9 (50). HRMS-EI (TOF) found: 193.0743. $[M]^+$. $C_{10}H_{11}NO_3$ requires 193.0739.

Synthesis of (*E*)-methyl 3-methoxy-3-(pyridin-3-yl)prop-2-enoate (3la)

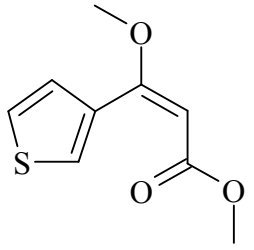


Compound **3la** was prepared following the general procedure GP1 from 3-ethynylpyridine (**1l**) (105 mg, 1.00 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient/trimethylamine (10%) gradient) yielded **3la** as a white solid (131 mg, 68 %).

mp. 62.0—62.5 °C. Elemental analysis found: N, 7.2, C, 62.2; H, 5.9. $C_{10}H_{11}NO_3$ requires N, 7.3, C, 62.2; H, 5.7%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3033, 2988, 2950, 2846, 1709, 1611, 1586, 1460, 1437, 1616, 1377, 1274, 1191, 1157, 1122, 1044, 1024, 983, 920, 818, 782, 710. ^{1}H—NMR

(400 MHz, $CDCl_3$) 8.62—8.66 (2 H, m), 7.77 (1 H, d, *J* = 8.0), 7.31—7.33 (1 H, m), 5.35 (1 H, s), 3.83 (3 H, s), 3.60 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 168.5, 166.8, 150.5, 149.5, 136.3, 130.9, 122.4, 93.2, 56.5, 51.1. MS (Ion trap, EI) *m/z* 192.9 (M^+, 24%), 192.0 (70), 162.0 (100), 118.1 (19), 91.0 (20), 78.0 (21), 50.0 (23). HRMS-EI (TOF) found: 193.0733. $[M]^+$. $C_{10}H_{11}NO_3$ requires 193.0739.

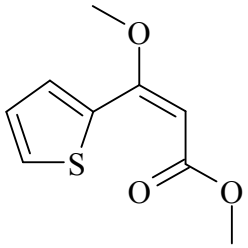
Synthesis of (*E*)-methyl 3-methoxy-3-(thiophen-3-yl)prop-2-enoate (3ma) [CAS: 1161948-25-9]



Compound **3ma** was prepared following the general procedure GP1 from 3-ethynylthiophene (**1m**) (112 mg, 101 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, toluene/ dichloromethane gradient) yielded **3ma** as a colourless oil (119 mg, 60 %).

Elemental analysis found: C, 54.5; H, 5.1, S, 16.0. $C_9H_{10}O_3S$ requires C, 54.5; H, 5.1, S, 16.2%. IR (ATR) $\tilde{\nu}_{max}/cm^{-1}$ 3110, 3009, 2947, 2843, 1712, 1605, 1435, 1345, 1253, 1191, 1143, 1107, 1034, 992, 924, 867, 793, 681. ^1H—NMR (400 MHz, $CDCl_3$) 7.80 (1 H, dd, *J* = 3.0, 1.3 Hz), 7.32 (1 H, dd, *J* = 5.1, 1.4 Hz), 7.22—7.28 (1 H, m), 5.24 (1 H, s), 3.77 (3 H, s), 3.64 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 167.1, 165.4, 134.9, 128.3, 128.2, 124.0, 91.5, 56.0, 50.9. MS (Ion trap, EI) *m/z* 197.8 (M+, 79%), 166.9 (100), 123.8 (43), 110.8 (33), 96.8 (25), 68.8 (23), 44.9 (32). HRMS-EI (TOF) found: 198.0356. $[M]^+$. $C_9H_{10}O_3S$ requires 198.0351.

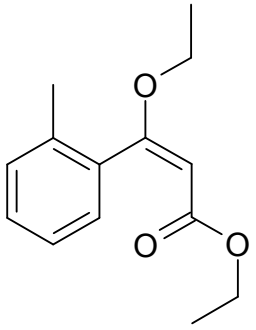
Synthesis of (*E*)-methyl 3-methoxy-3-(thiophen-2-yl)prop-2-enoate (3na)



Compound **3na** was prepared following the general procedure GP1 from 2-ethynylthiophene (**1n**) (114 mg, 99.9 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3na** as a brown oil (153 mg, 77 %).

Elemental analysis found: C, 54.8; H, 5.0, S, 16.3. $C_9H_{10}O_3S$ requires C, 54.5; H, 5.1, S, 16.2%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3107, 2955, 1736, 1657, 1519, 1436, 1412, 1357, 1325, 1273, 1217, 1146, 1062, 1017, 926, 859, 723. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.95 (1 H, dd, *J* = 3.8, 1.4 Hz), 7.46 (1 H, dd, *J* = 5.0, 1.3 Hz), 7.08 (1 H, dd, *J* = 5.3, 3.8 Hz), 5.27 (1 H, s), 3.81 (3 H, s), 3.70 (3 H, s. ^{13}C–NMR (101 MHz, $CDCl_3$) 166.9, 162.2, 135.4, 131.5, 128.8, 126.8, 91.2, 56.2, 51.0. MS (Ion trap, EI) *m/z* 198.0 (M^+, 20%), 125.8 (49), 110.9 (100), 82.9 (22), 45.0 (28), 43.9 (34), 43.0 (41). HRMS-EI (TOF) found: 198.0351. $[M]^+$. $C_9H_{10}O_3S$ requires 198.0351.

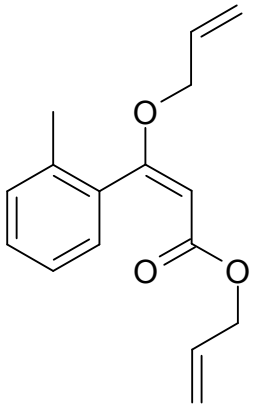
Synthesis of (*E*)-ethyl 3-ethoxy-3-(2-methylphenyl)prop-2-enoate (3bb) [CAS:147499-01-2]



Compound **3bb** was prepared following the general procedure GP1 from 2-ethynyltoluene (**1b**) (120 mg, 130 µl, 1.00 mmol) and diethyl carbonate (**2b**) (143 mg, 147 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3bb** as a colourless oil (140 mg, 60 %).

Elemental analysis found: C, 71.6; H, 7.7. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.7%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3065, 2982, 1718, 1695, 1620, 1599, 1446, 1374, 1355, 1262, 1262, 1217, 1201, 1155, 1123, 1095, 1043, 1021, 896, 815, 761, 726. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.27-7.33 (m, 1 H), 7.14-7.26 (m, 3 H), 5.34 (s, 1 H), 3.96-4.04 (m, 4 H), 2.28 (s, 3 H), 1.41 (t, *J* = 7.0 Hz, 3 H), 1.08 (t, *J* = 7.0 Hz, 3 H). ^{13}C–NMR (101 MHz, $CDCl_3$) 171.0, 166.6, 136.0, 135.6, 129.8, 129.0, 128.3, 125.3, 93.9, 84.7, 59.4, 19.1, 14.3, 14.1. MS (Ion trap, EI) *m/z* 235.0 (M^+, 55%), 219.1 (44), 189.1 (100), 161.2 (25), 119.0 (48), 118.1 (29), 91.1 (23). HRMS-EI (TOF) found: 234.1267. $[M]^+$. $C_{14}H_{18}O_3$ requires 234.1256.

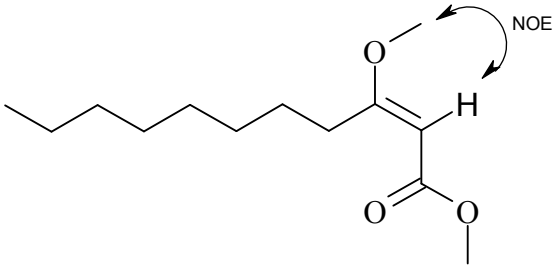
Synthesis of prop-2-en-1-yl (2*E*)-3-(2-methylphenyl)-3-(prop-2-en-1-yloxy)prop-2-enoate (3bc)



Compound **3bc** was prepared following the general procedure GP1 from 2-ethynyltoluene (**1b**) (120 mg, 130 µl, 1.00 mmol) and diallyl carbonate (**2c**) (172 mg, 174 µl, 1.20 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3bc** as a yellow oil (162 mg, 63 %).

Elemental analysis found: C, 74.4; H, 7.0. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3080, 3023, 2923, 2872, 1720, 1695, 1619, 1599, 1380, 1260, 1155, 1119, 1090, 1029, 987, 925, 822, 767, 728. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.29—7.33 (1 H, m), 7.21—7.24 (3 H, m), 6.02 (1 H, ddt, *J* = 17.3, 10.7, 5.5), 5.80 (1 H, ddt, *J* = 17.3, 10.4, 5.7), 5.42 (1 H, dq, *J* = 17.3, 1.3), 5.41 (1 H, s), 5.32 (1 H, dq, *J* = 10.5, 1.2), 5.13—5.21 (2 H, m), 4.51 (2 H, dt, *J* = 5.6, 1.6), 4.46 (2 H, dt, *J* = 5.8, 1.5), 2.29 (3 H, s). ^{13}C–NMR (101 MHz, $CDCl_3$) 170.8, 165.9, 135.6, 135.4, 132.5, 131.7, 129.9, 129.1, 128.4, 125.3, 118.8, 117.6, 94.2, 69.8, 64.3, 19.1. MS (Ion trap, EI) *m/z* 120.0 (9%), 119.0 (100), 91.0 (36), 65.0 (14). HRMS-EI (TOF) found: 258.1267. $[M]^+$. $C_{16}H_{18}O_3$ requires 258.1256.

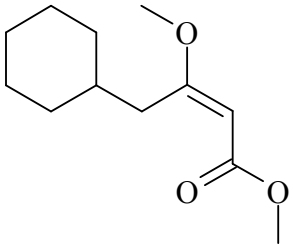
Synthesis of (*E*)-methyl 3-methoxyundec-2-enoate (3oa) [CAS: 1161948-21-5]



Compound **3oa** was prepared following the general procedure GP2 from 1-decyne (**1o**) (146 mg, 190 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (273 mg, 255 µl, 3.00 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3oa** as a colourless oil (128 mg, 56 %).

Elemental analysis found: C, 68.6; H, 10.7. $C_{13}H_{24}O_3$ requires C, 68.4; H, 10.6%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 2927, 2856, 1714, 1620, 1435, 1378, 1136, 1113, 1053, 930, 819. ^{1}H—NMR (400 MHz, $CDCl_3$) 4.98 (1 H, s), 3.67 (3 H, s), 3.62 (3 H, s), 2.73 (2 H, t, *J* = 6.8), 1.53 (2 H, quin, *J* = 7.5), 1.26—1.33 (2 H, m), 0.87 (3 H, t, *J* = 7.5). ^{13}C–NMR (101 MHz, $CDCl_3$) 177.2, 168.0, 89.9, 55.3, 50.7, 32.0, 31.8, 29.4, 29.3, 29.2, 27.5, 22.7, 14.1. MS (Ion trap, EI) *m/z* 197.0 (40), 142.9 (90), 129.8 (68), 111.0 (60), 101.0 (100), 87.0 (57), 72.0 (45). HRMS-EI (TOF) found: 197.1547. [M-OMe]$^+$. $C_{12}H_{21}O_2$ requires 197.1542 (M$^+$-Peak too small for appropriate detection).

Synthesis of (*E*)-methyl 4-cyclohexyl-3-methoxybut-2-enoate (3pa)

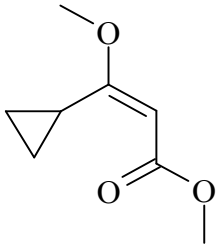


Compound **3pa** was prepared following the general procedure GP2 from 3-cyclohexyl-1-propyne (**1p**) (126 mg, 149 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (273 mg, 255 µl, 3.00 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3pa** as a colourless oil (127 mg, 60 %).

Elemental analysis found: C, 67.7; H, 9.5. $C_{12}H_{20}O_3$ requires C, 67.9; H, 9.5%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 2923, 2851, 1713, 1618, 1435, 1376, 1288, 1249, 1191, 1172, 1140, 1120, 1052,

1012, 930, 894, 817, 747. ^{1}H—NMR (400 MHz, $CDCl_3$) 5.02 (1 H, s), 3.66 (3 H, s), 3.61 (3 H, s), 2.65 (2 H, d, *J* = 6.8), 1.63—1.69 (6 H, m), 1.11—1.26 (3 H, m), 0.95—1.03 (2 H, m). ^{13}C–NMR (101 MHz, $CDCl_3$) 176.0, 168.1, 90.8, 55.2, 50.7, 39.1, 36.6, 32.9, 26.3, 26.1. MS (Ion trap, EI) *m/z*.131.0 (79), 129.8 (100), 89.0 (50), 87.0 (63), 72.0 (61), 55.0 (51), 40.0 (64). HRMS-EI (TOF) found: 181.1234 $[M\text{-}OMe]^+$. $C_{11}H_{17}O_2$ requires 181.1229 (M^+-Peak too small for appropriate detection).

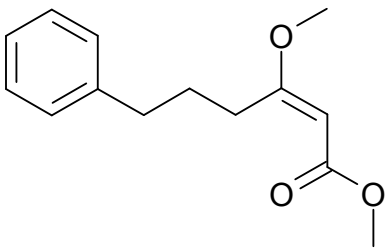
Synthesis of (*E*)-methyl 3-cyclopropyl-3-methoxyprop-2-enoate (3qa) [CAS: 182617-98-7]



Compound **3qa** was prepared following the general procedure GP2 from ethynylcyclopropane (**1q**) (68.1 mg, 87.3 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (273 mg, 255 µl, 3.00 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3qa** as a colourless oil (90 mg, 58 %).

Elemental analysis found: C, 61.5; H, 7.6. $C_8H_{12}O_3$ requires C, 61.5; H, 7.7%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3097, 3014, 2950, 1706, 1602, 1435, 1405, 1282, 1235, 1189, 1145, 1104, 1044, 989, 915, 812, 768. ^{1}H—NMR (400 MHz, $CDCl_3$) 5.06 (1 H, s), 3.70 (3 H, s), 3.57 (3 H, s), 3.16—3.22 (1 H, m), 0.92—0.96 (2 H, m), 0.77—0.82 (2 H, m). ^{13}C–NMR (101 MHz, $CDCl_3$) 175.6, 168.8, 89.7, 55.3, 50.7, 11.6, 7.19. MS (Ion trap, EI) *m/z* 127.9 (100%), 125.0 (15), 113.0 (39), 96.9 (20), 68.9 (13), 67.0 (16), 53.0 (12). HRMS-EI (TOF) found: 156.0780. $[M]^+$. $C_8H_{12}O_3$ requires 156.0786.

Synthesis of (*E*)-methyl 3-methoxy-6-phenylhex-2-enoate (3ra) [CAS: 1161948-18-0]

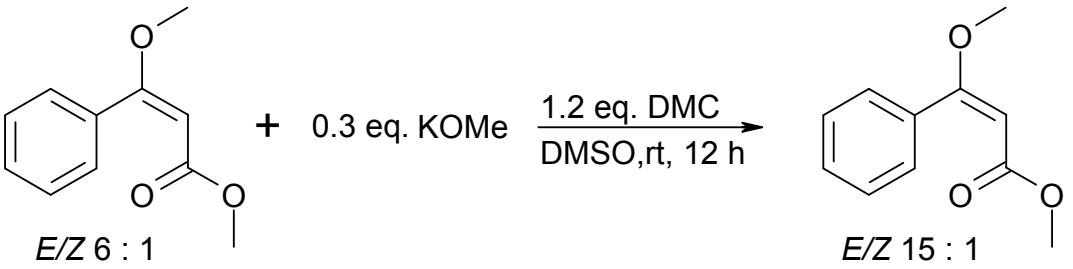


Compound **3ra** was prepared following the general procedure GP2 from 5-phenyl-1-pentyne (**1r**) (144 mg, 152 µl, 1.00 mmol) and dimethyl carbonate (**2a**) (273 mg, 255 µl, 3.00 mmol). Purification by column flash chromatography (SiO_2, cyclohexane/ethyl acetate gradient) yielded **3ra** as a colourless oil (112 mg, 48 %).

Elemental analysis found: C, 71.6; H, 7.7. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.7%. IR (ATR) $\tilde{\nu}_{max}$/cm^{-1} 3065, 3027, 2981, 2937, 2905, 1719, 1696, 1620, 1599, 1492, 1477, 1445, 1375, 1355, 1283, 1263, 1217, 1202, 1155, 1124, 1098, 1045, 1021, 1000, 981, 816, 763, 727. ^{1}H—NMR (400 MHz, $CDCl_3$) 7.26—7.30 (2 H, m), 7.18—7.22 (3 H, m), 5.01 (1 H, s), 3.68 (3 H, s), 3.62 (3 H, s), 2.82 (2 H, t, *J* = 7.8), 2.67 (2 H, t, *J* = 7.8), 1.85—1.93 (2 H, m). ^{13}C–NMR (101 MHz, $CDCl_3$) 176.5, 168.0, 142.2, 128.4, 128.2, 125.7, 90.3, 55.4, 50.7, 36.6, 31.8, 29.2. MS (Ion trap, EI) *m/z* 129.8 (67), 111.0 (69), 104.0 (100), 101.1 (65), 99.0 (78), 97.9 (66), 91.1 (68). HRMS-EI (TOF) found: 203.1082 $[M\text{-}OMe]^+$. $C_{13}H_{15}O_2$ requires 203.1072 (M^+-Peak too small for appropriate detection).

Control Experiments

Isomerization Experiments

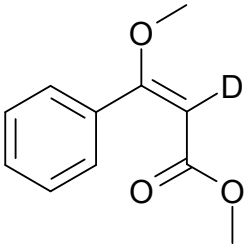


E/Z 6 : 1 *E/Z* 15 : 1

An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with potassium methoxide (21.0 mg, 0.30 mmol) and closed with a septum cap. The atmosphere was changed three times with argon; afterwards dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol) and a stock solution of **3aa** (*E/Z* ratio 6:1) (192 mg, 1.00 mmol) in DMSO (1.5 mL) were added via syringe. The resulting mixture was stirred (500 rpm) at room temperature for 12 h. GC analysis after reaction showed an *E/Z* ratio of 15 : 1.

Deuterium Labeling Experiments

Synthesis of (*E*)-methyl 3-methoxy-3-phenyl(^{2}H)prop-2-enoate (3aa-d_1)



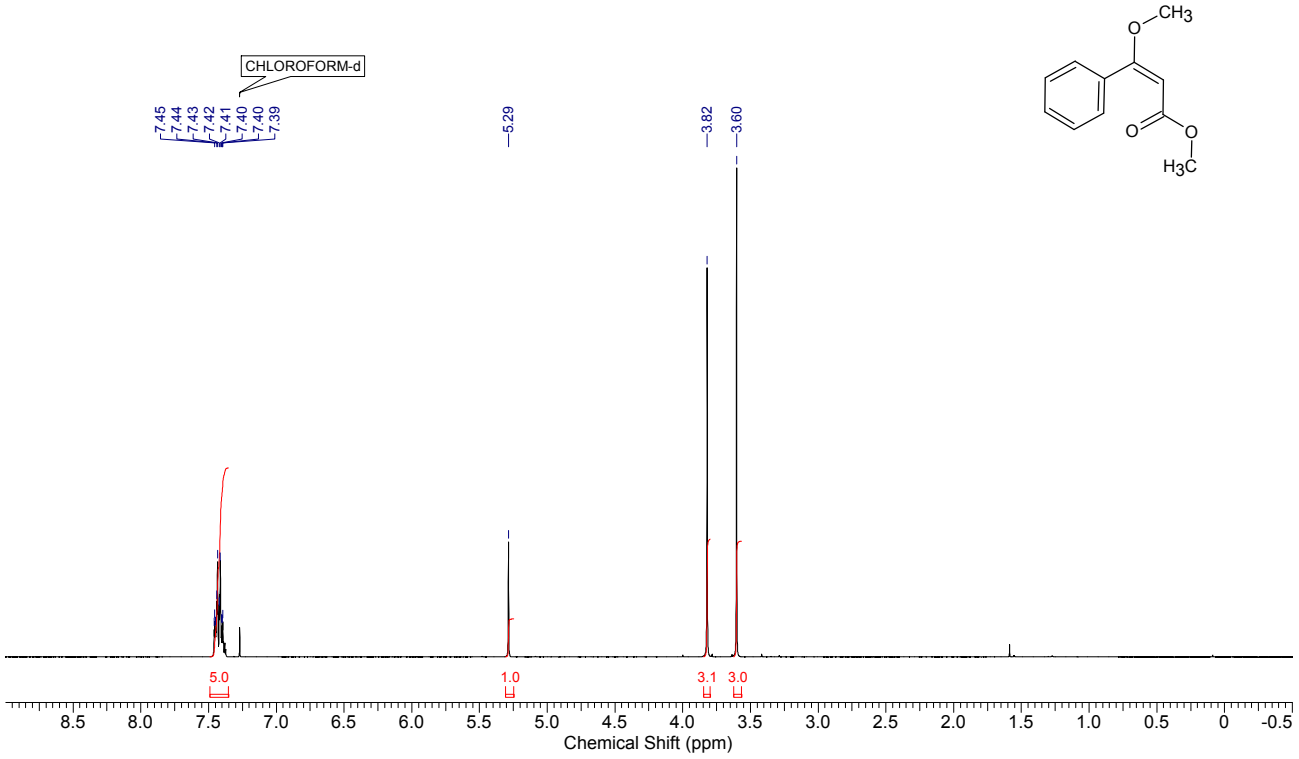
A: An oven-dried 20 mL headspace vial with Teflon-coated stirring bar was charged with potassium methoxide (21.0 mg, 0.30 mmol) and closed with a septum cap. The atmosphere was changed three times with argon; afterwards DMSO-d_6 (168 mg, 141 µL, 2.00 mmol), dimethyl carbonate (**2a**) (109 mg, 102 µl, 1.20 mmol) and phenylacetylene (**1a**) (102 mg, 110 µl, 1.00 mmol) were added via syringe. The resulting mixture was stirred (500 rpm) at room temperature for 12 h. The crude reaction mixture was diluted with DMSO-d_6 (0.5 mL), filtered and used for NMR analysis. ^{1}H-NMR showed a deuterium incorporation of 94 % according to a residual proton signal at 5.35 ppm with a relative integral of 0.06.

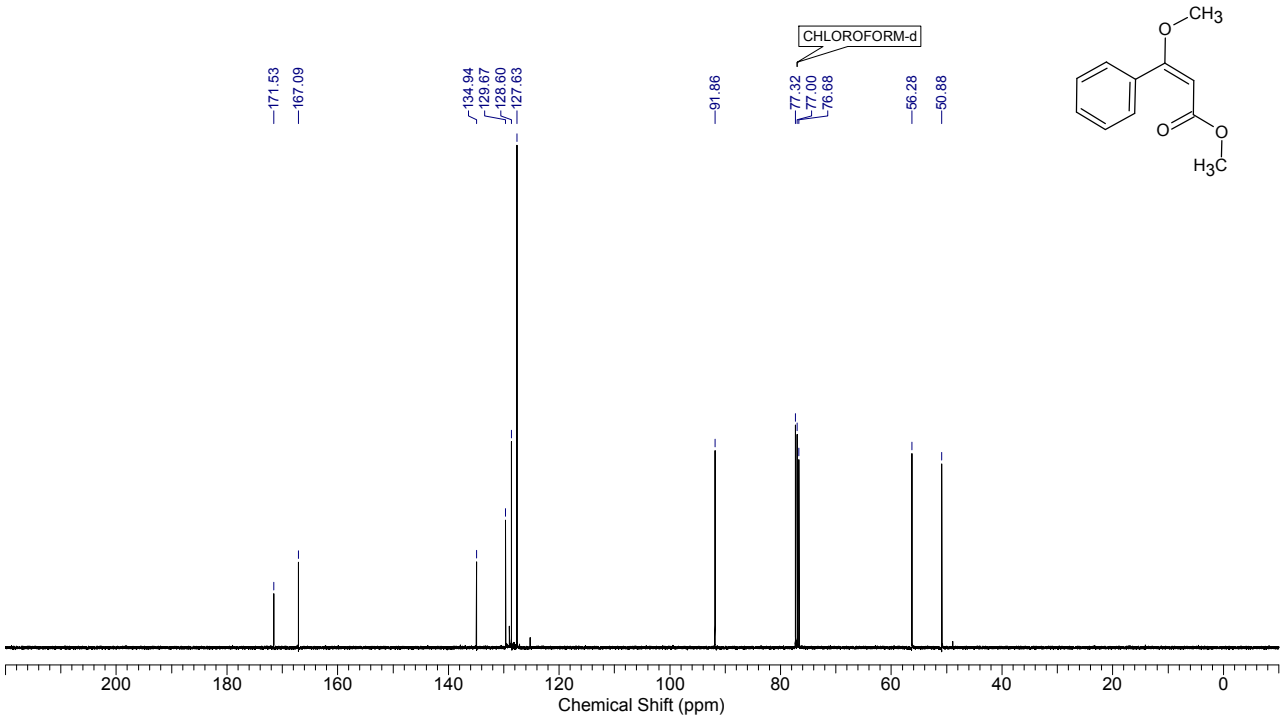
B: According to **A** phenylacetylene-d_1 (**1a-*d*$_1$**) (102 mg, 110 µl, 1.00 mmol) was reacted in non-deuterated DMSO (168 mg, 141 µL, 2.00 mmol). ^{1}H-NMR analysis showed no deuterium incorporation.

C: According to **A** phenylacetylene-d_1 (**1a-*d*$_1$**) (102 mg, 110 µl, 1.00 mmol) was reacted with dimethyl carbonate (**2a**) (455 mg, 425 µl, 5.00 mmol). ^{1}H-NMR showed a deuterium incorporation of 96 % according to a residual proton signal at 5.34 ppm with a relative integral of 0.04.

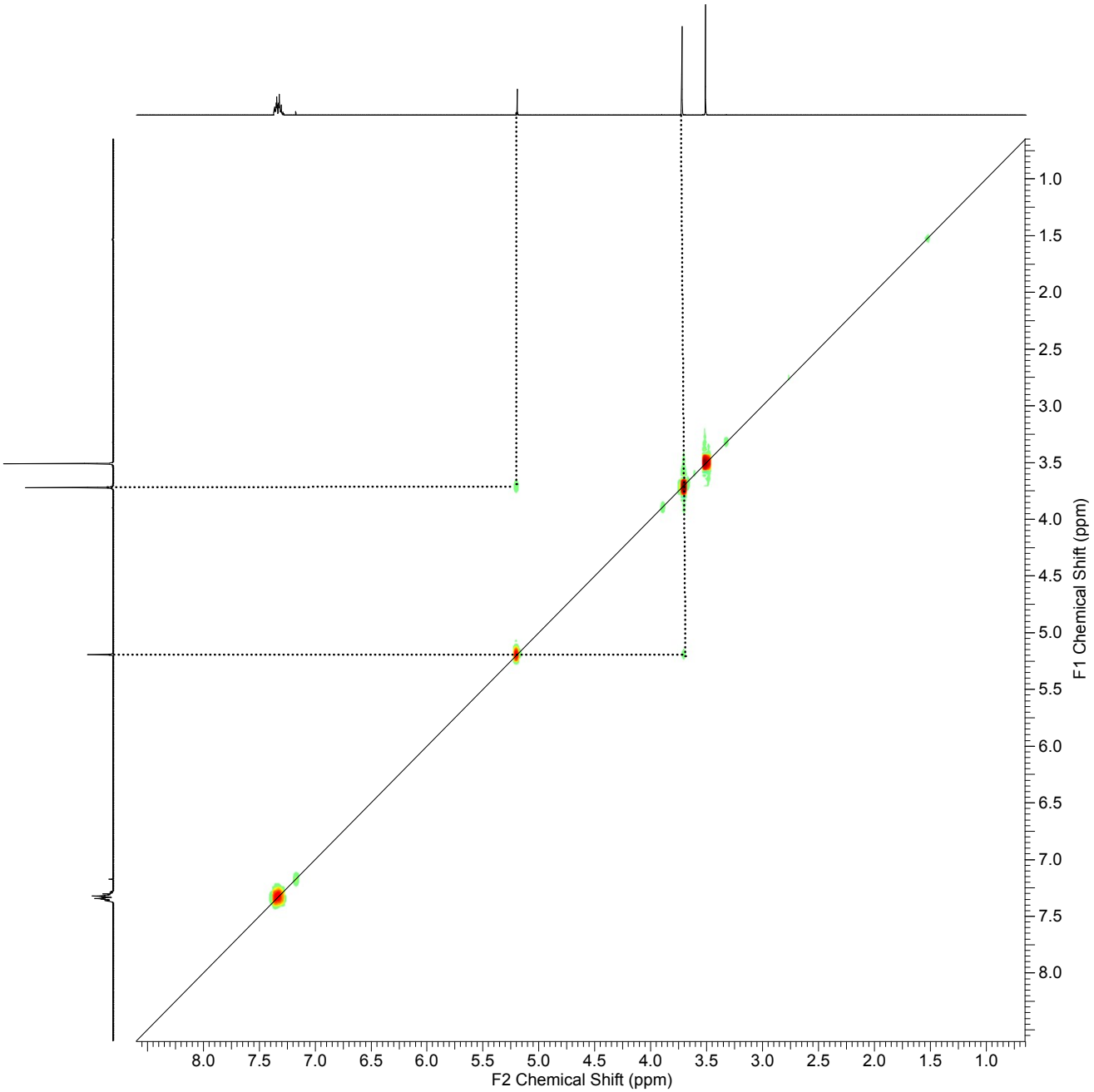
Spectra

(*E*)-methyl 3-methoxy-3-phenylprop-2-enoate (3aa)

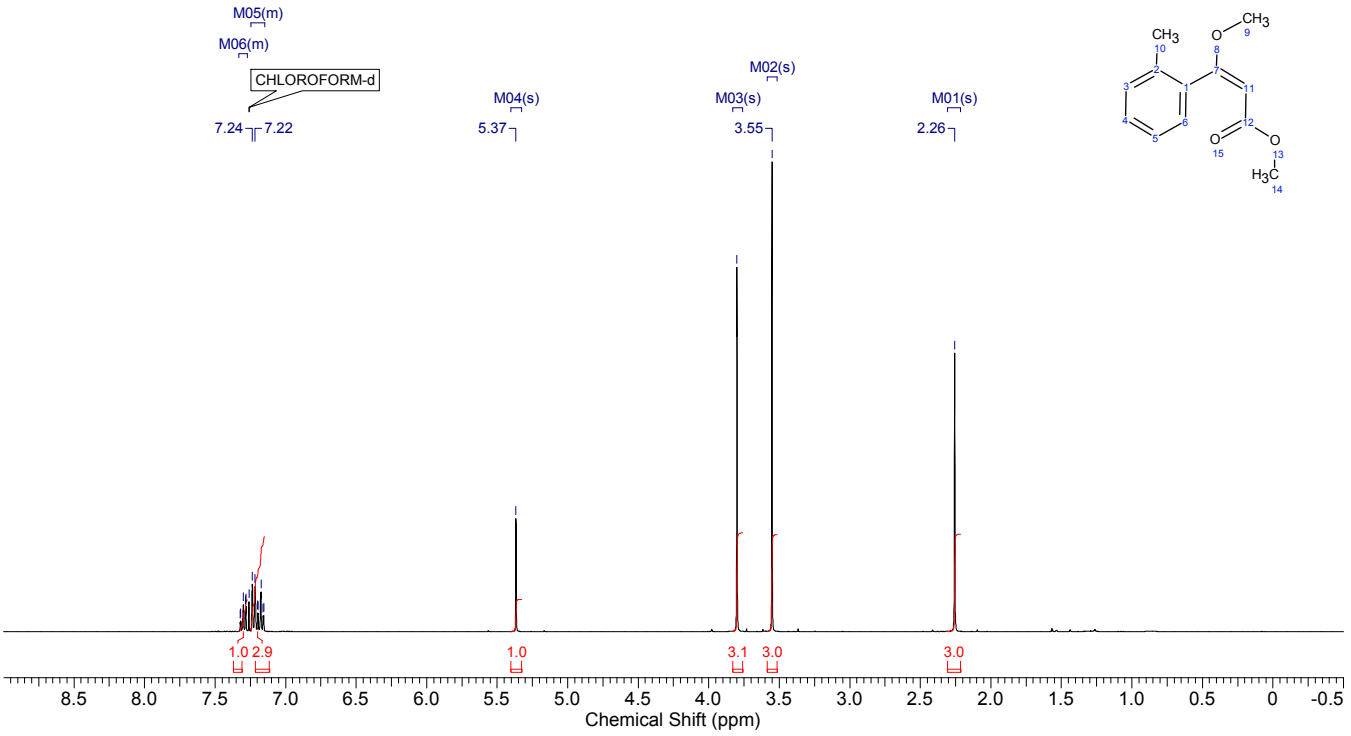


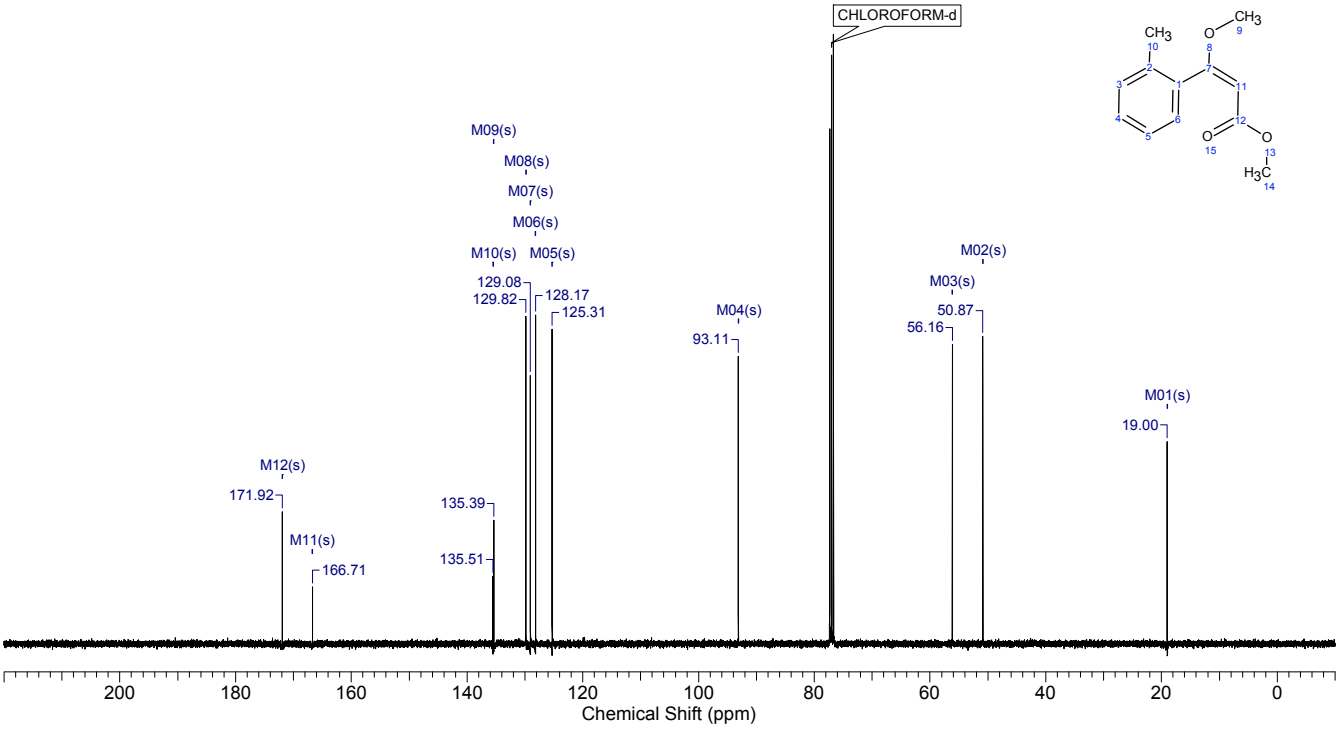


NOE Experiment

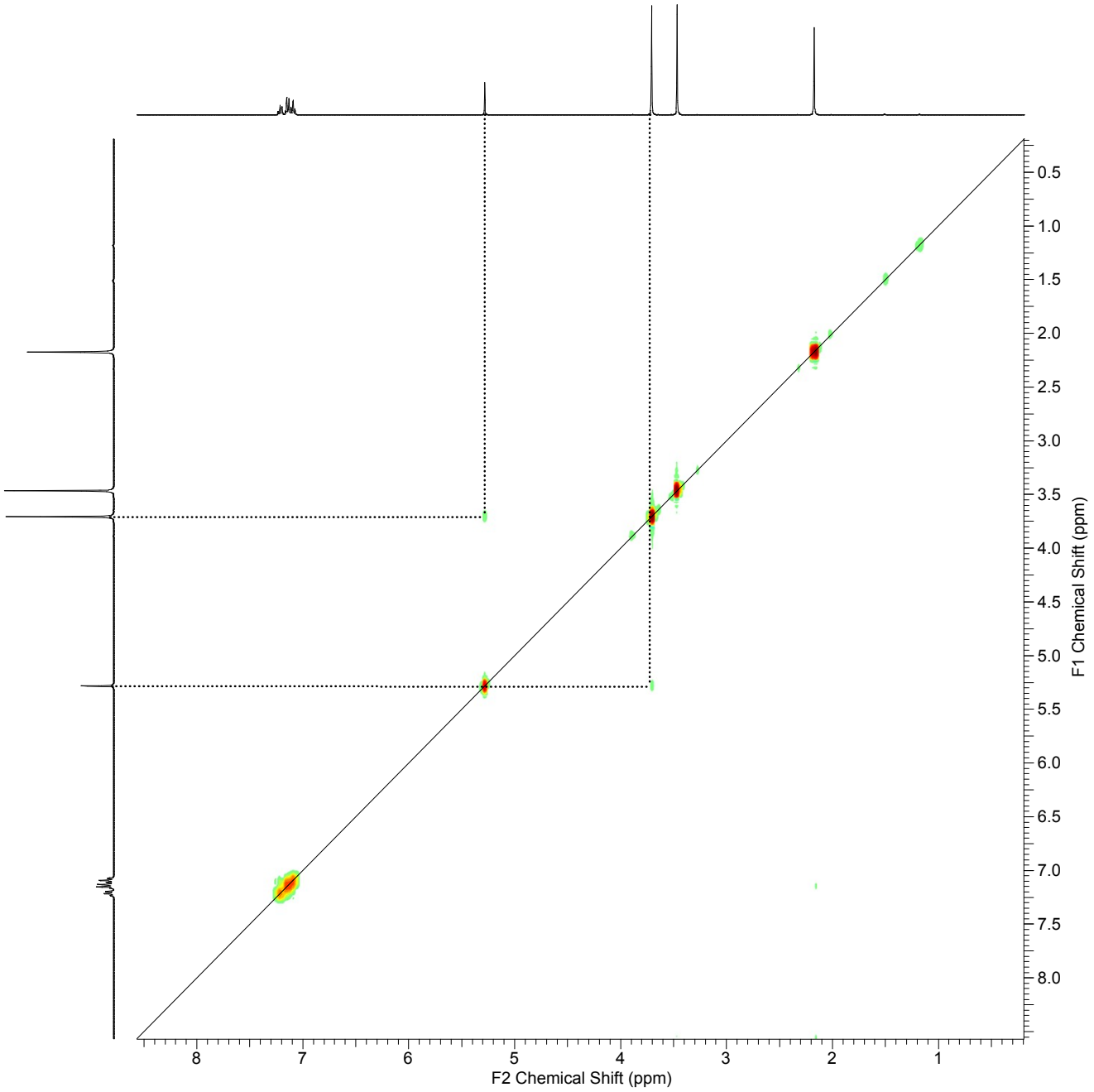


(*E*)-methyl 3-methoxy-3-(2-methylphenyl)prop-2-enoate (3ba)

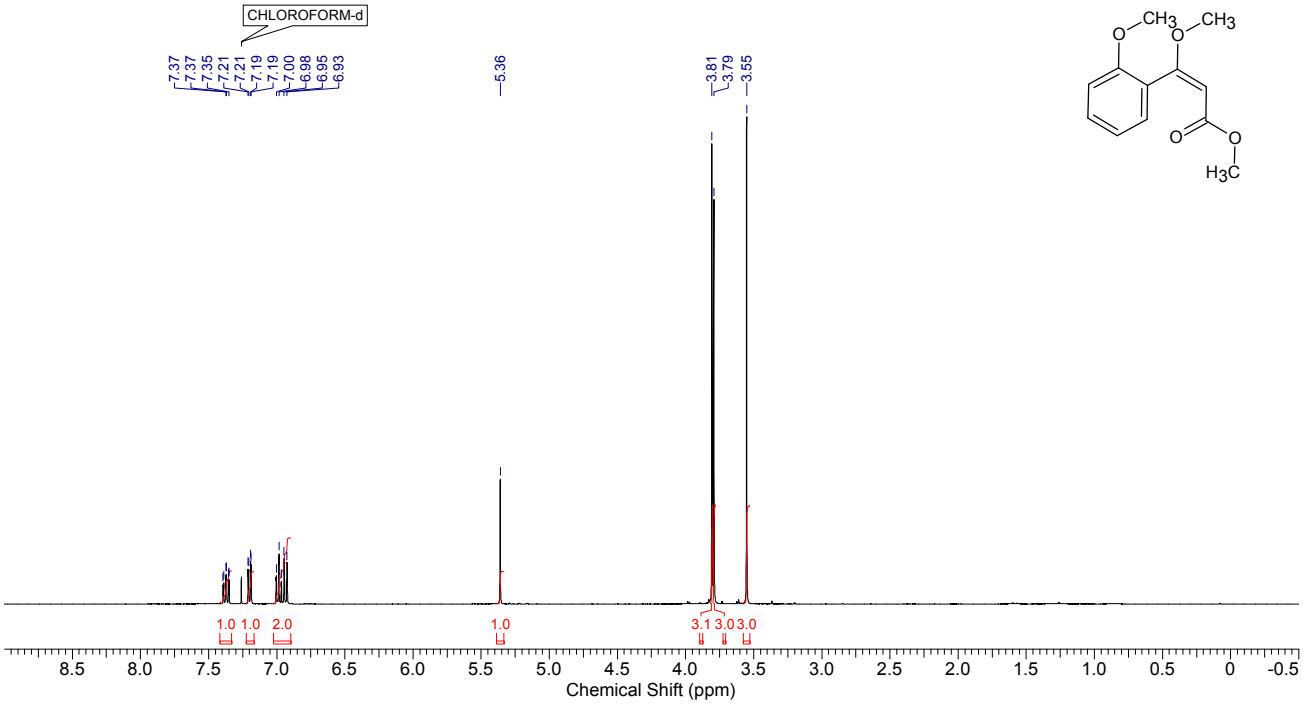


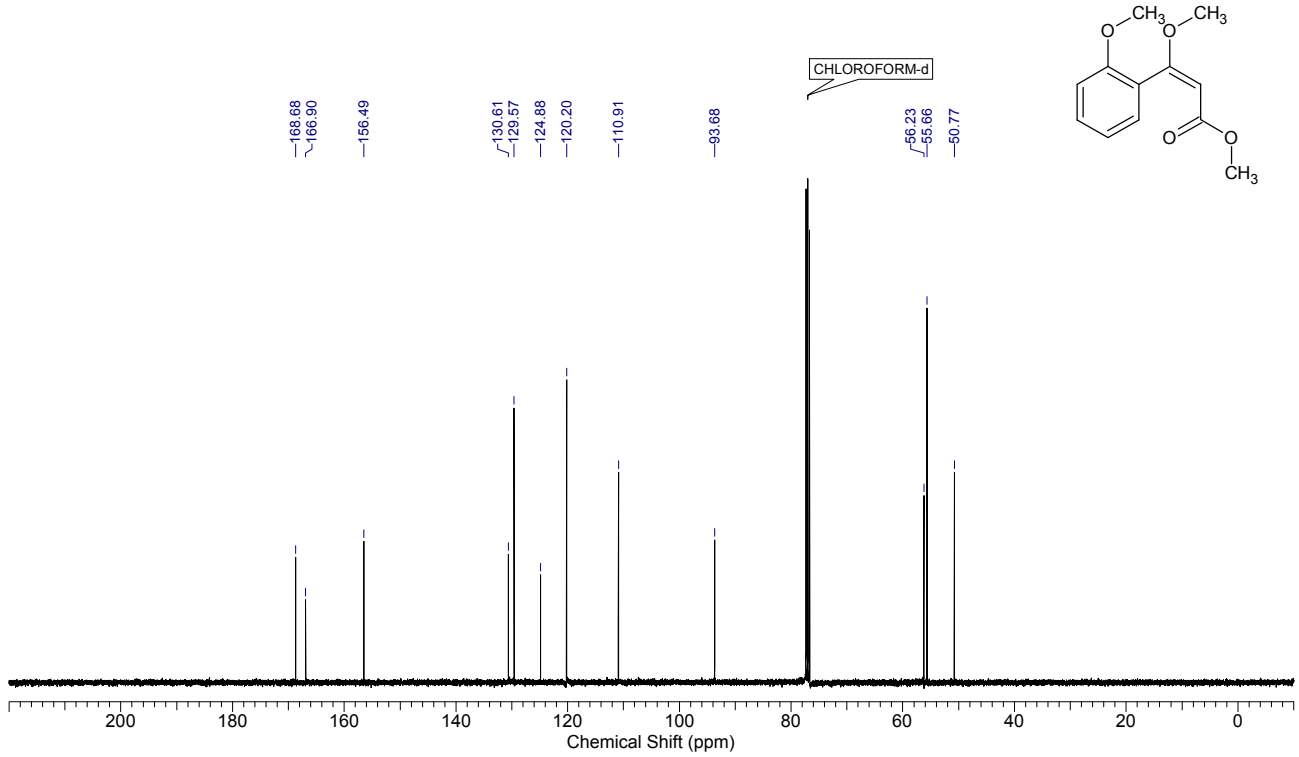


NOE Experiment

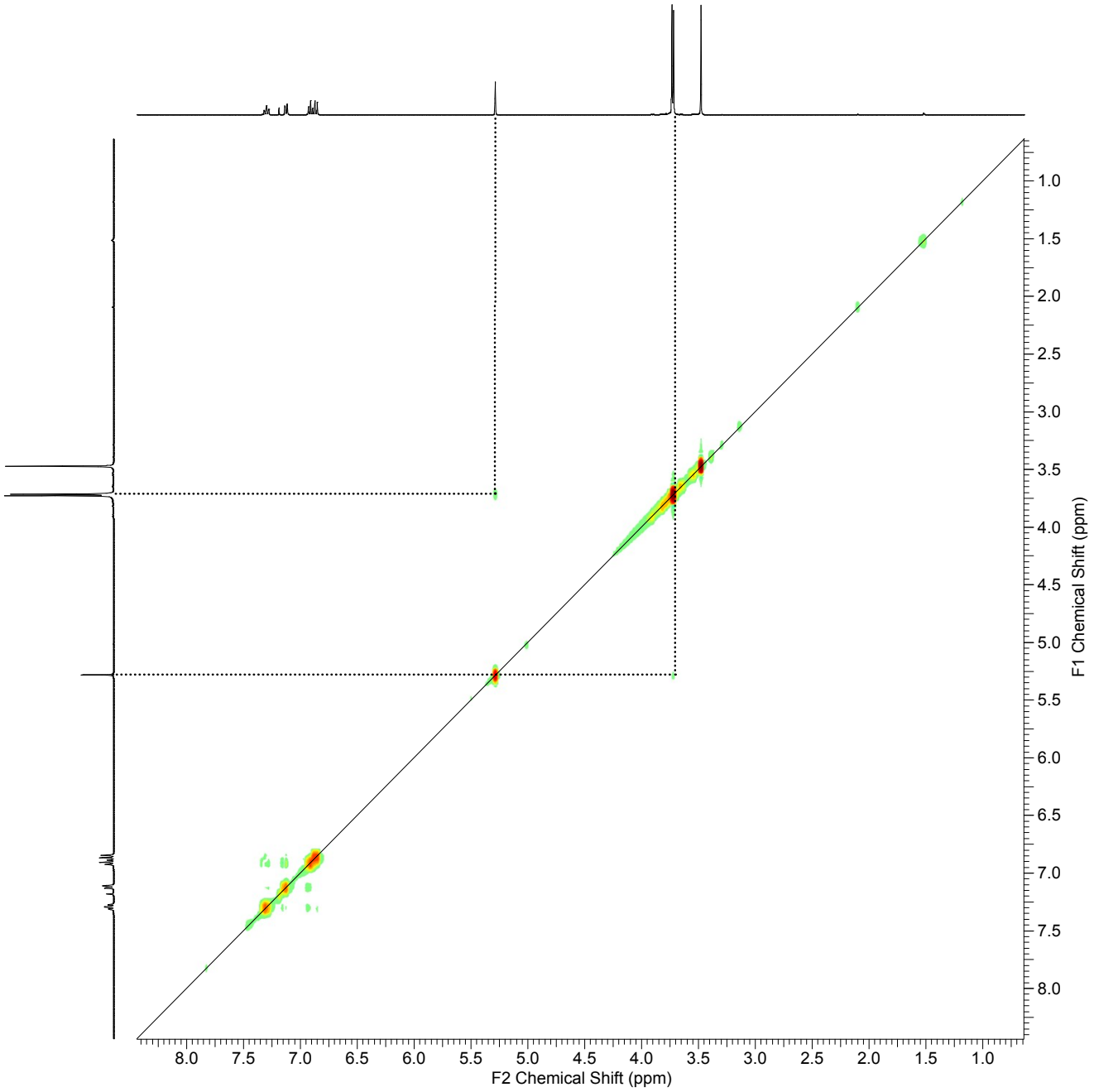


(*E*)-methyl 3-methoxy-3-(2-methoxyphenyl)prop-2-enoate (3ca)

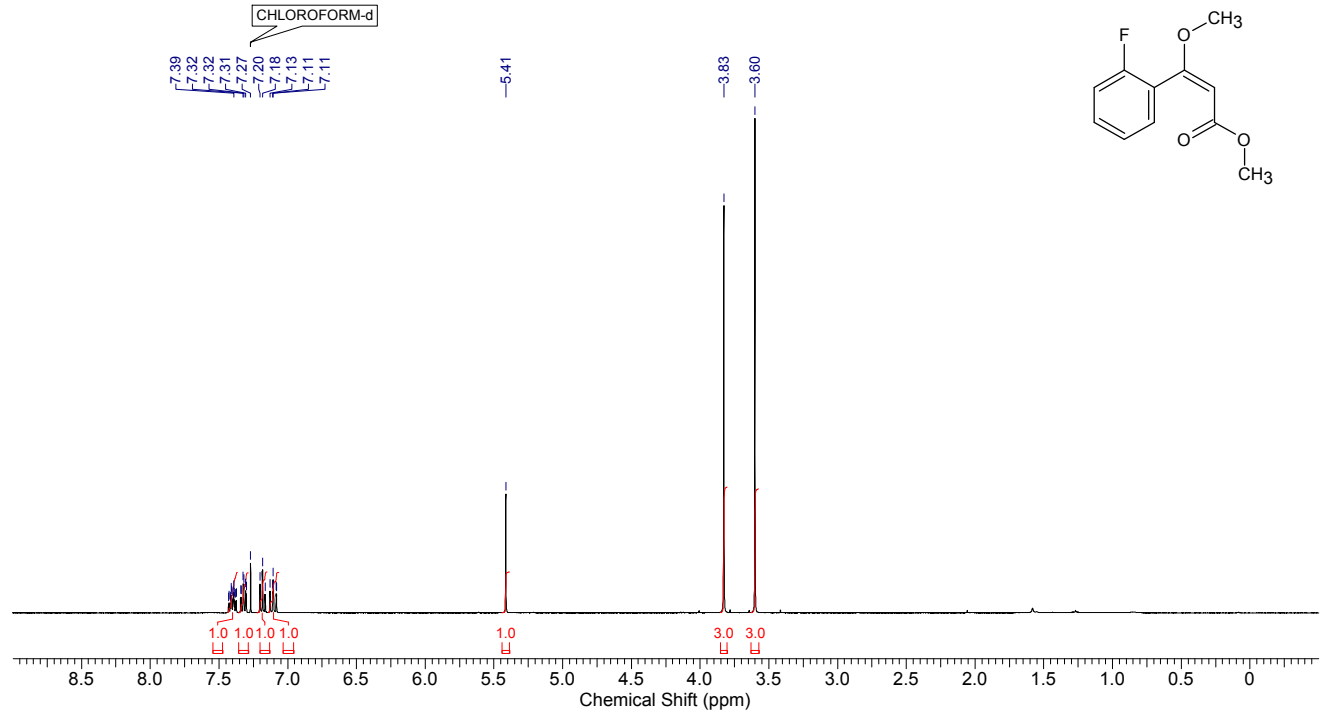


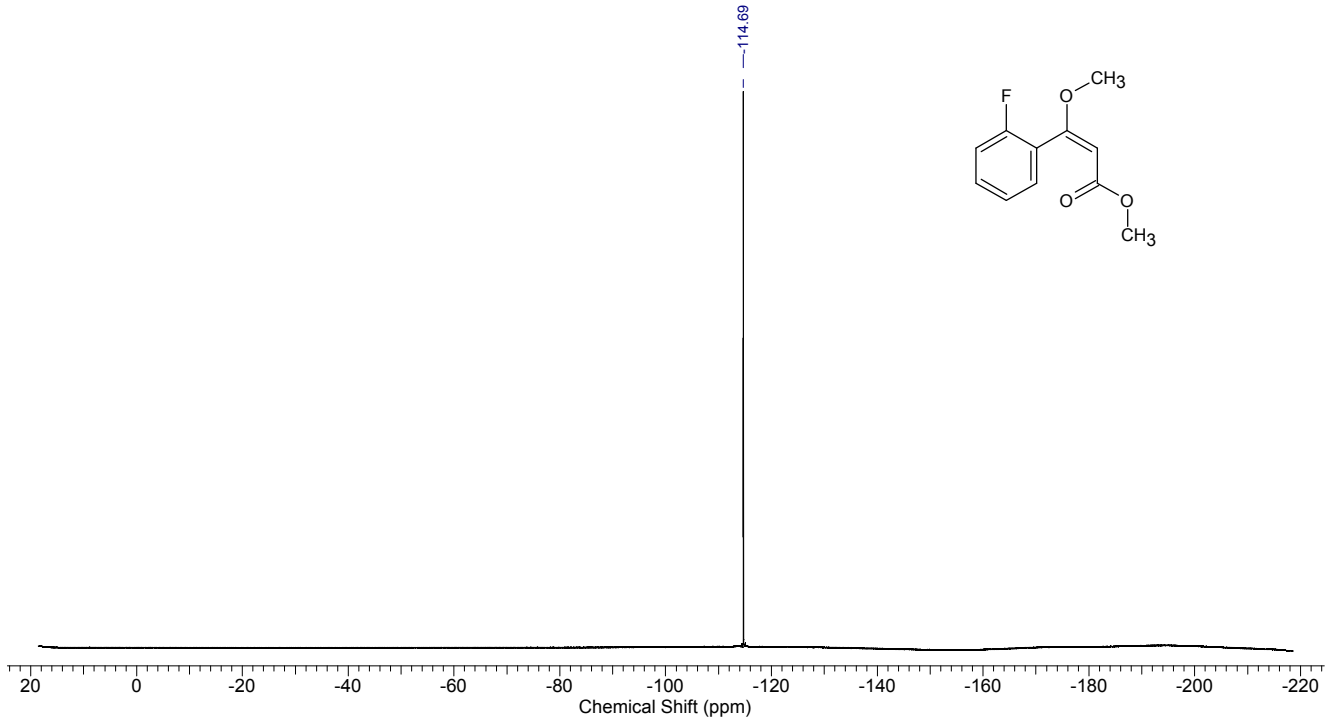


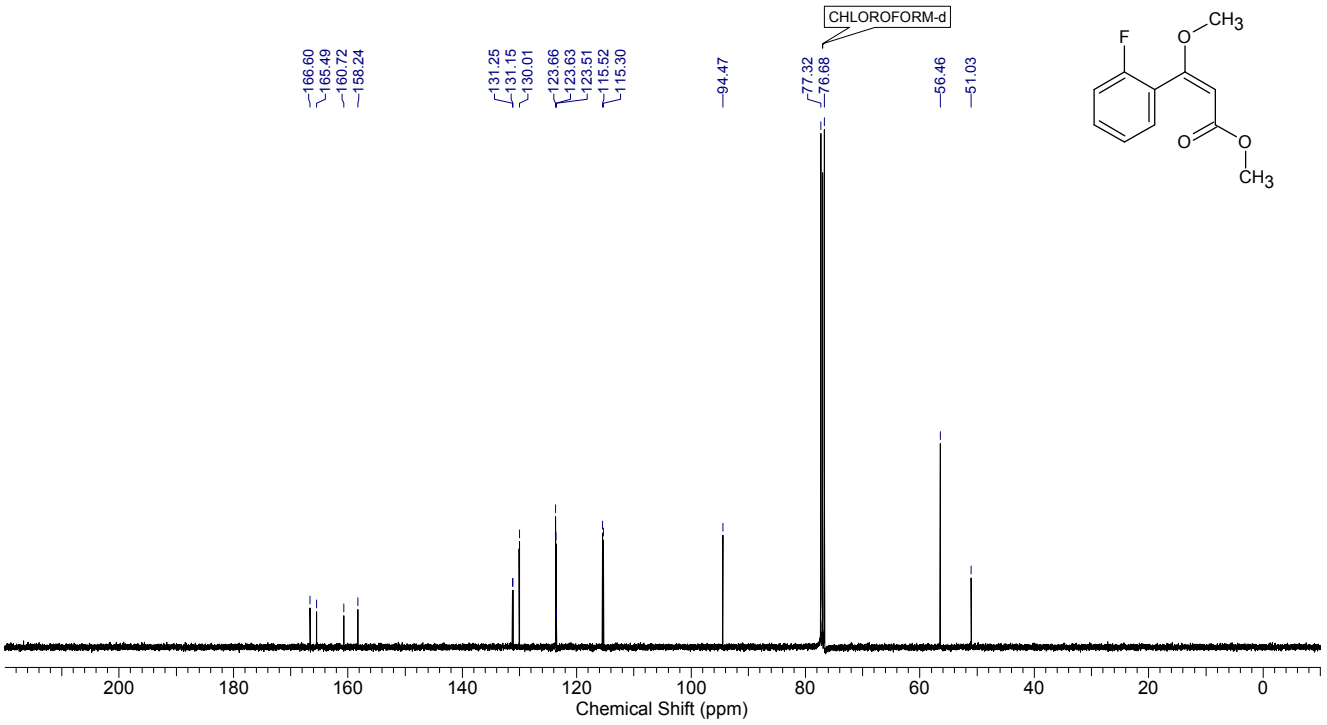
NOE Experiment



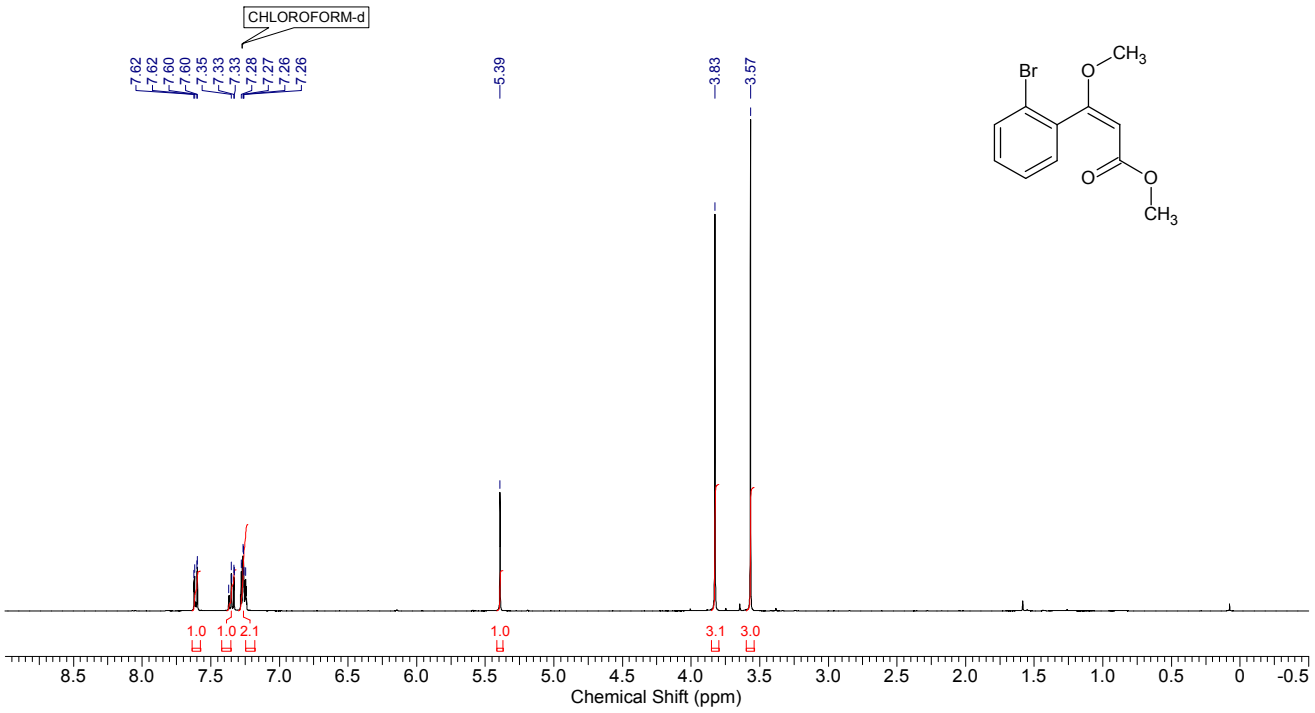
(*E*)-methyl 3-(2-fluorophenyl)-3-methoxyprop-2-enoate (3da)

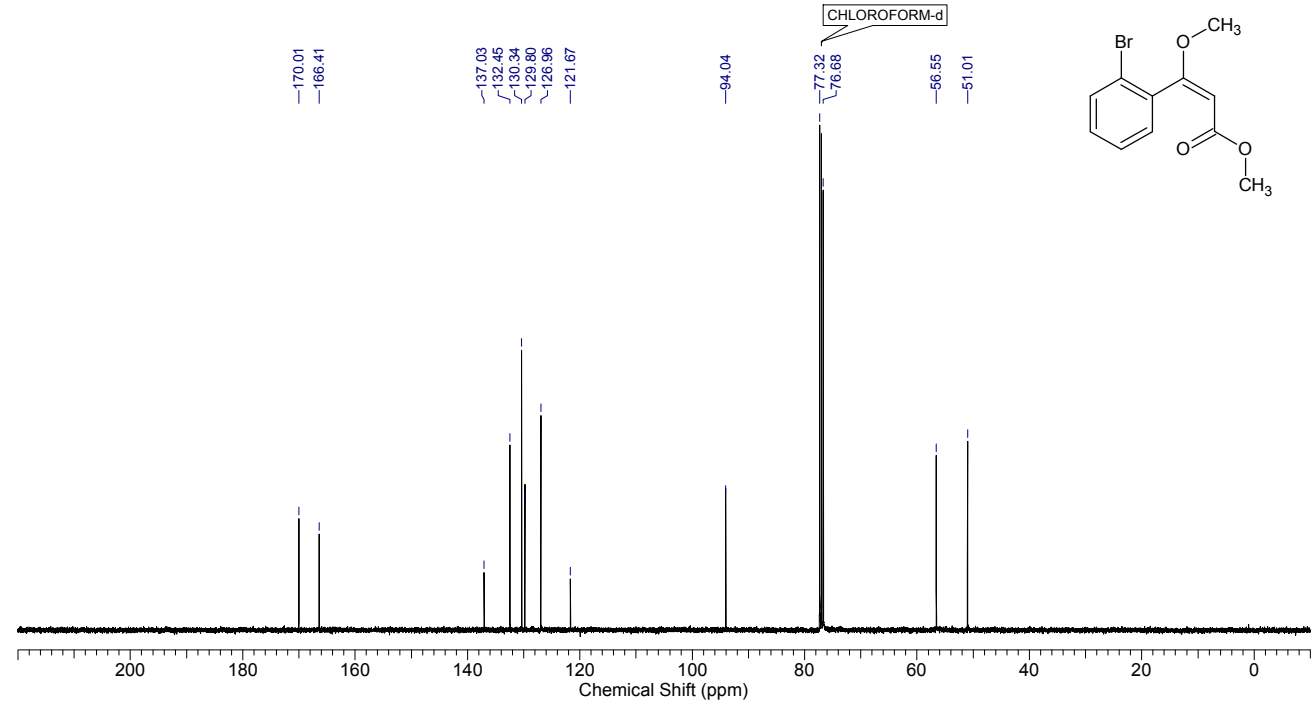




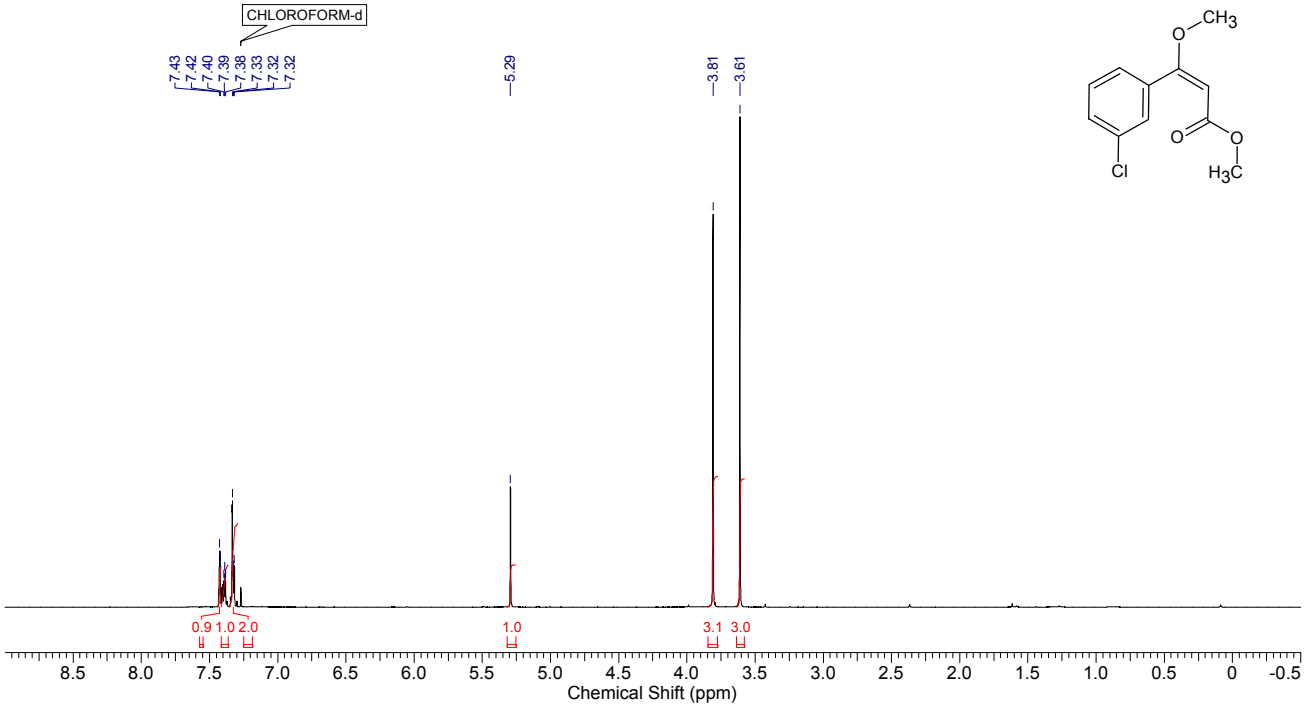

CHLOROFORM-d
166.60
165.49
160.72
158.24
131.25
131.15
130.01
123.66
123.63
123.51
115.52
115.30
94.47
77.32
76.68
56.46
51.03
F
O
CH3
O
O
CH3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

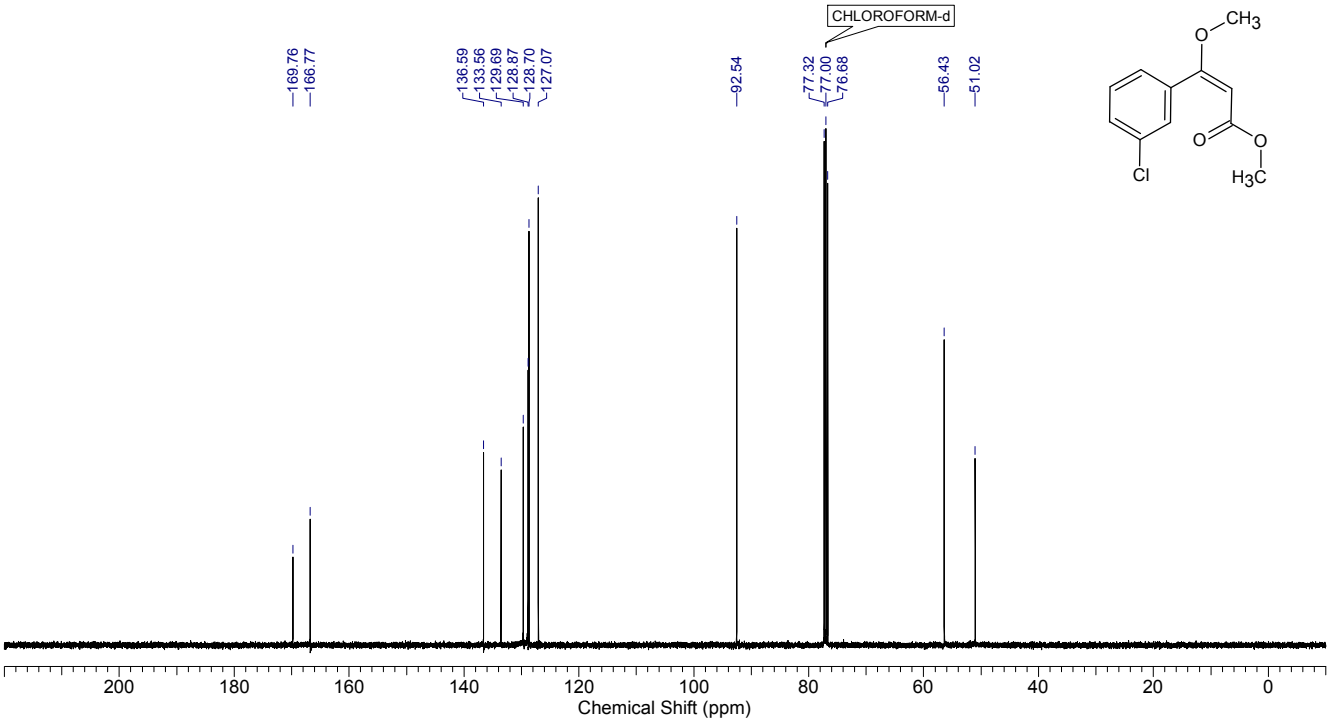
(*E*)-methyl 3-(2-bromophenyl)-3-methoxyprop-2-enoate (3ea)



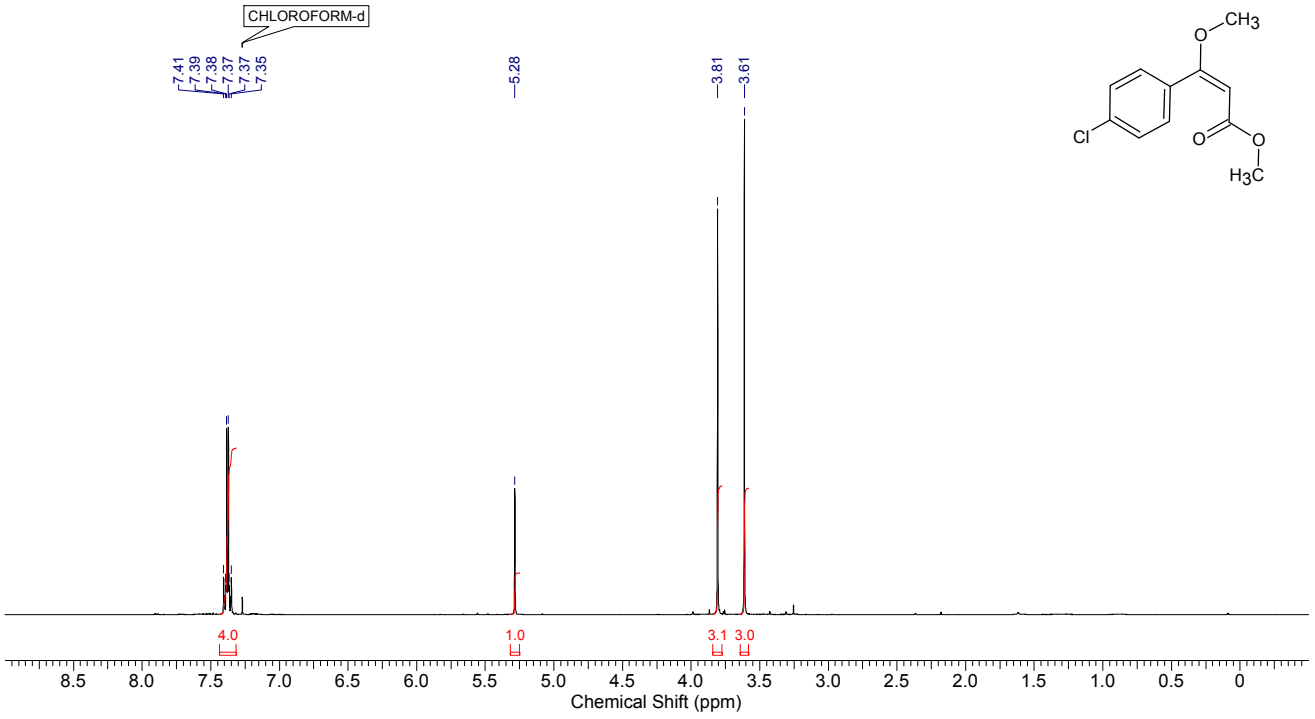


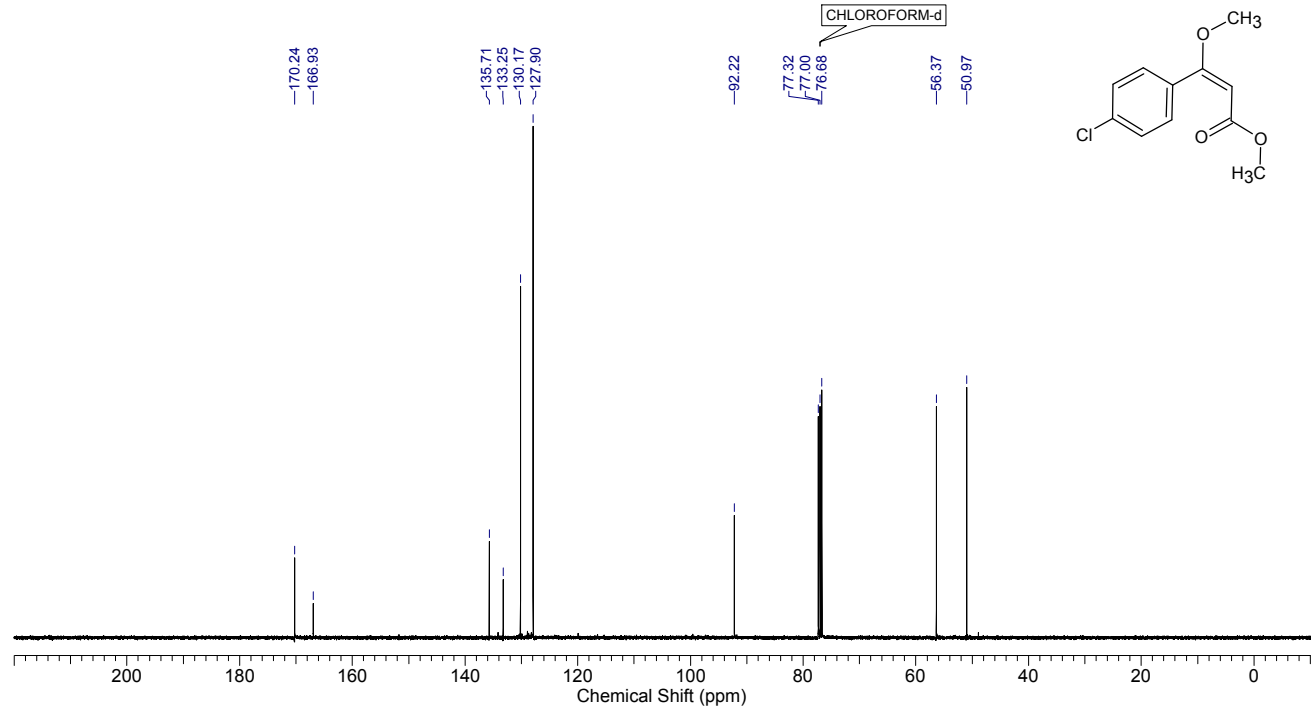
(*E*)-methyl 3-(3-chlorophenyl)-3-methoxprop-2-enoate (3fa)



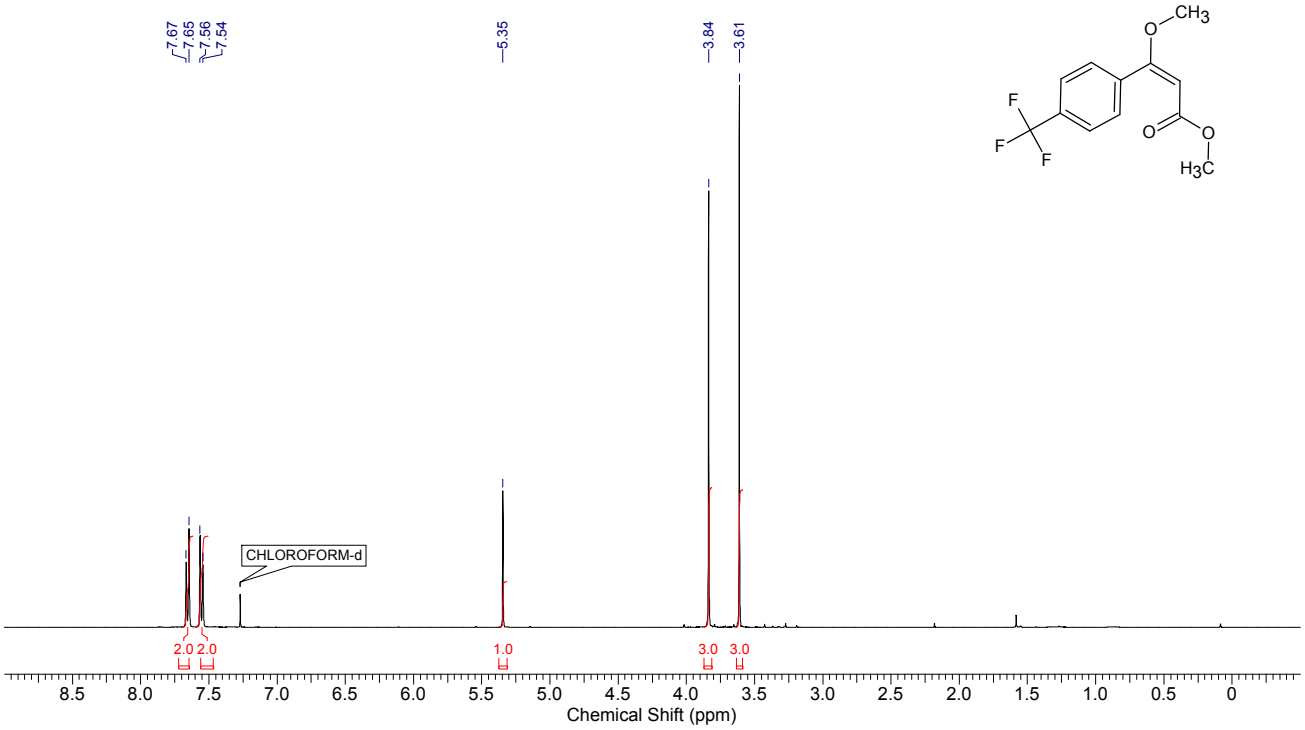


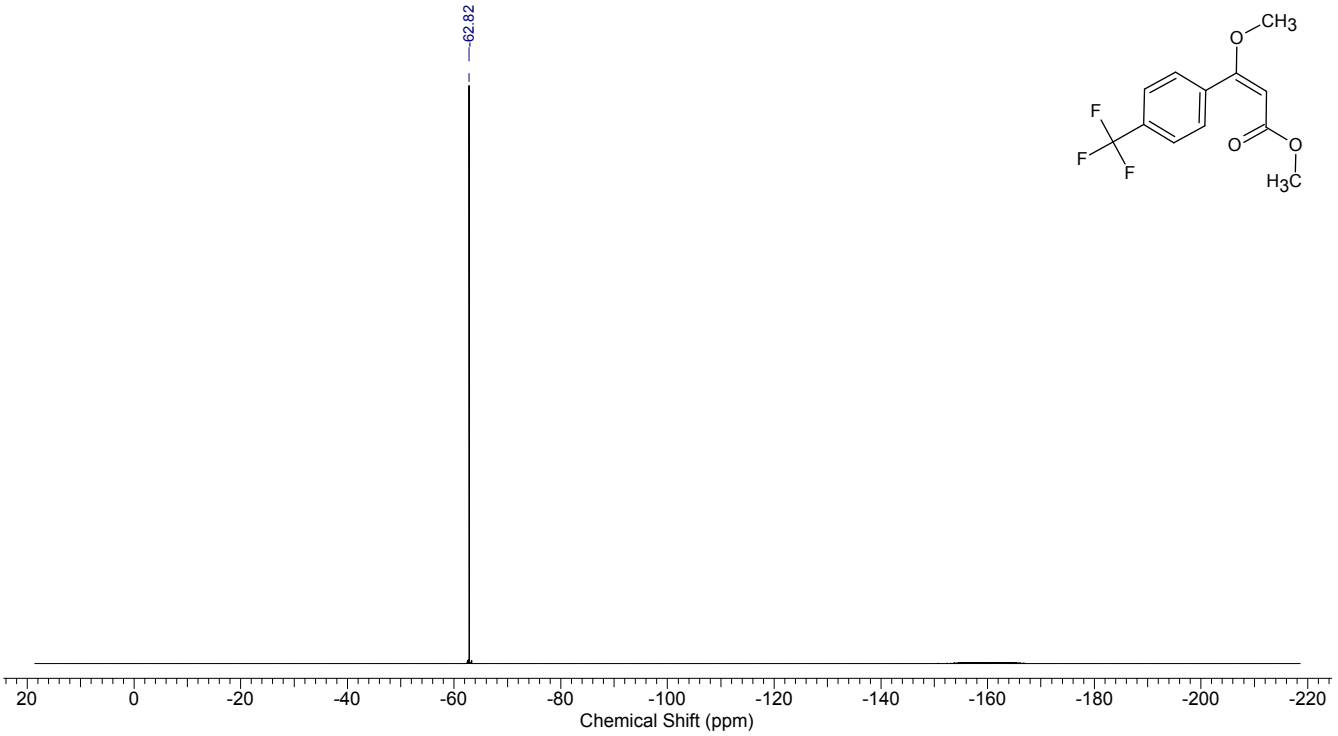
(*E*)-methyl 3-(4-chlorophenyl)-3-methoxyprop-2-enoate (3ga)

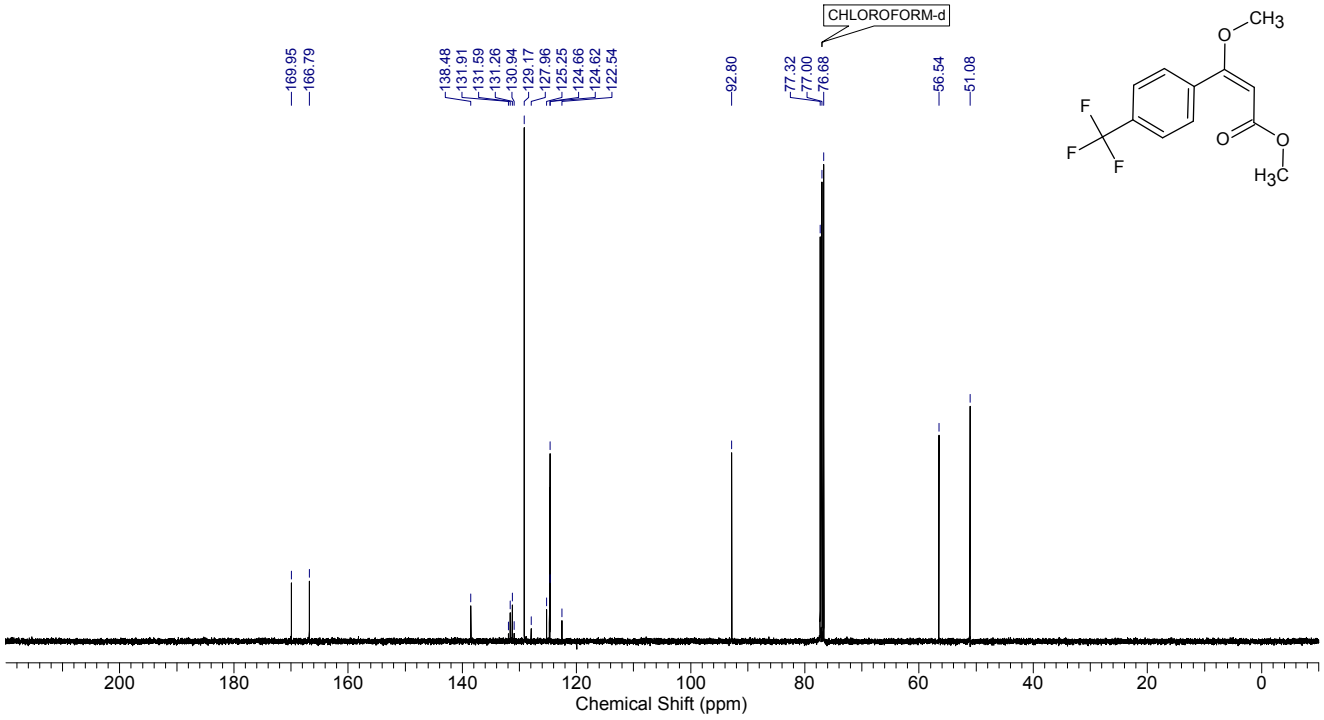




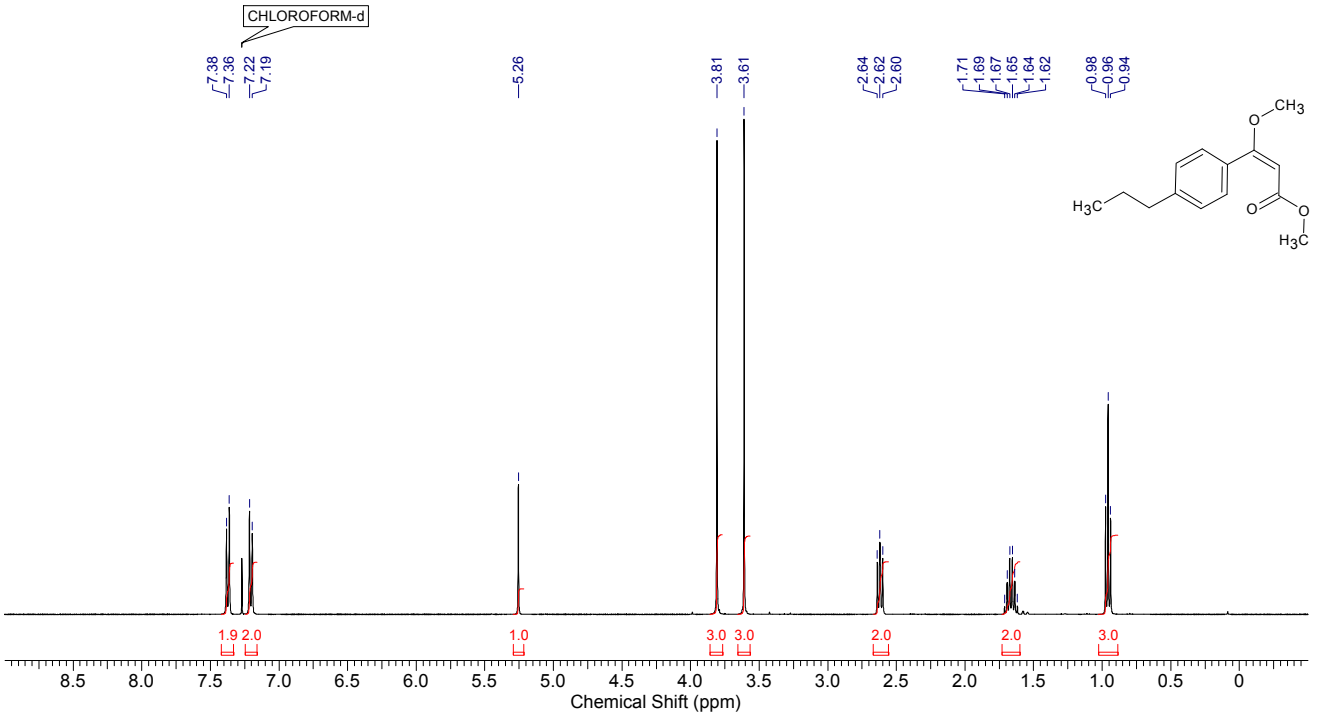
(*E*)-methyl 3-methoxy-3-[4-(trifluoromethyl)phenyl]prop-2-enoate (3ha)

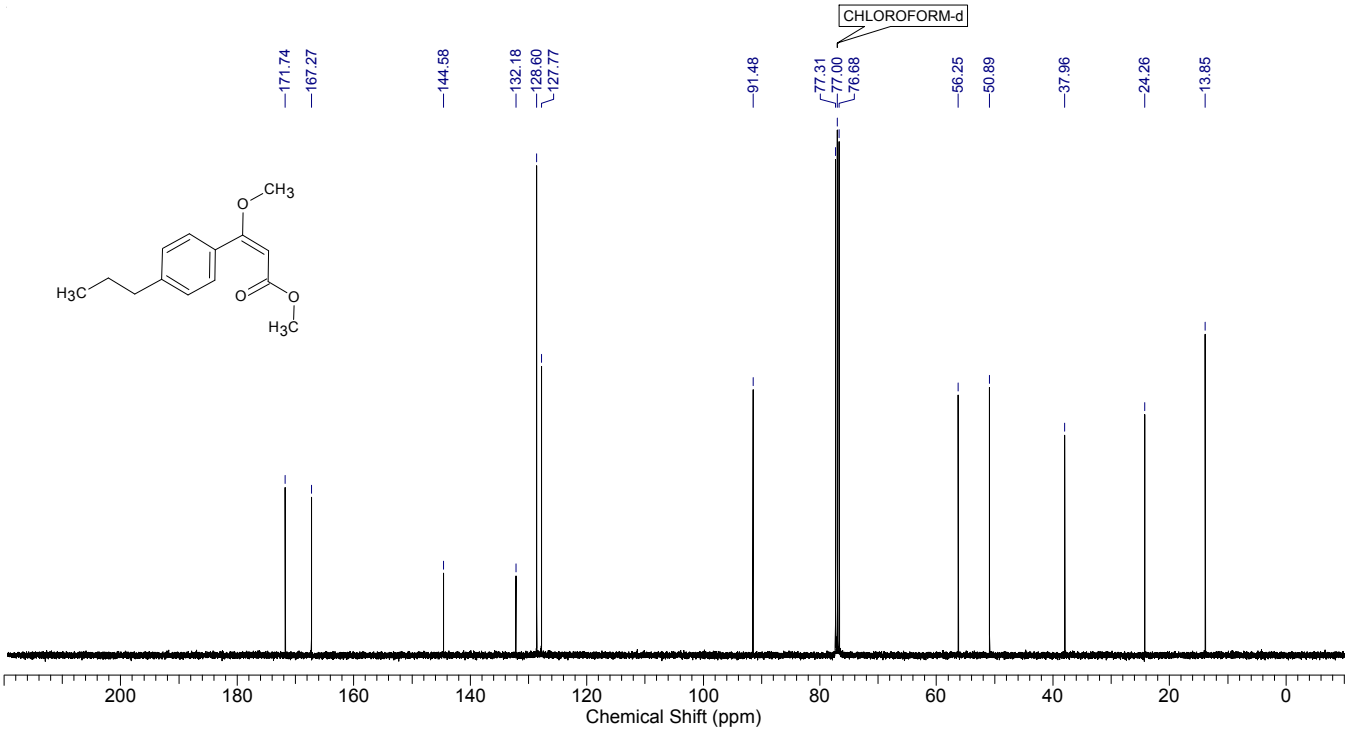




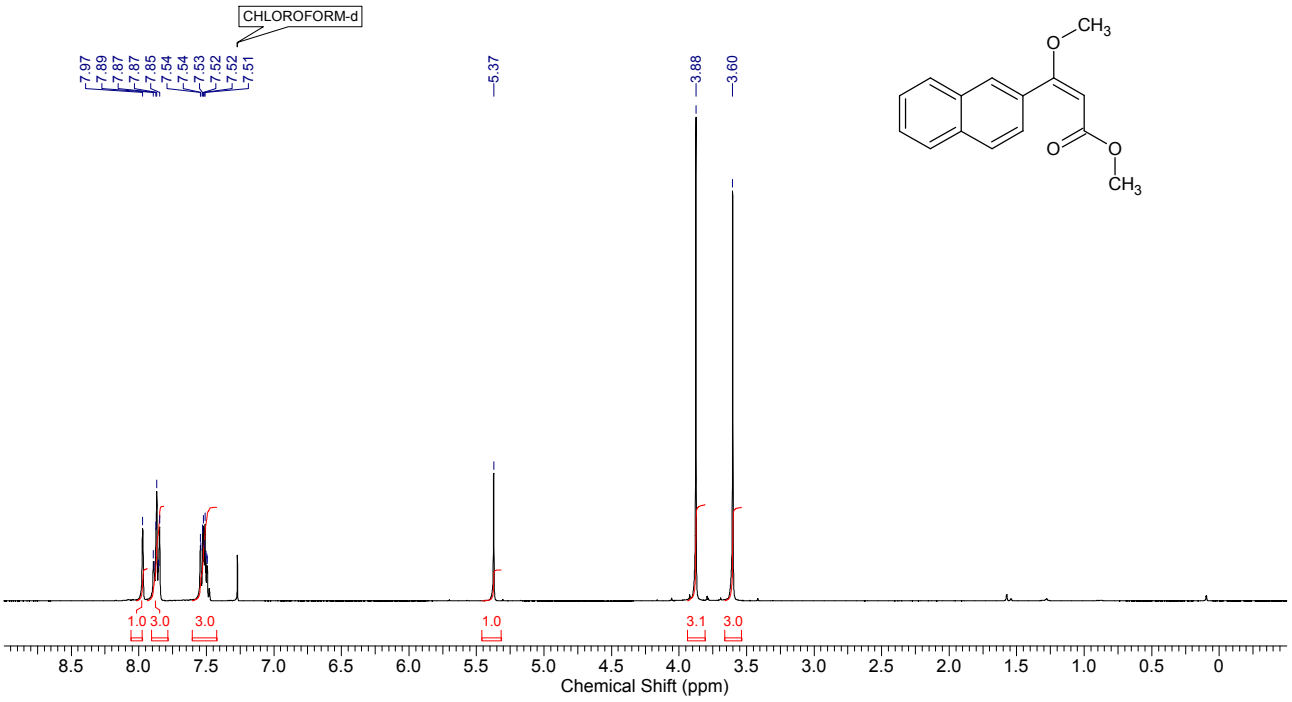

CHLOROFORM-d
169.95
166.79
138.48
131.91
131.59
131.26
130.94
129.17
127.96
125.25
124.66
124.62
122.54
92.80
77.32
77.00
76.68
56.54
51.08
CH3
O
F
F
F
O
O
H3C
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

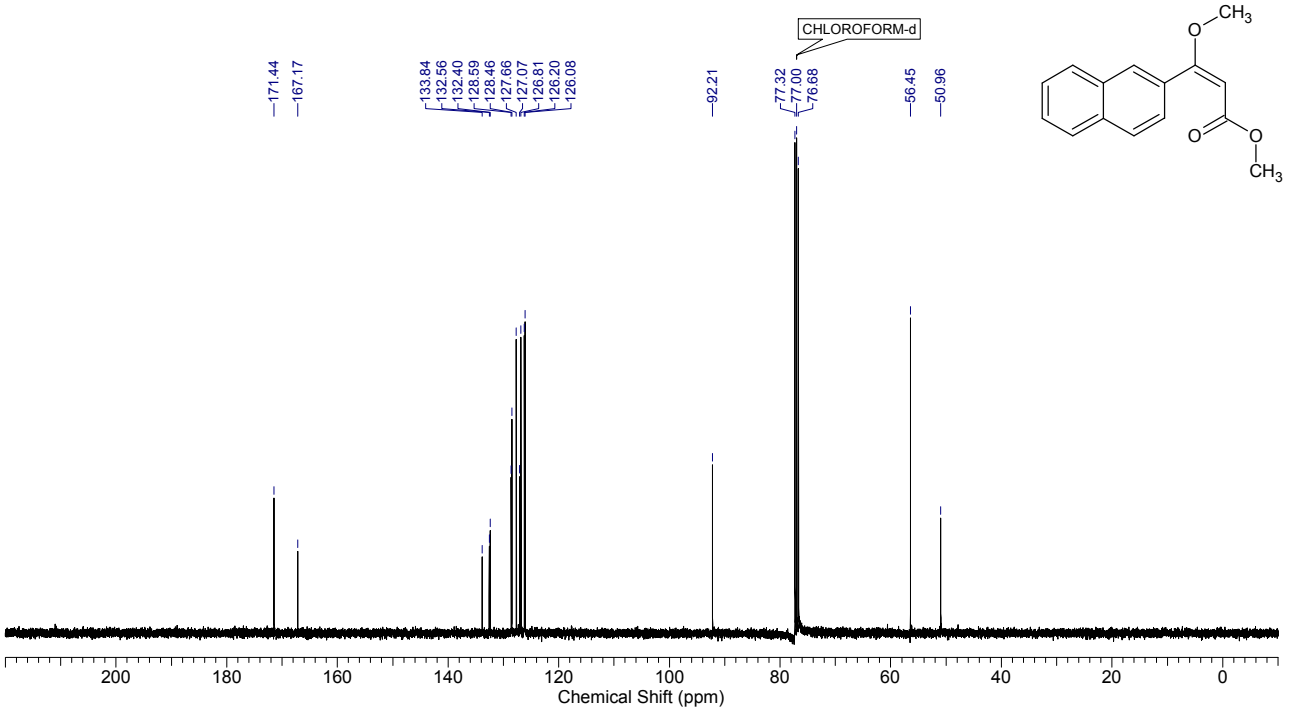
((*E*)-methyl 3-methoxy-3-(4-propylphenyl)prop-2-enoate (3ia)



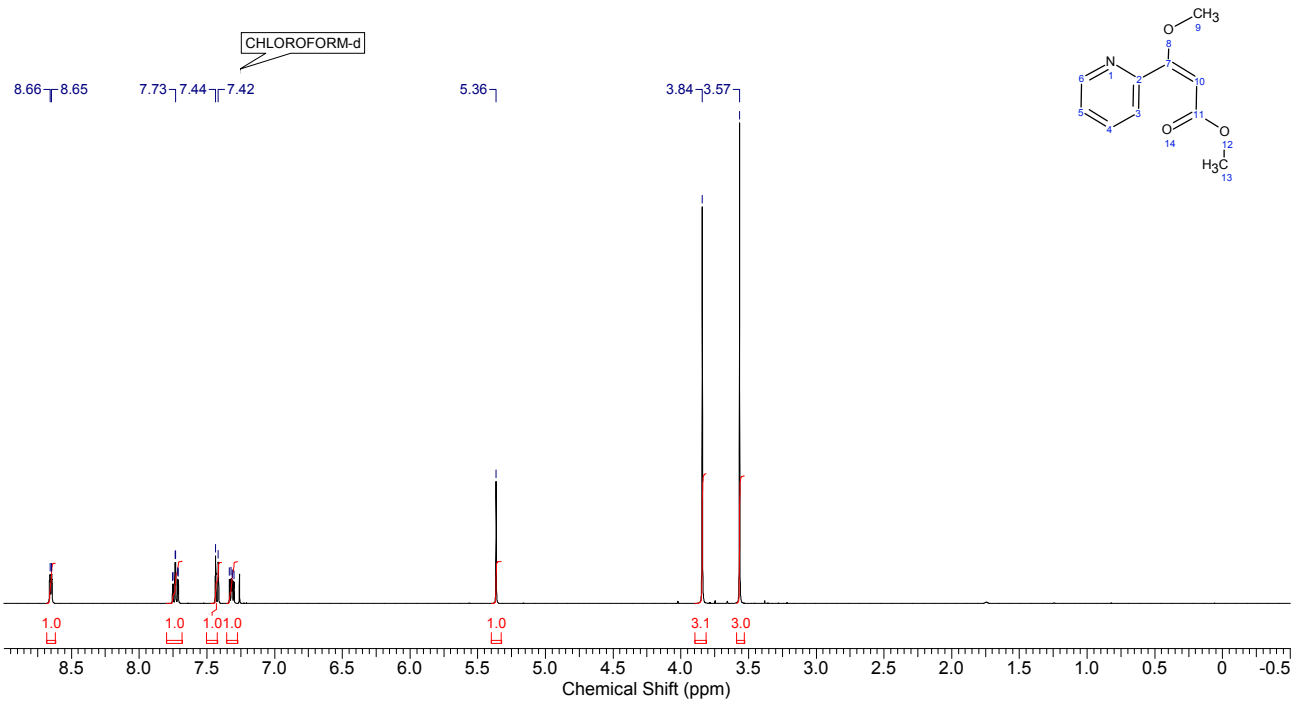


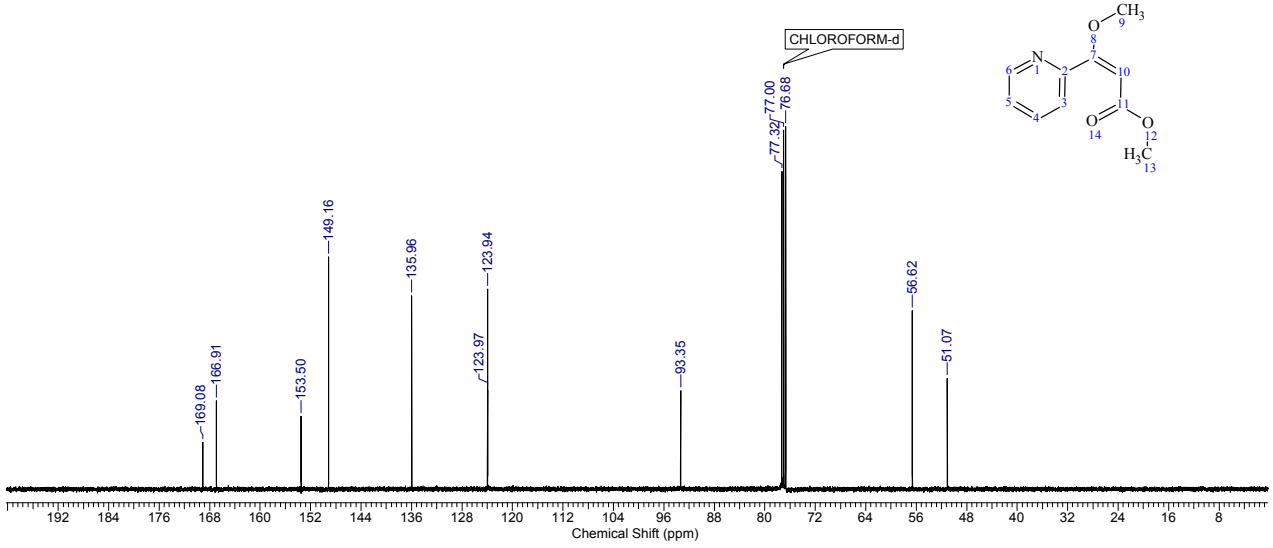
(*E*)-methyl 3-methoxy-3-(naphthalen-2-yl)prop-2-enoate (3ja)



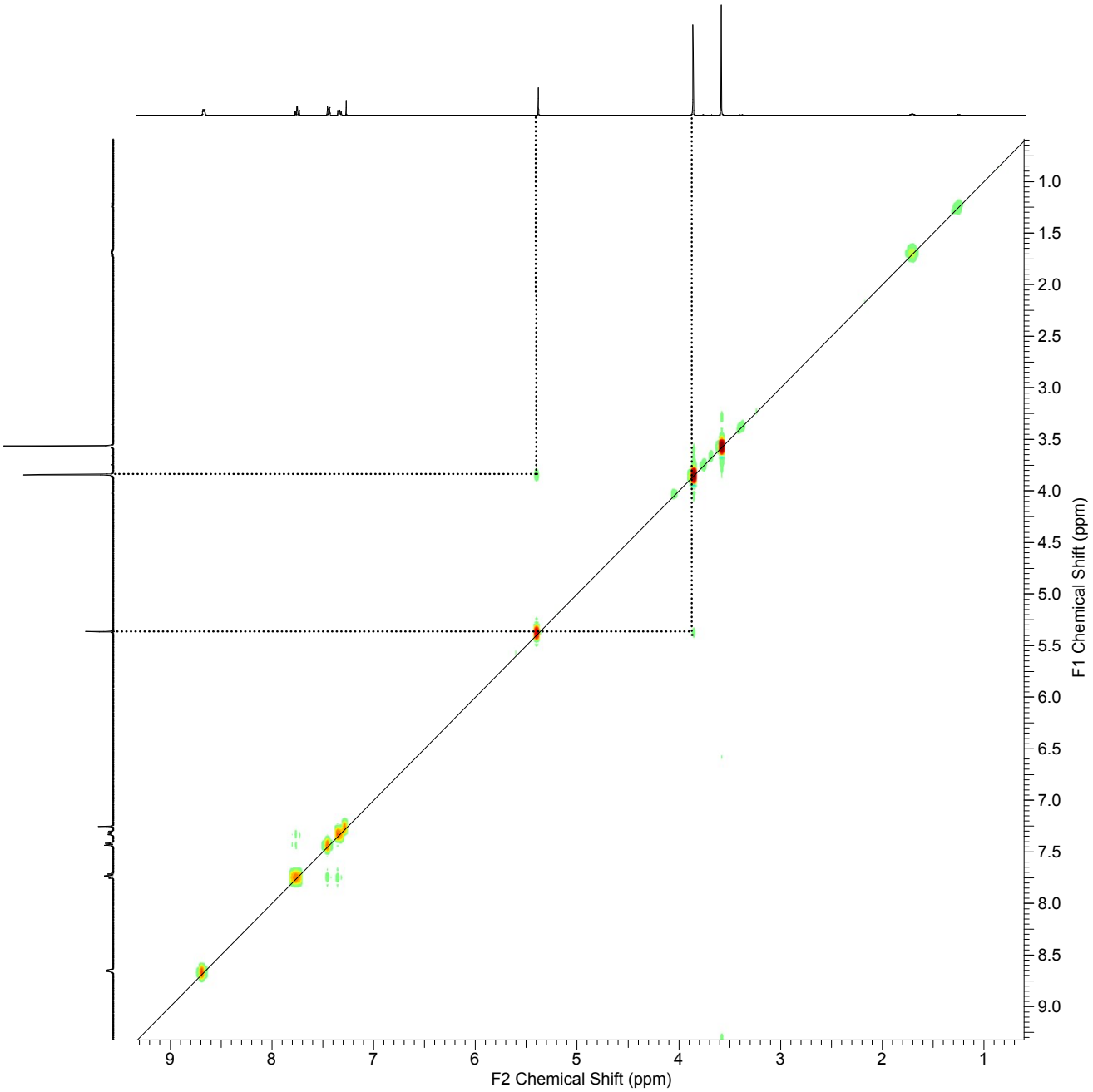


(*E*)-methyl 3-methoxy-3-(pyridin-2-yl)prop-2-enoate (3ka)

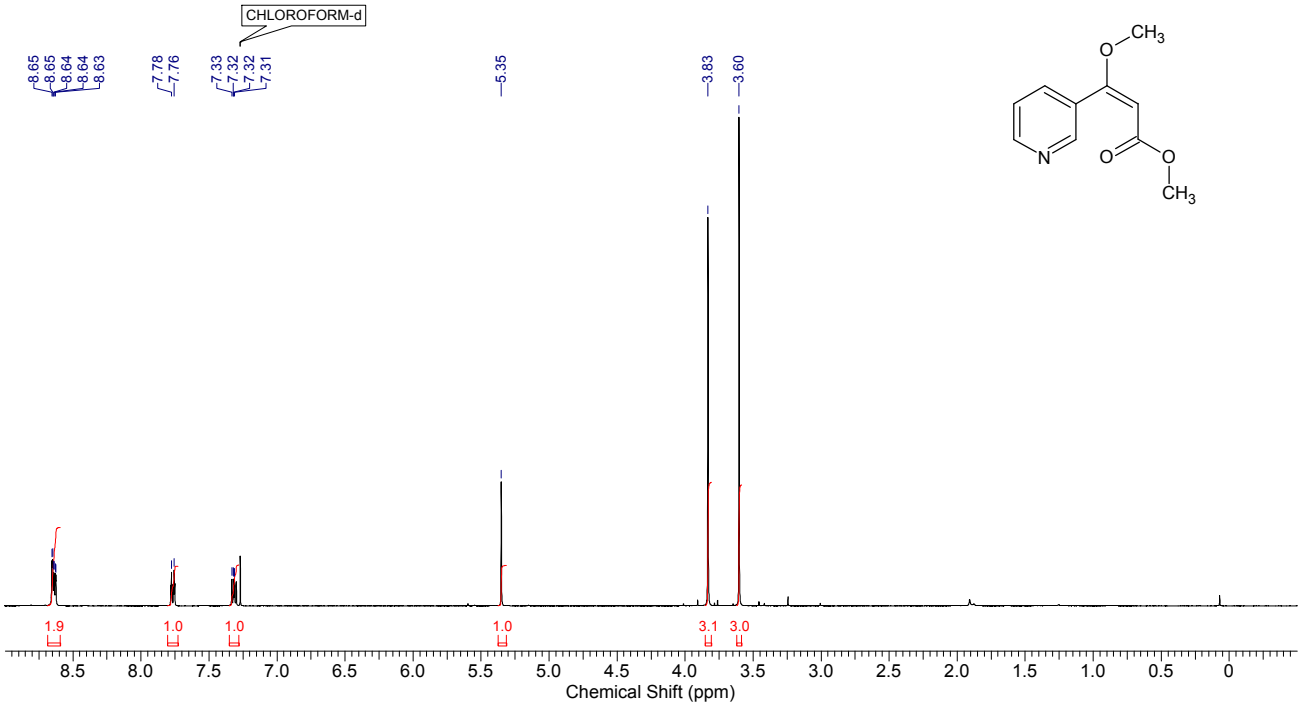


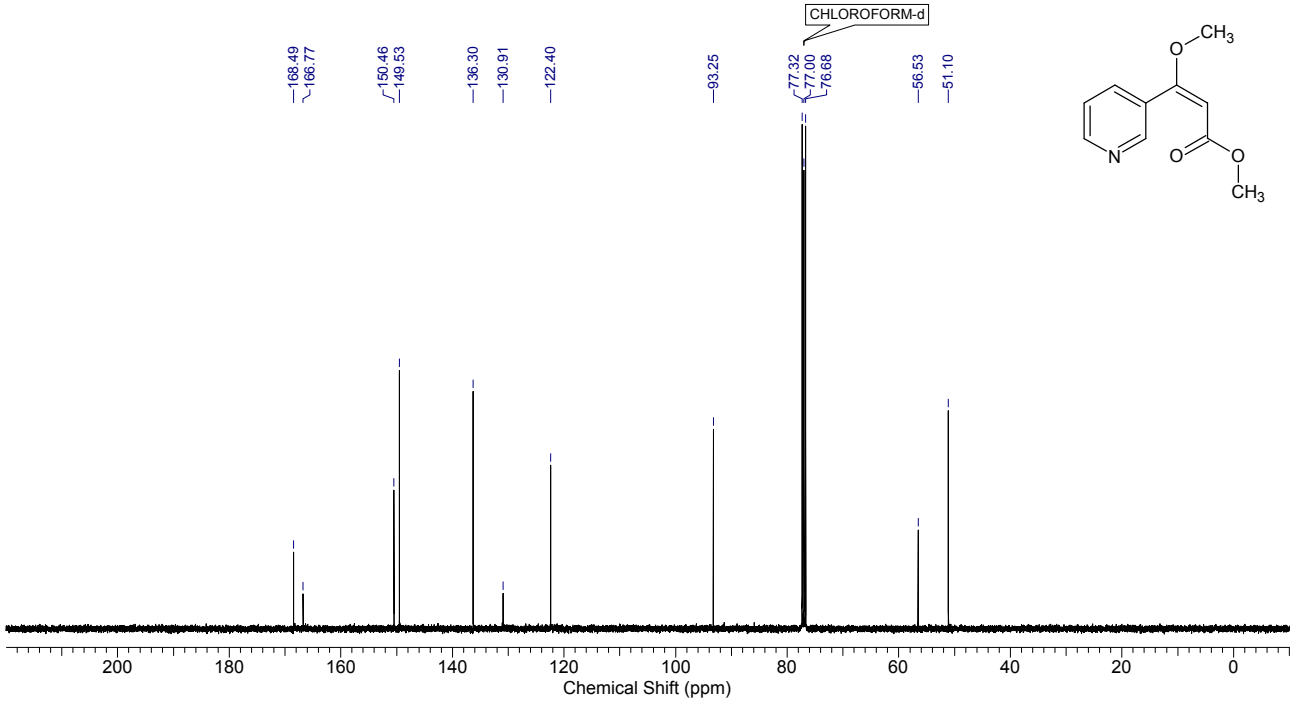


NOE Experiment

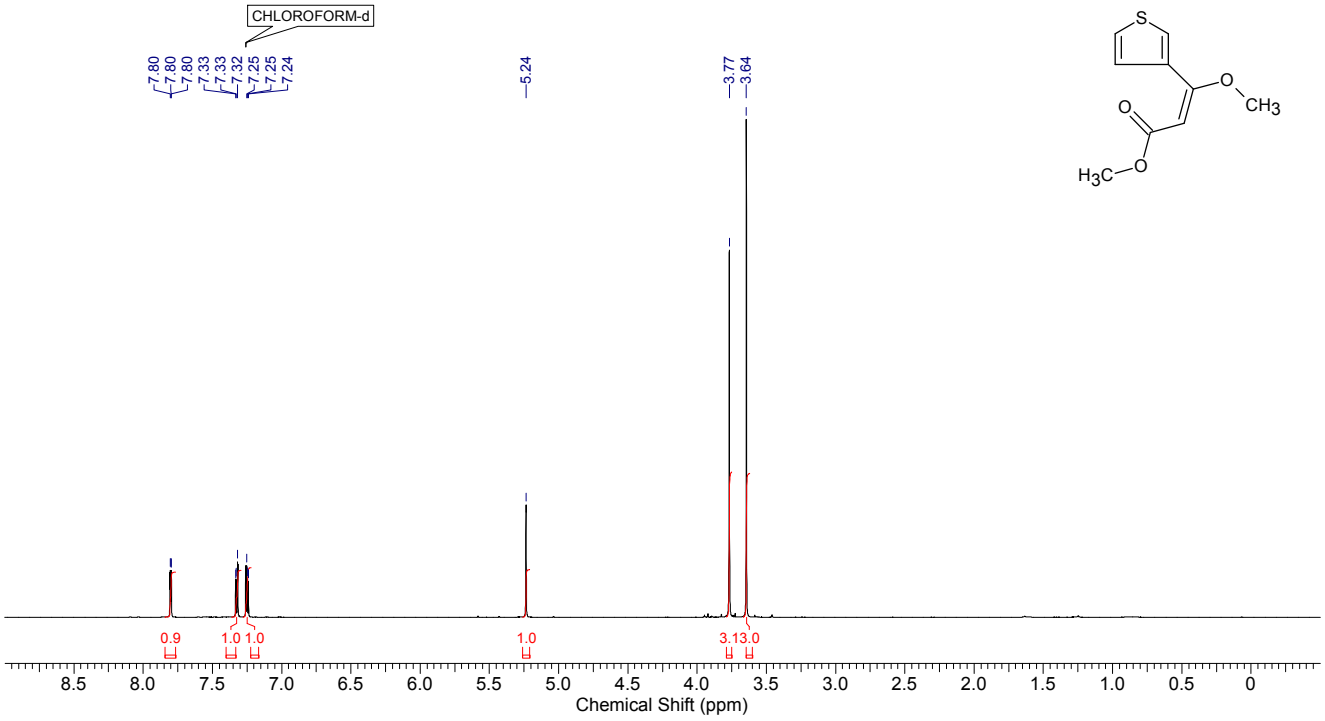


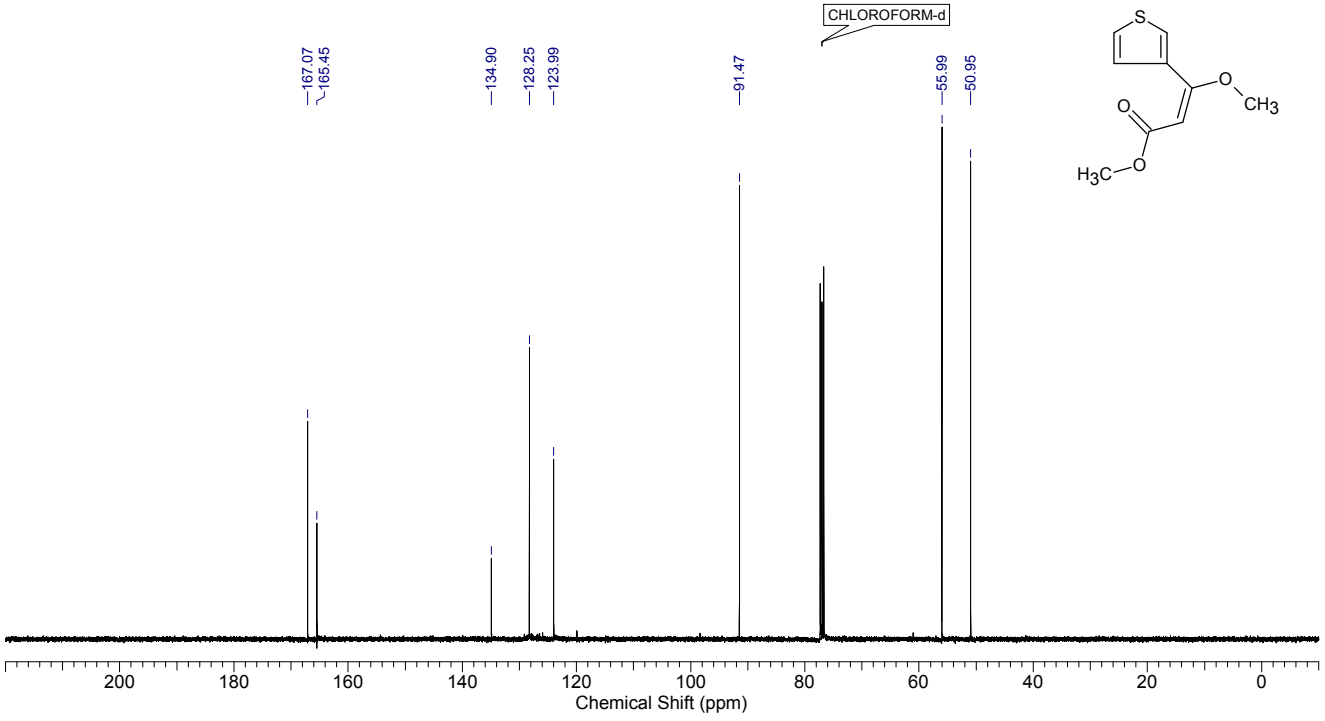
(*E*)-methyl 3-methoxy-3-(pyridin-3-yl)prop-2-enoate (3la)



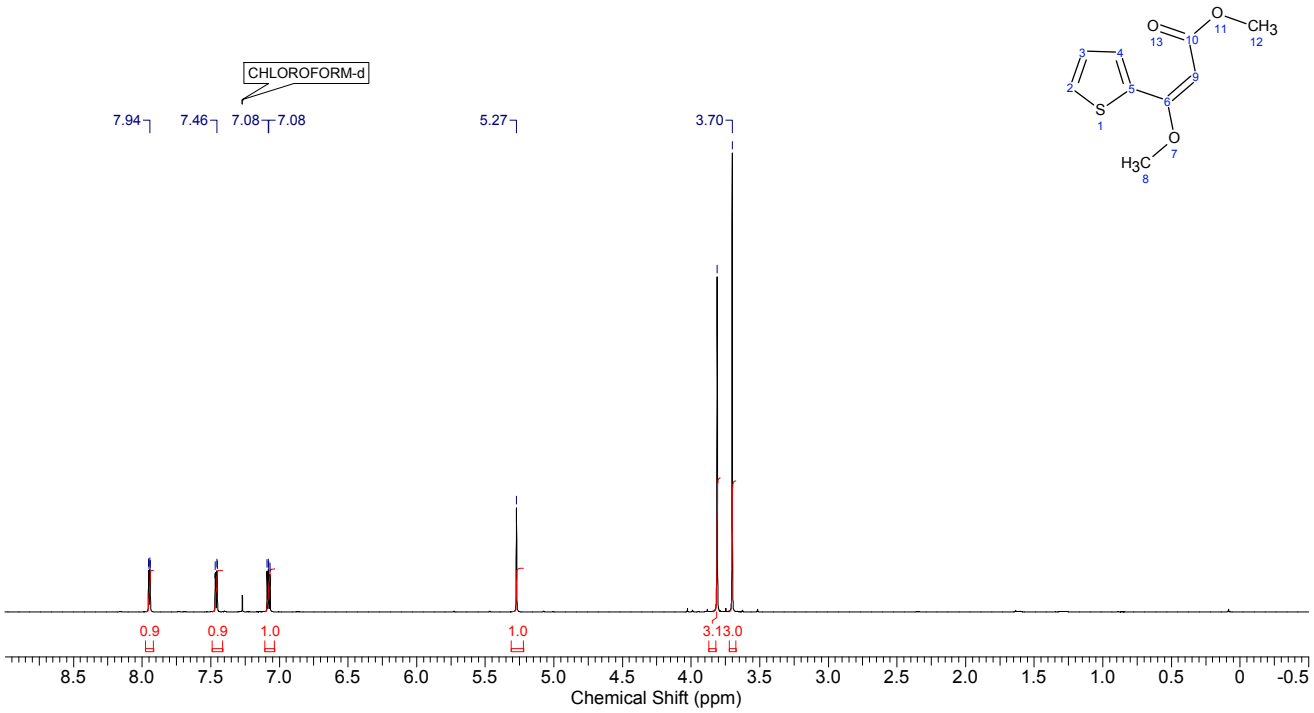


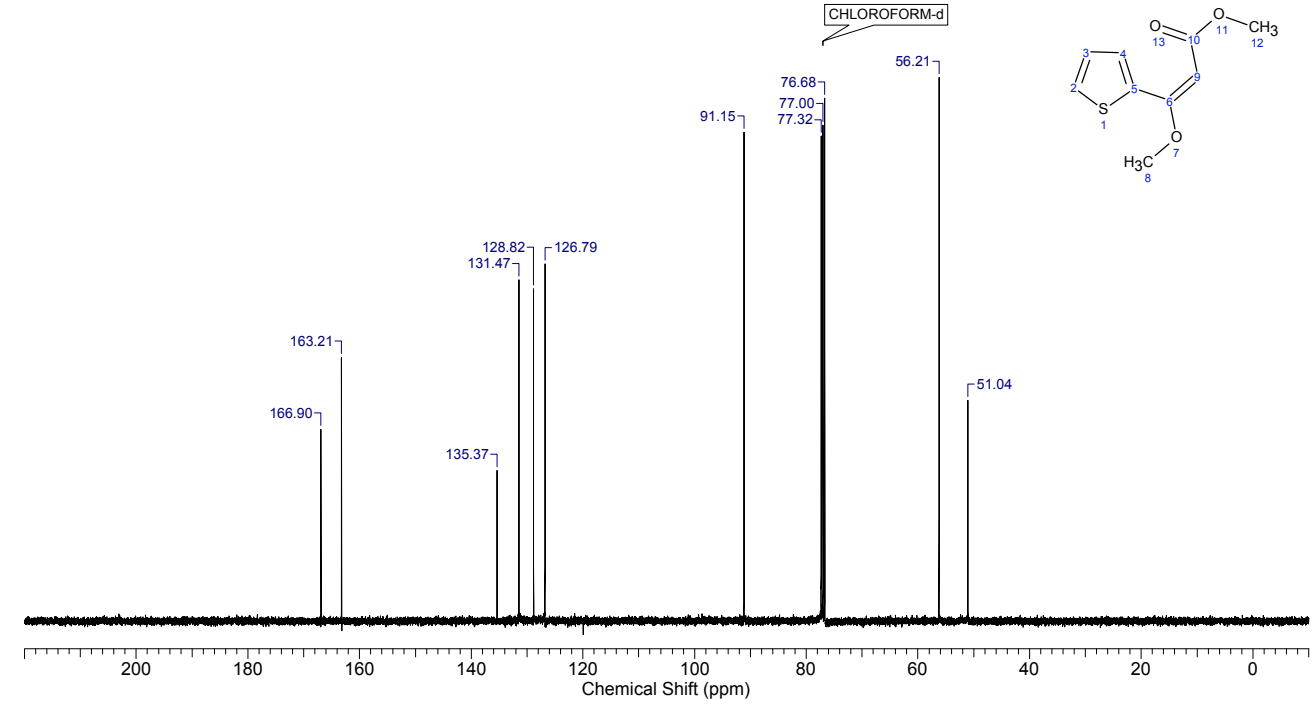
(*E*)-methyl 3-methoxy-3-(thiophen-3-yl)prop-2-enoate (3ma)



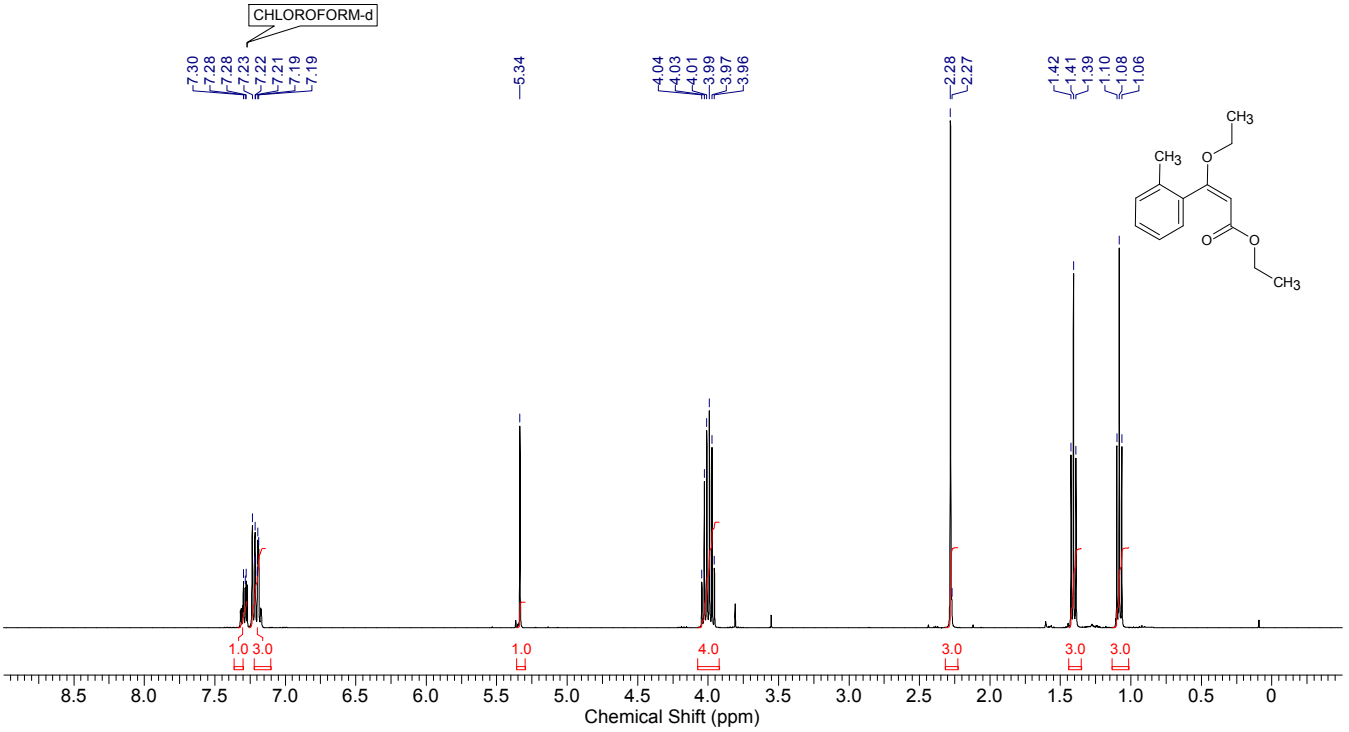


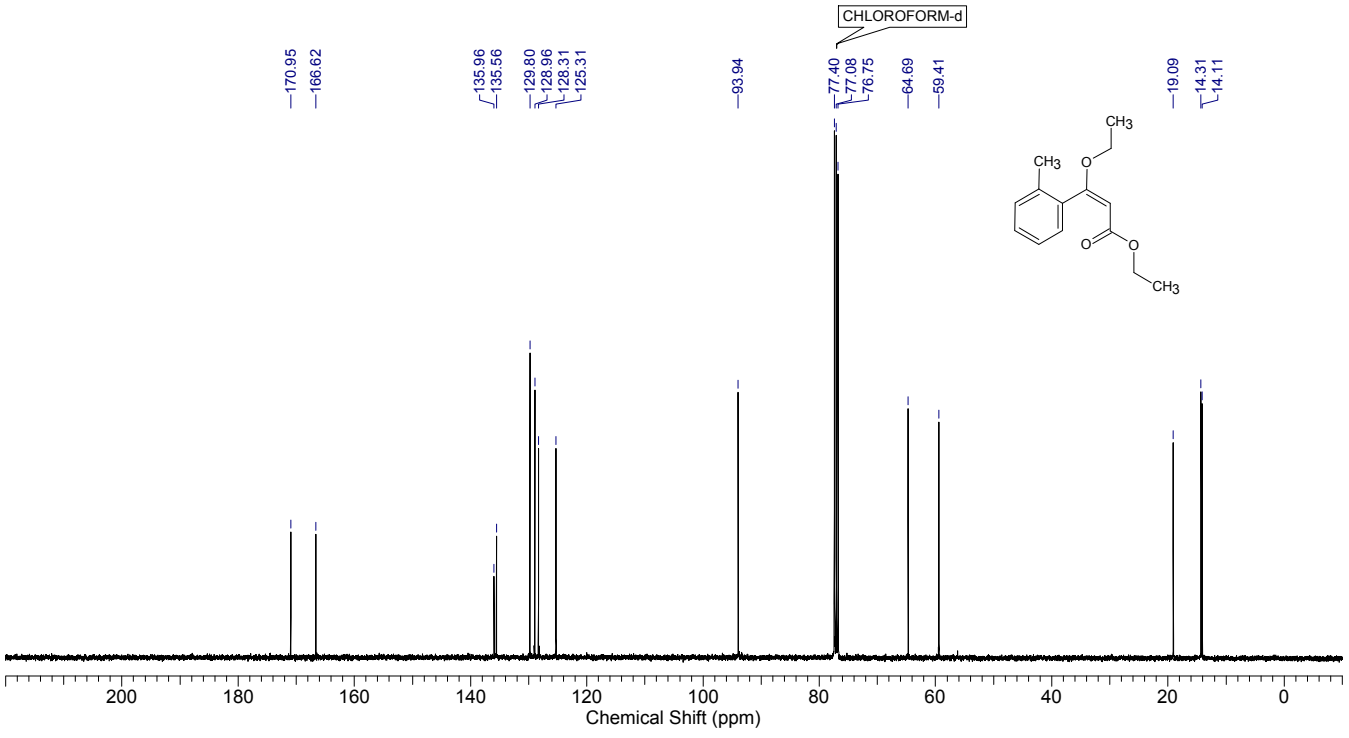
(*E*)-methyl 3-methoxy-3-(thiophen-2-yl)prop-2-enoate (3na)



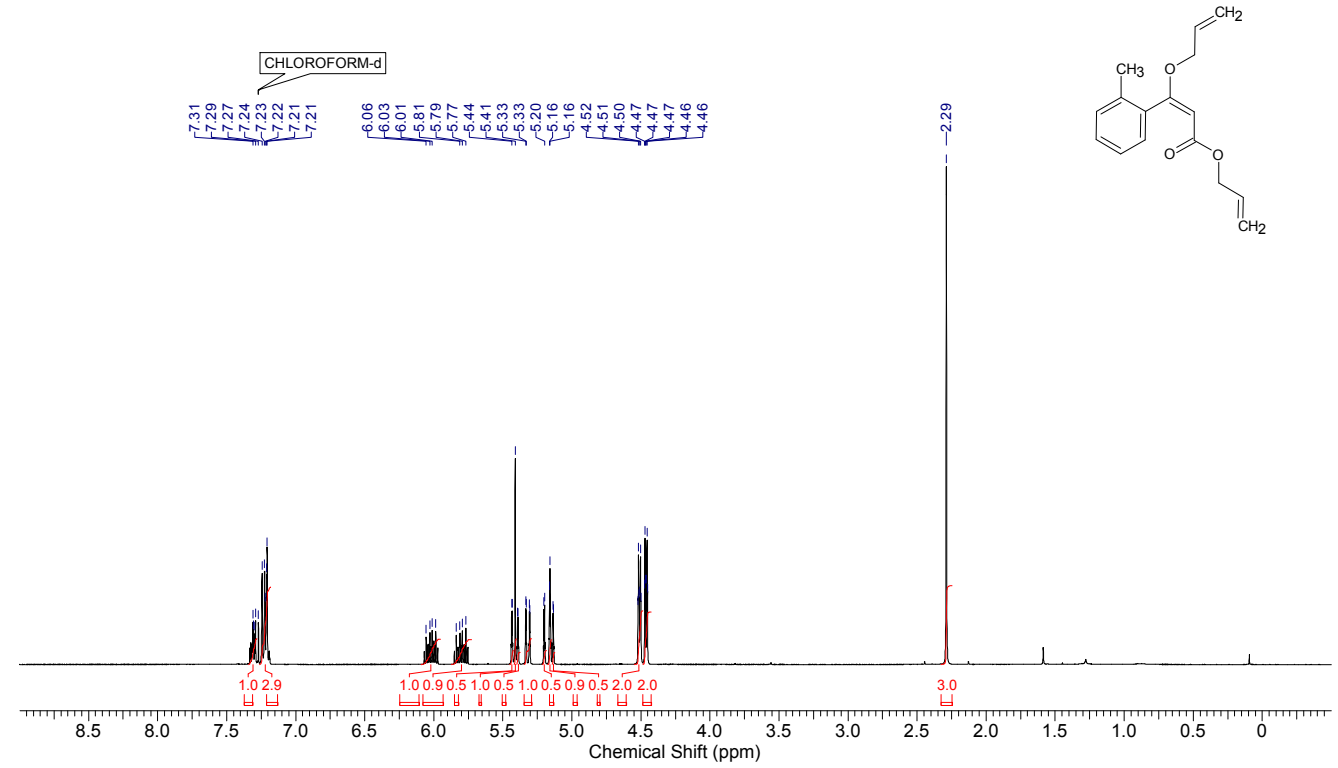


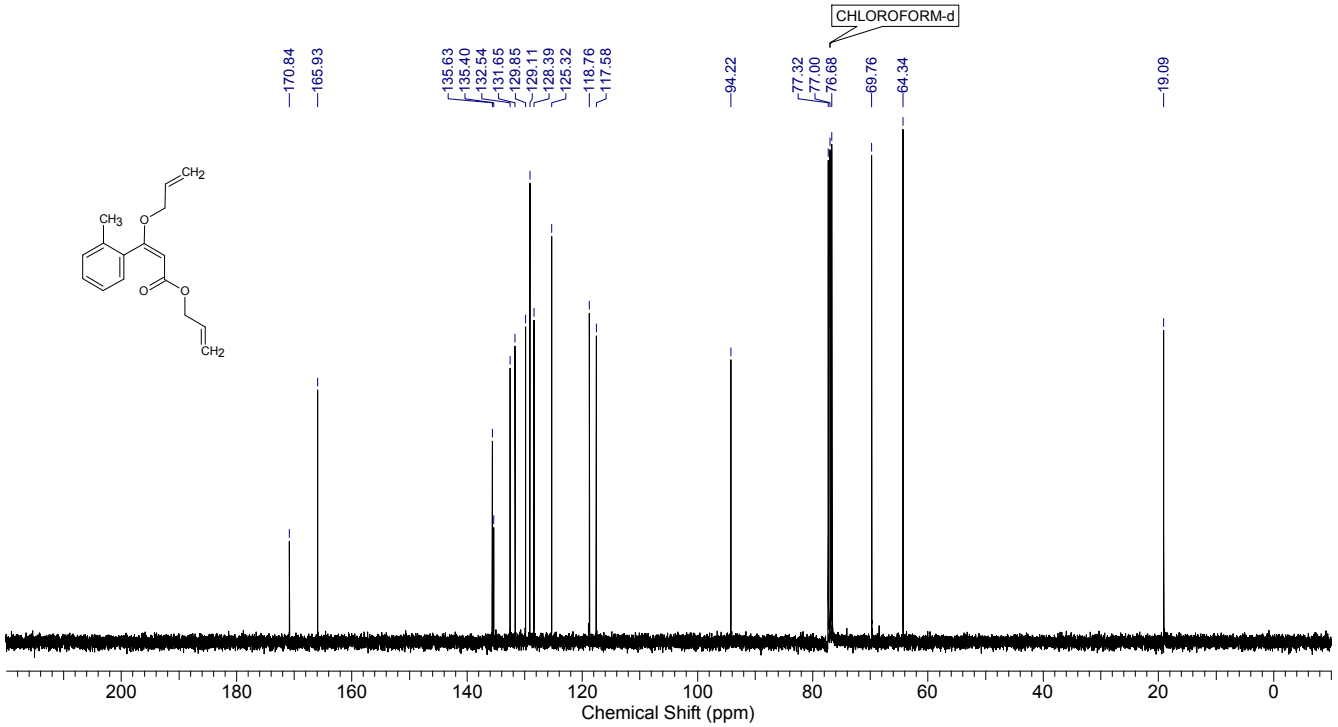
(*E*)-ethyl 3-ethoxy-3-(2-methylphenyl)prop-2-enoate (3bb)



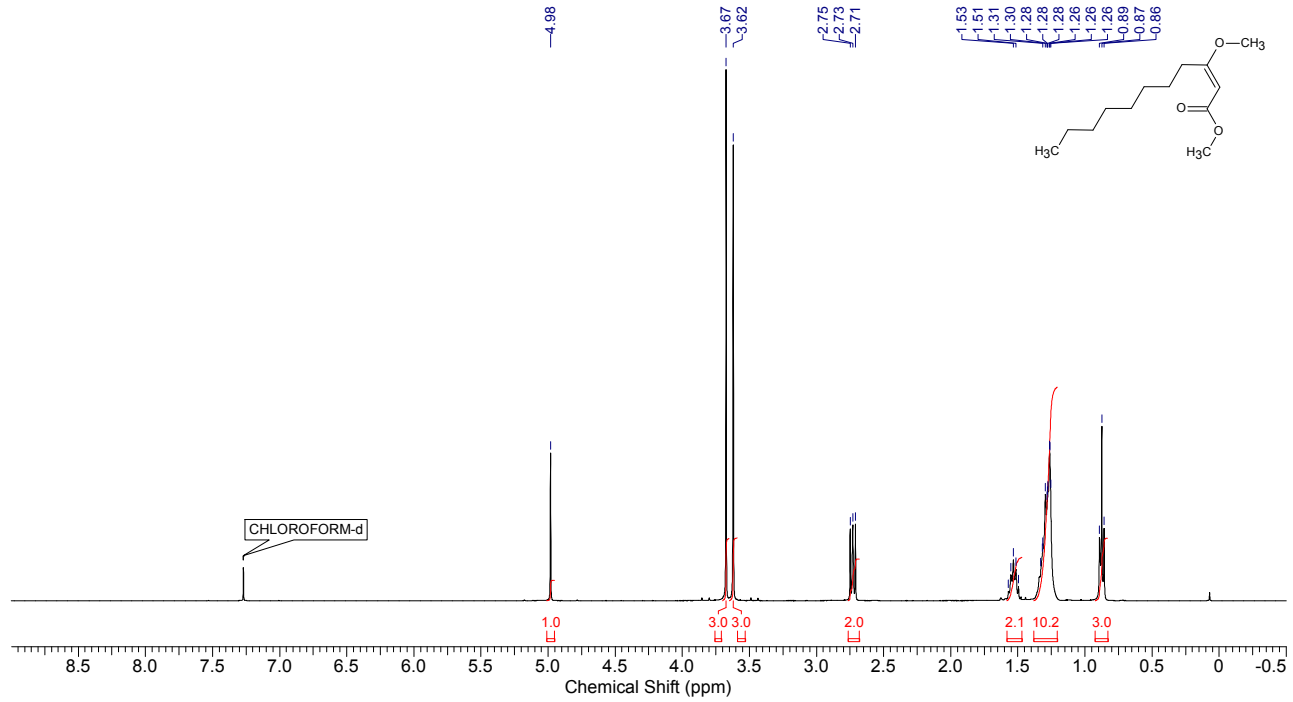


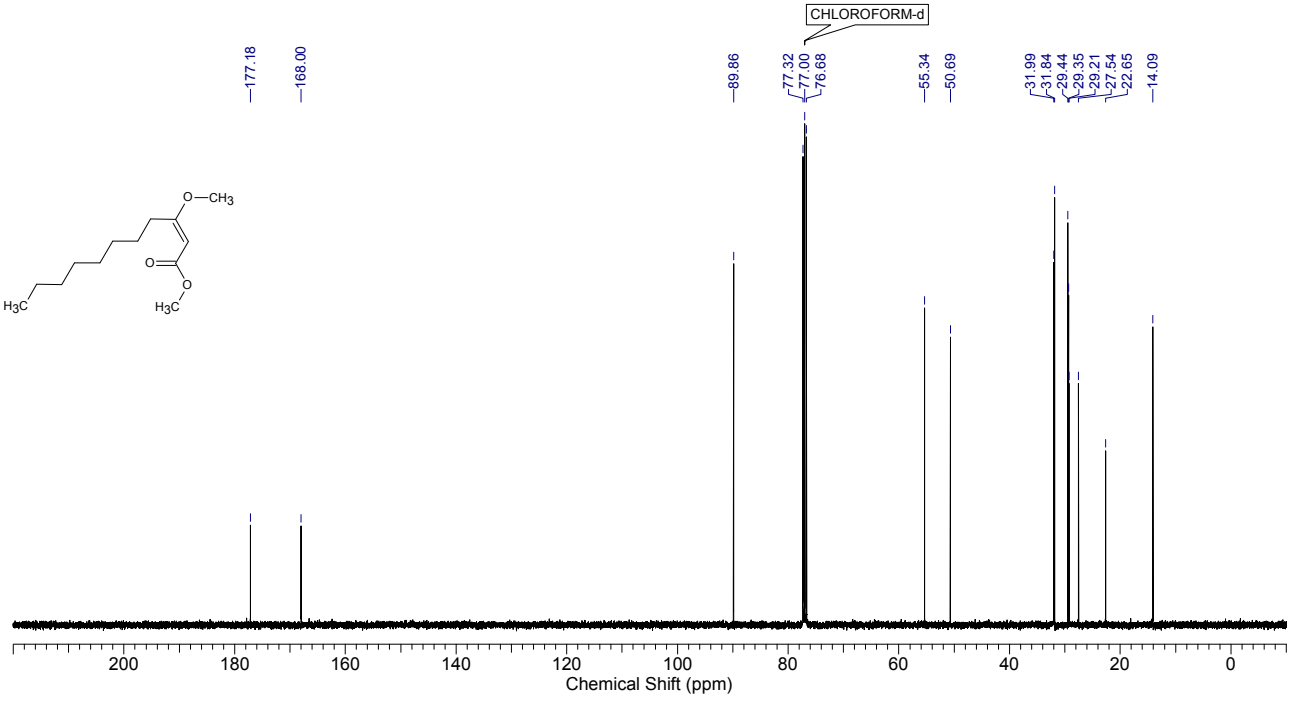
Prop-2-en-1-yl (2*E*)-3-(2-methylphenyl)-3-(prop-2-en-1-yloxy)prop-2-enoate (3bc)



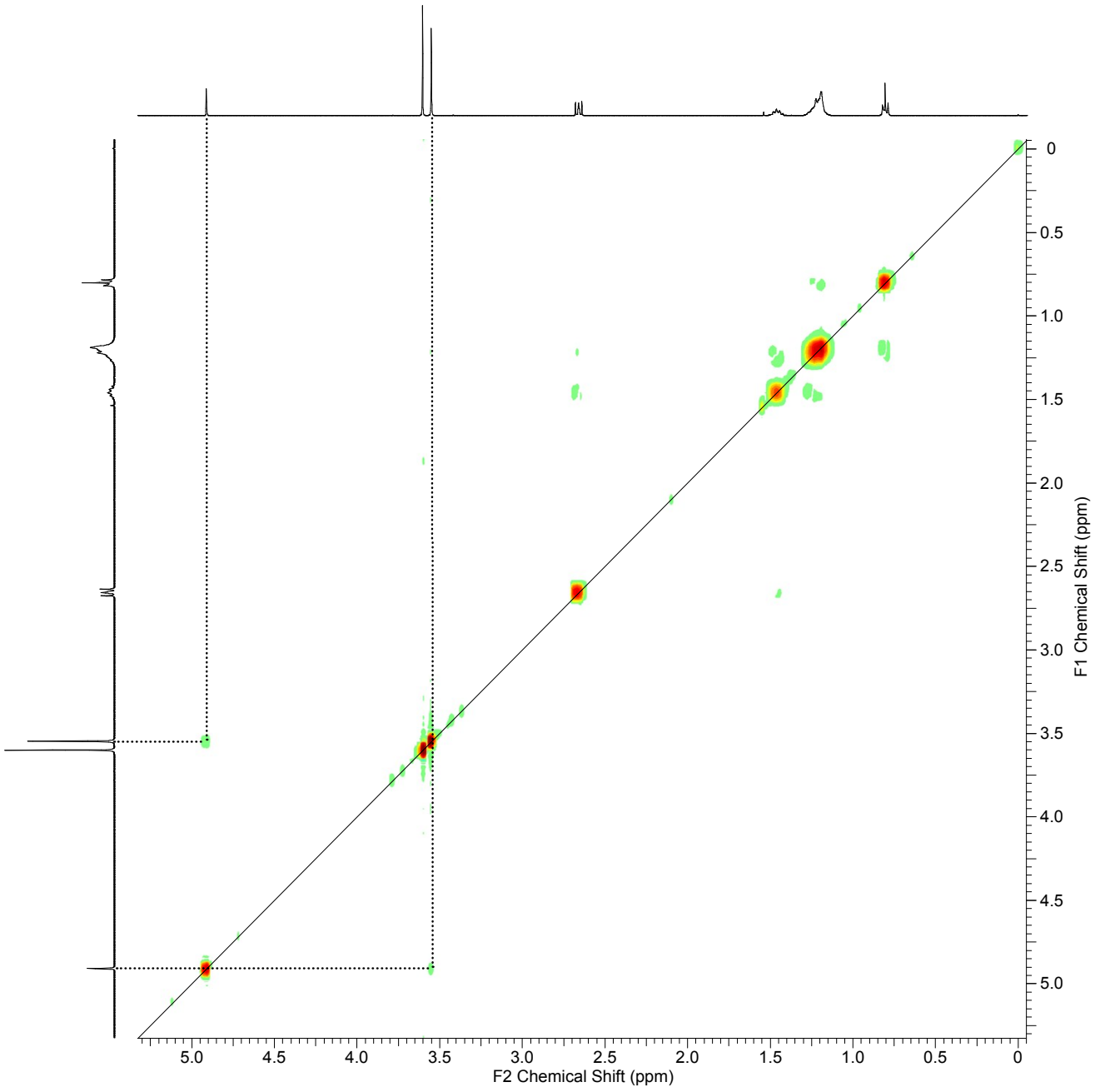


(*E*)-methyl 3-methoxyundec-2-enoate (3oa)

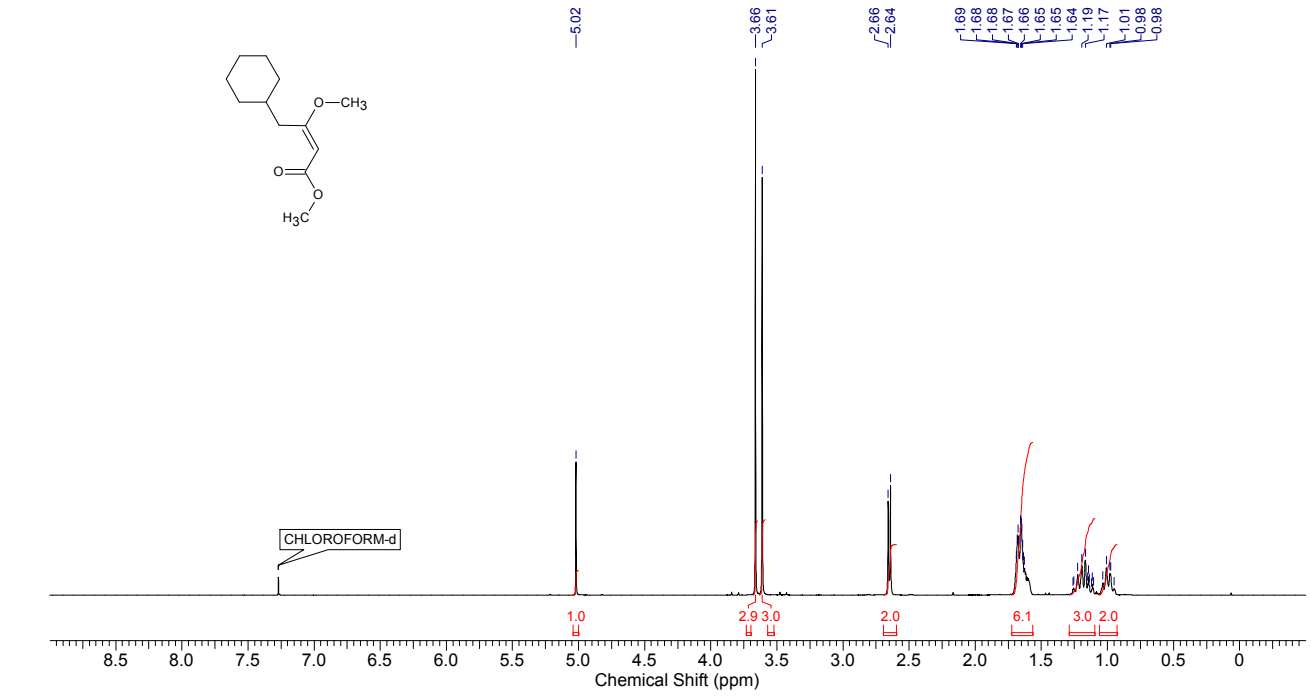


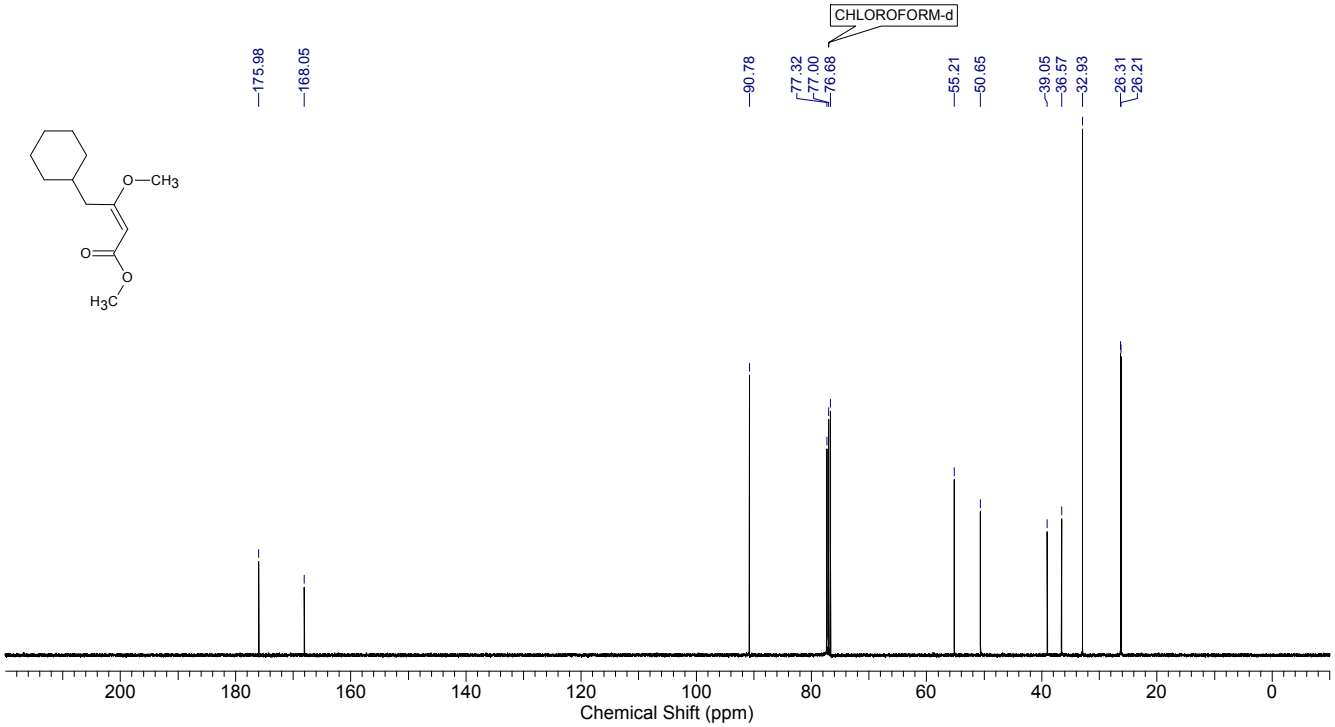


NOE Experiment

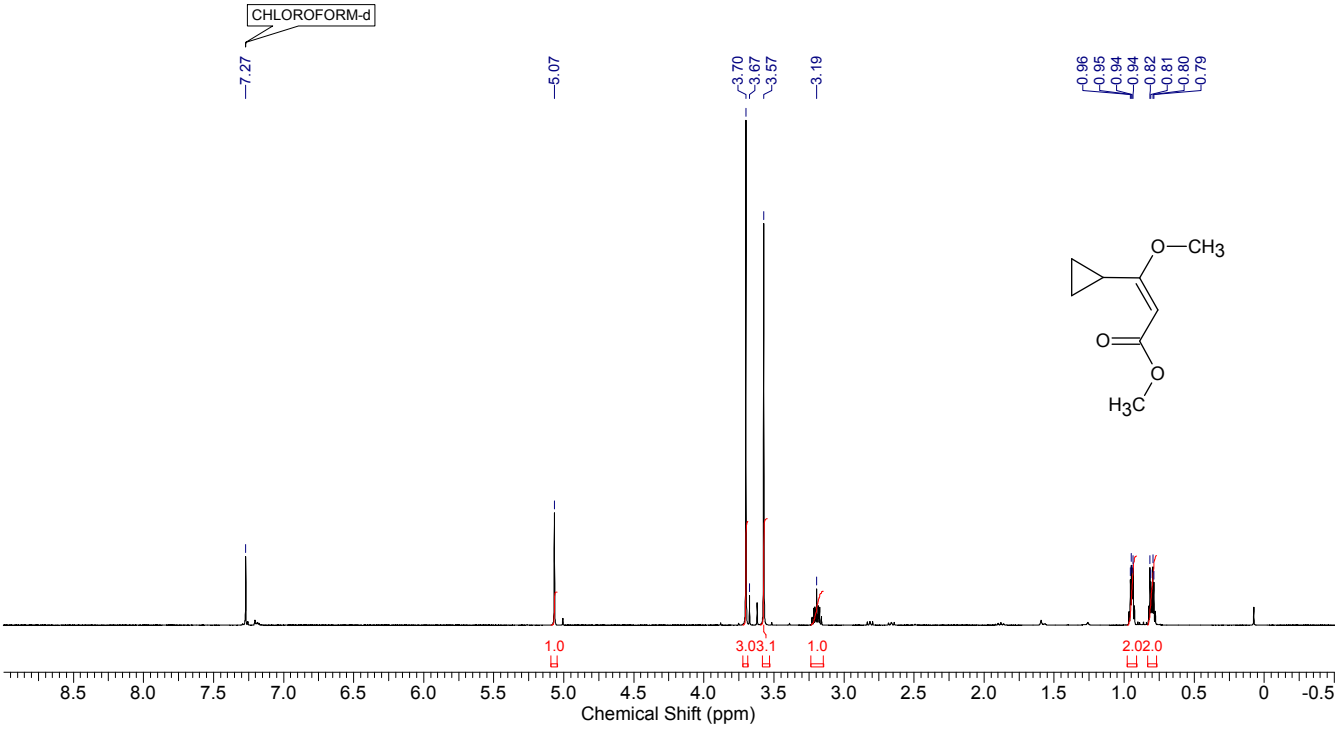


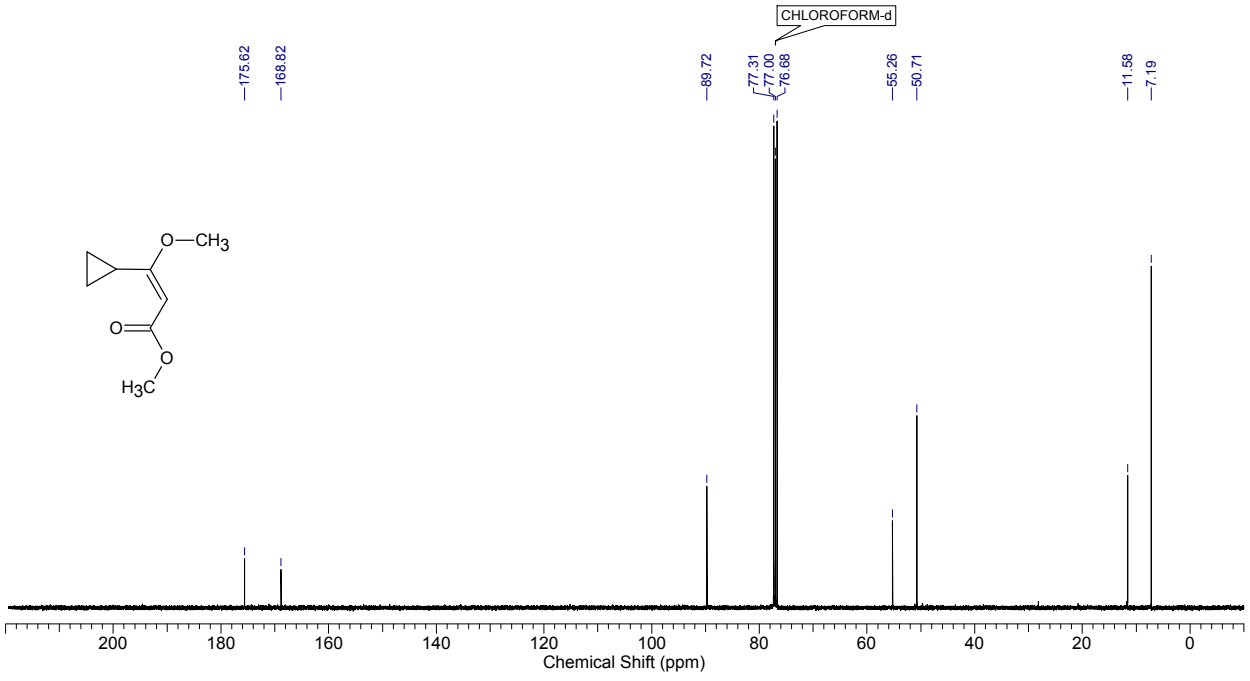
(*E*)-methyl 4-cyclohexyl-3-methoxybut-2-enoate (3pa)



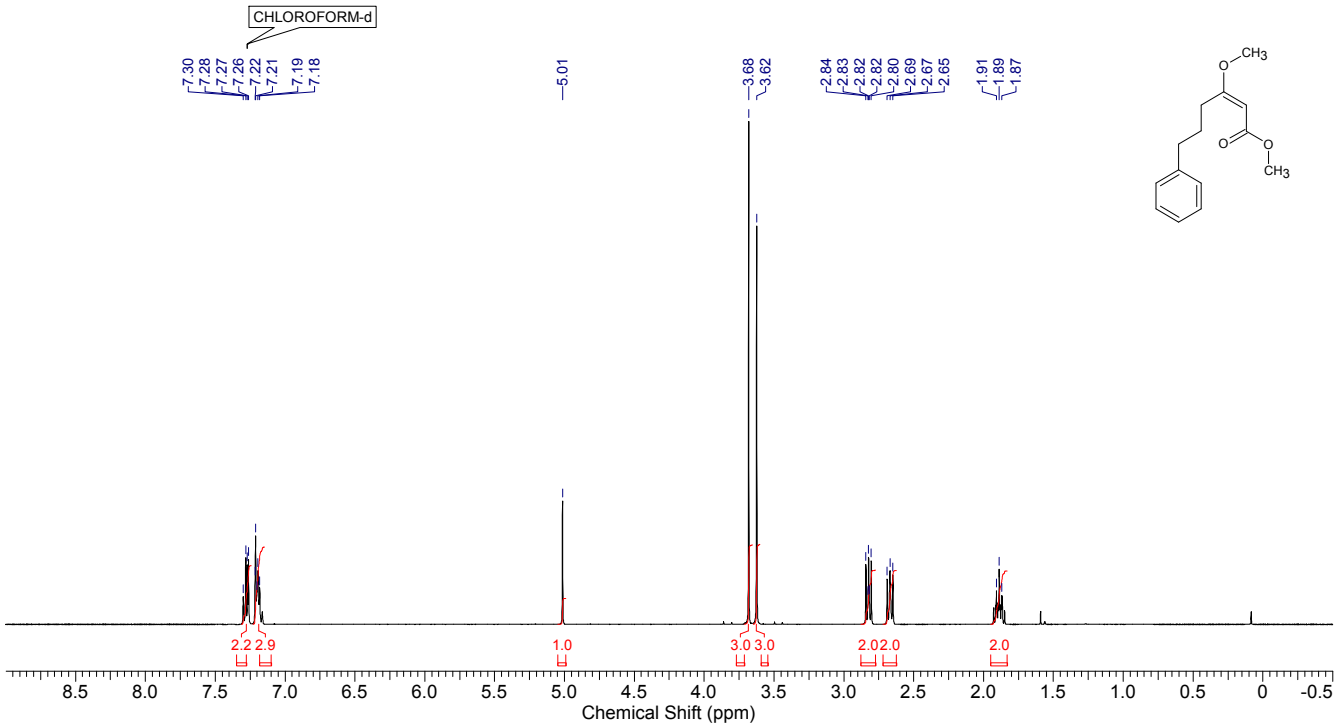


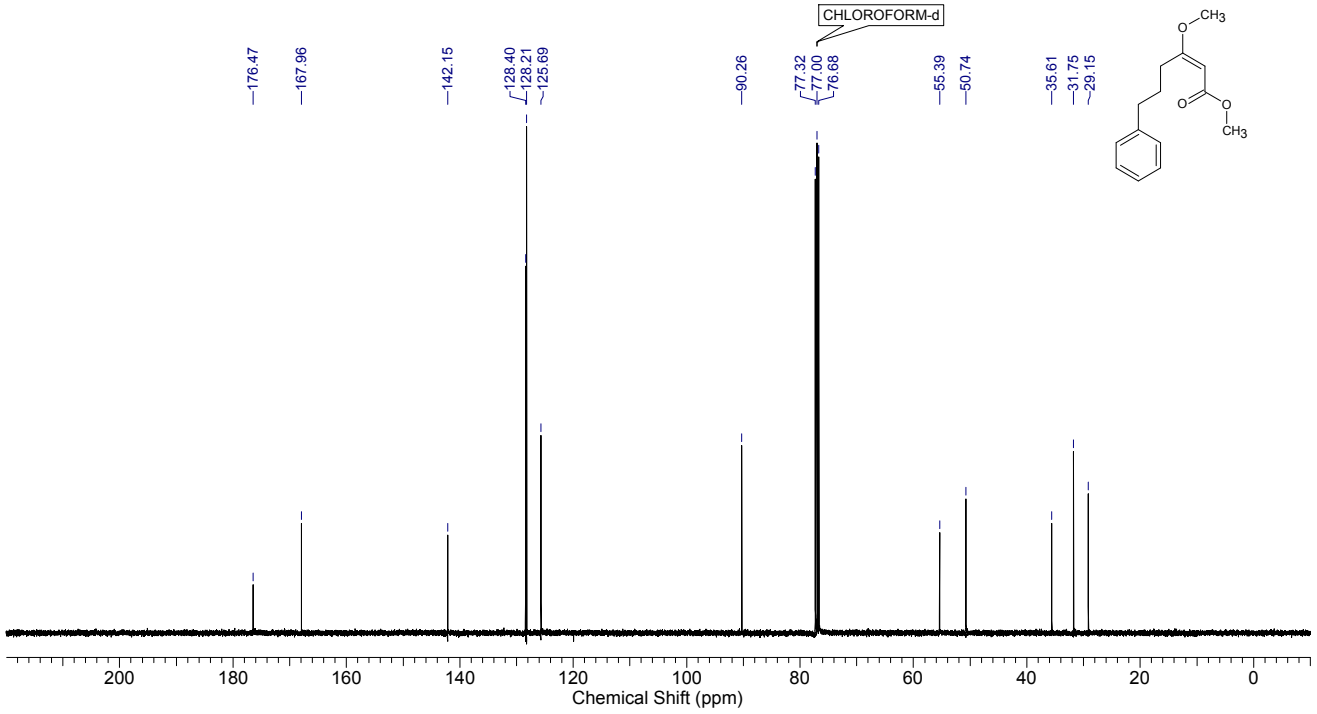
(*E*)-methyl 3-cyclopropyl-3-methoxyprop-2-enoate (3qa)



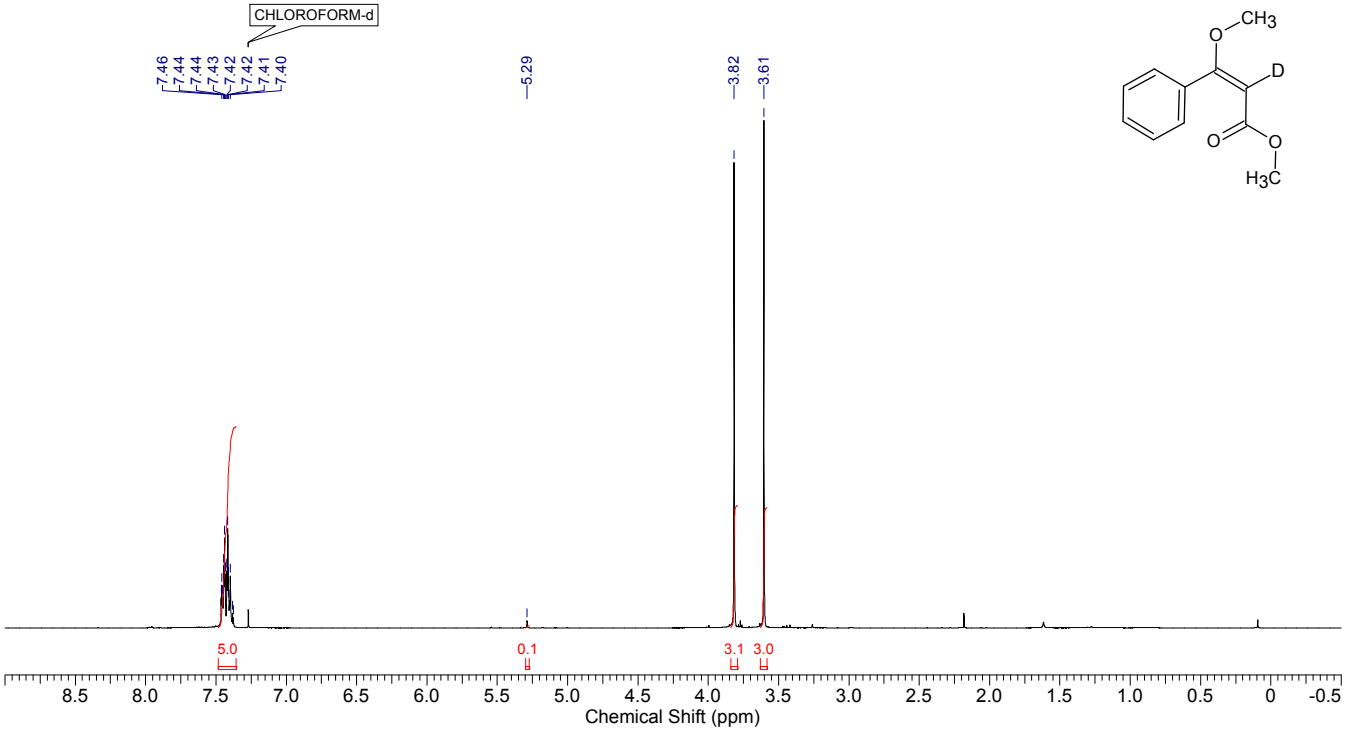


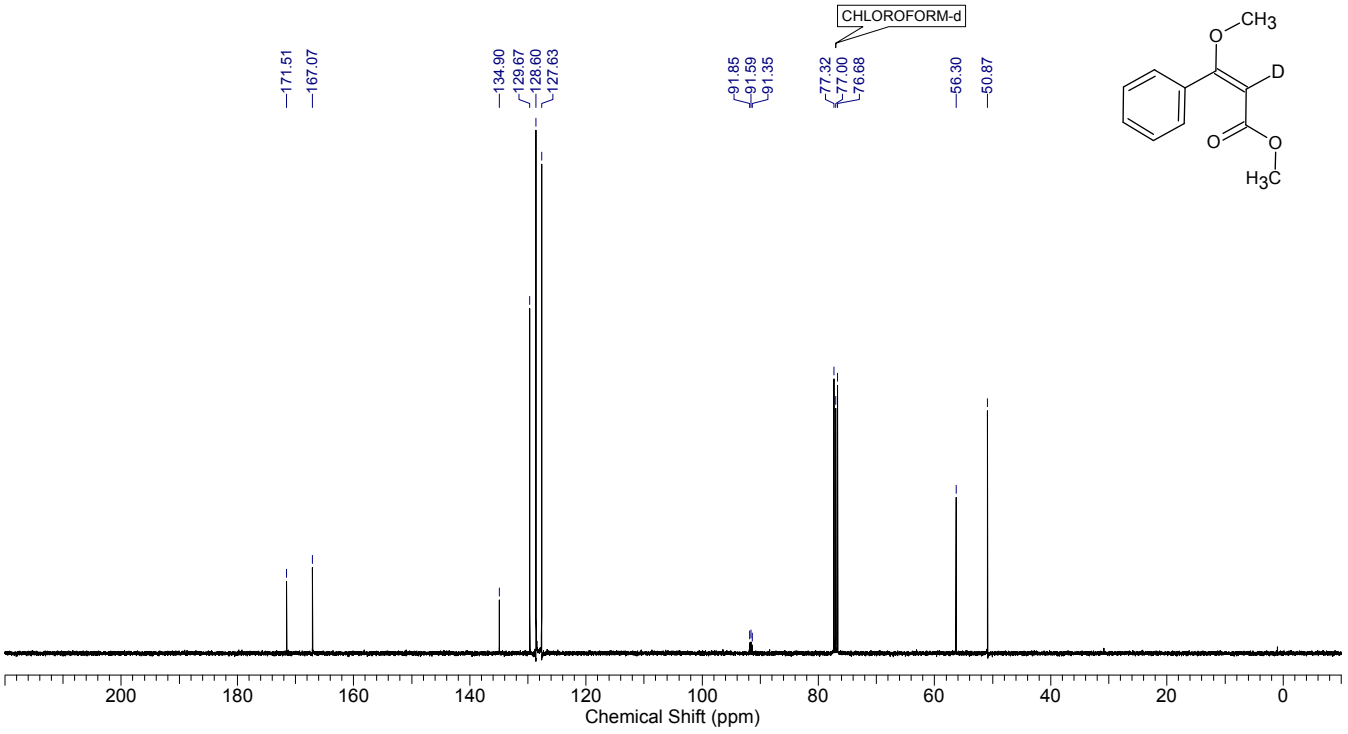
(*E*)-methyl 3-methoxy-6-phenylhex-2-enoate (3ra)





(*E*)-methyl 3-methoxy-3-phenyl(^{2}H)prop-2-enoate (3aa-d_1)





References

[1] F. Pünner and G. Hilt, *Chem. Commun.*, 2012, **48**, 3617–3619.

[2] L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *Chem. Eur. J.,* 2012, **18**, 2931-2937.