Supporting Information

Electrocatalyzed Direct Arene Alkenylations without Directing Groups: Selective Late-Stage Drug Diversification

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General Remarks

Catalytic reactions were carried out in a divided electrochemical cell using pre-dried glassware, if not noted otherwise. Arenes **1**, drug **51**, acrylates **2**, and ligands (**L1-L3**, **L5-L8**, **L13-35**) were used as obtained by commercial sources, **L4** was prepared following the procedure described in the literature,[1] acrylates **2m** and **2n** were synthesized according to known methods,[2,3] drug derivatives **51b**, **51d**, **51e**, **51g**, **51h**, **51j-51m** were synthesized according to previous literature.[4-7] Other chemicals were obtained from commercial sources and were used without further purification. Platinum electrodes (10 mm × 15 mm × 0.25 mm, 99.9%; obtained from ChemPur® Karlsruhe, Germany) and Graphite felt (GF) electrodes (10 mm × 15 mm × 6 mm, SIGRACELL®GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using a Metrohm MULTI AUTOLAB M204 potentiostat in two-electrode constant current mode. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H-NMR. Chromatography: Merck silica gel 60 (40–63 µm). NMR: Spectra were recorded on a Varian Unity 300, Mercury 300, Inova 500 or Bruker Avance III 300, Bruker Avance III HD 400 and Bruker Avance III HD 500 in the solvent indicated; chemical shifts (δ) are given in ppm relative to the residual solvent peak. All IR spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS- and ESI-MS-spectra were recorded with Finnigan MAT 95, 70 eV and Finnigan LCQ; High resolution mass spectrometry (HRMS) with APEX IV 7T FTICR. M. p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected. LC/MS chromatograms were recorded on an Agilent 1260/1290 Infinity system with an Agilent 6100s Series Single Quad using the ZORBAX SB-C18 column, 5 µm. The flow rate was set to 0.5 mL/min, detection at 270 and 290 nm. The method used is MB_RP_gradACN60to100(default_Method) with acetonitrile (0.5% TFE) as eluent.

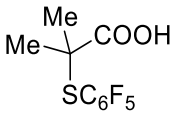
General Procedure A: Non-directed Electrocatalyzed C–H Olefinations

The electrocatalysis was carried out in a pre-dried divided cell, with a GF anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). Arene **1**, or **51** (5.0–20 equiv), acrylates **2** (0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), **L3** (6.5 mg, 20 mol %) or **L12** (7.9 mg, 20 mol %), 1,4-benzoquinone (4.3 mg, 20 mol %) and NaOAc (66.0 mg, 4.0 equiv) were placed in the anodic chamber and dissolved in AcOH (2.6 mL) and HFIP (1.3 mL). 1,4-Benzoquinone (4.3 mg, 20 mol %) and NaOAc (66.0 mg, 4.0 equiv) were placed in the cathodic chamber and dissolved in AcOH (2.6 mL) and HFIP (1.3 mL). Electrocatalysis was performed at 60 °C with a constant current of 1.0 mA and a stirring rate of 500 rpm maintained for 20 h. At ambient temperature, the reaction mixture was diluted with EtOAc (5.0 mL). The GF anode was washed with EtOAc (3 × 10 mL) in an ultrasonic bath and the washings were added to the reaction mixture. The resulting mixture was loaded in a column chromatography with a pad of silica and washed with 50 mL EtOAc. The combined solvents were removed *in vacuo*. The NMR yield was determined by adding CH_2Br_2 (14.0 µL, 0.20 mmol, 1.0 equiv) as internal standard. The crude mixture was purified by flash column chromatography on silica gel to yield the products **3-65**. The isomer ratios were measured by ^{1}H-NMR of both crude mixtures and product mixtures. If the two ratios are same, we used the one from the product mixture; otherwise, we used the one from the crude mixture.

General Procedure B: Non-directed Electrocatalyzed C–H Olefinations

The electrocatalysis was carried out in a pre-dried divided cell, with a GF anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). Arene **1**, or **51** (5.0 – 20 equiv), acrylates **2** (0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), **L3** (6.5 mg, 20 mol %) or **L12** (7.9 mg, 20 mol %), 1,4-benzoquinone (4.3 mg, 20 mol %) and NaOAc (66.0 mg, 4.0 equiv) were placed in the anodic chamber and dissolved in AcOH (2.6 mL) and HFIP (1.3 mL). 1,4-Benzoquinone (4.3 mg, 20 mol %) and NaOAc (66.0 mg, 4.0 equiv) were placed in the cathodic chamber and dissolved in AcOH (2.6 mL) and HFIP (1.3 mL). Electrocatalysis was performed at 60 °C with a constant current of 1.0 mA and a stirring rate of 500 rpm maintained for 20 h. At ambient temperature, the GF anode was washed with EtOAc (3 × 10 mL) in an ultrasonic bath and the washings were added to the reaction mixture. The solvents were removed *in vacuo*. The residues were added sat. $NaHCO_3$ (30 mL), extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The NMR yield was determined by adding CH_2Br_2 (14.0 µL, 0.20 mmol, 1.0 equiv) as internal standard. The crude mixture was purified by flash column chromatography on silica gel to yield the products **3-65**. The isomer ratios were checked by ^{1}H-NMR of both crude mixtures and product mixtures. If the two ratios are same, we used the one from the product mixture; otherwise, we used the one from the crude mixture.

Syntheses of Ligands



2-Methyl-2-[(perfluorophenyl)thio]propanoic acid (L11)

2-Methyl-2-[(perfluorophenyl)thio]propanoic acid (**L11**) was prepared following the procedure described in the literature.[8] 2,3,4,5,6-Pentafluorothiophenol (1.33 mL, 10 mmol, 1.0 equiv) was added to a mixture of 2-bromo-2-methylpropionic acid (1.68 g, 10 mmol, 1.0 equiv) and NaOH (1.0 g, 20 mmol, 2.0 equiv) in *t*-BuOH (30 mL) and H_2O (5.0 mL) at room temperature. Then the reaction mixture was refluxed overnight. At ambient temperature, the reaction mixture was concentrated in *vacuo*. The resulting pale, yellow crude mixture was acidified with 2M HCl solution. The aqueous layer was extracted with Et_2O (3 x 100 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. Then, the mixture was filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel using *n*-hexane/EtOAc (100:1 to 10:1) as an eluent provided **L11** as white crystals solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.76 (brs, 1H), 1.55 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 179.3 (C_q), 150.2 (dq, *J* = 10.7, 3.7 Hz), 147.7 (dq, *J* = 10.9, 3.8 Hz), 144.2 (tt, *J* = 13.6, 5.2 Hz, C_q), 141.6 (tt, *J* = 13.6, 5.2 Hz, C_q), 139.4 – 138.4 (m, C_q), 137.0 – 135.9 (m, C_q), 51.7 (C_q), 24.7 (CH_3). ^{19}F-NMR (377 MHz, $CDCl_3$): δ = -128.9 – -129.4 (m, 2F), -148.6 (tt, *J* = 20.8, 4.0 Hz, 1F), -160.5 – -161.0 (m, 2F). IR (ATR): 2919, 2633, 2534, 1710, 1447, 1281, 1092, 979, 861, 547 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 285 $[M - H]^-$. HR-MS (ESI): *m*/*z* calcd. for $[C_{13}H_{16}O_2 - H]^-$ 285.0014, found 285.0005.

Other *S,O*-ligands (**L9, L10, L12, L36**) were prepared following a modified procedure adapted from previous literature synthesis.[8] 15% water was used as co-solvent along with *t*-BuOH or EtOH.

Reaction set-up

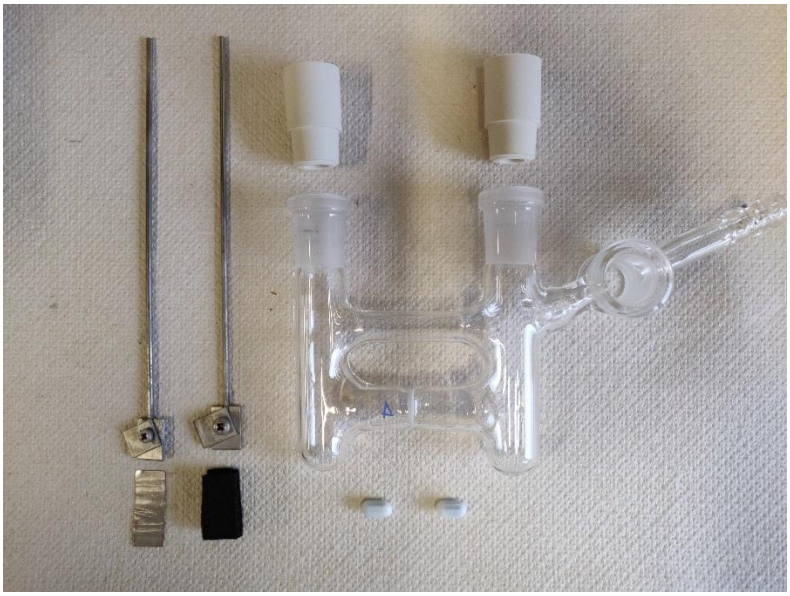


Figure S1 Divided cell

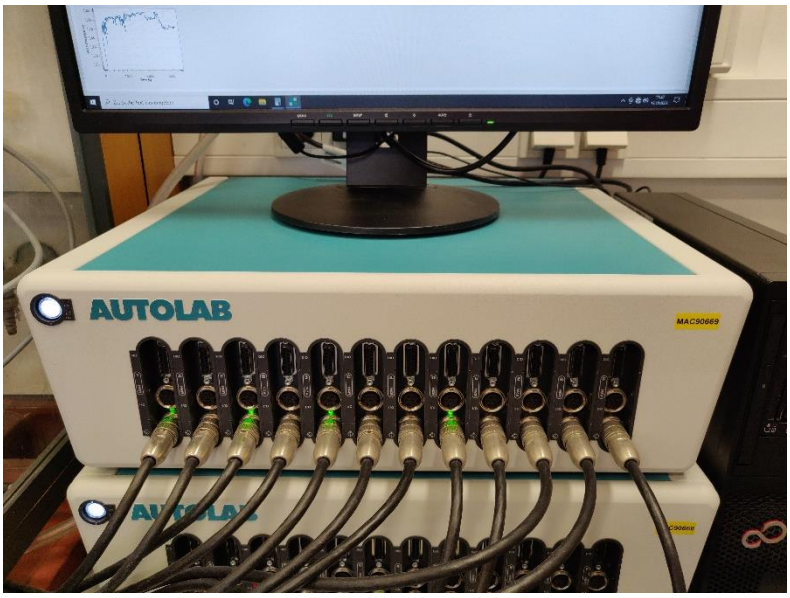
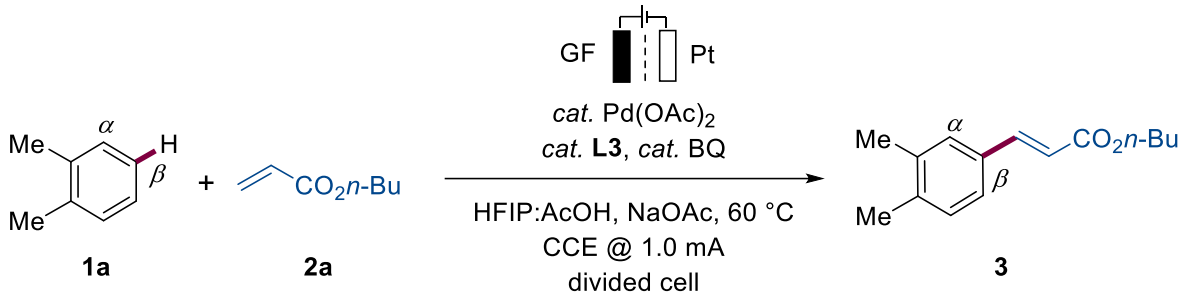


Figure S2 Metrohm MULTI AUTOLAB M204 potentiostat S1

Figure S3 ROHDE & SCHWARZ HMP4040 Potentiostat S2

Optimization Studies

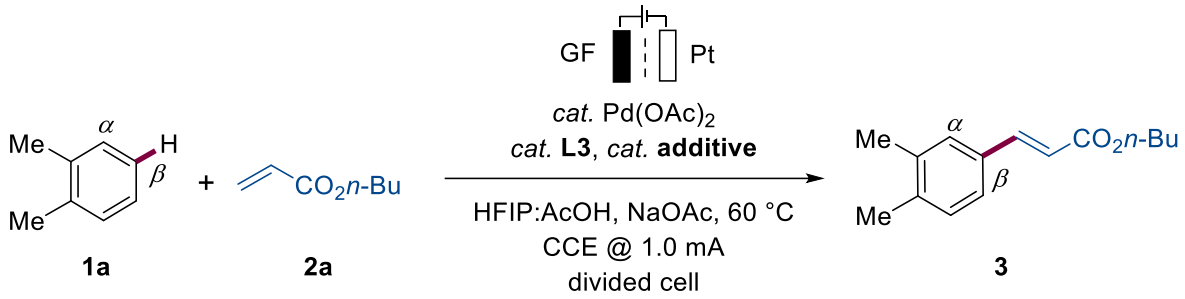
Table S1 Optimization of the non-directed electrocatalyzed C–H olefination



Entry	Deviation from standard condition	Yield [%]	*α*:*β*
1	None	69[a]	1:6
2	No electricity	27	1:7
3	No BQ	37[b]	1:8
4	No BQ in cathodic cell	45	1:6
5	No $Pd(OAc)_2$	---[b,d]	---
6	No NaOPiv	11[b,d]	1:6
7	Undivided cell	<5[b,c,d]	---
8	No ligand	36[c]	1:4
9	Under N_2	38[c]	1:12
10	BQ (1.0 equiv) without electricity, under N_2	8[c]	---
11	10 mol % BQ instead of 20 mol % BQ	59[c]	1:5

Reaction conditions: divided cell, anodic chamber: **1a** (4.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L3** (20 mol %), NaOPiv (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL), cathodic chamber: NaOPiv (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 20 h, graphite felt (GF) anode, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard. [a] Isolated yield. [b] No BQ. [c] NaOAc (4.0 equiv). [d] HFIP:AcOH (2.0 mL:2.0 mL).

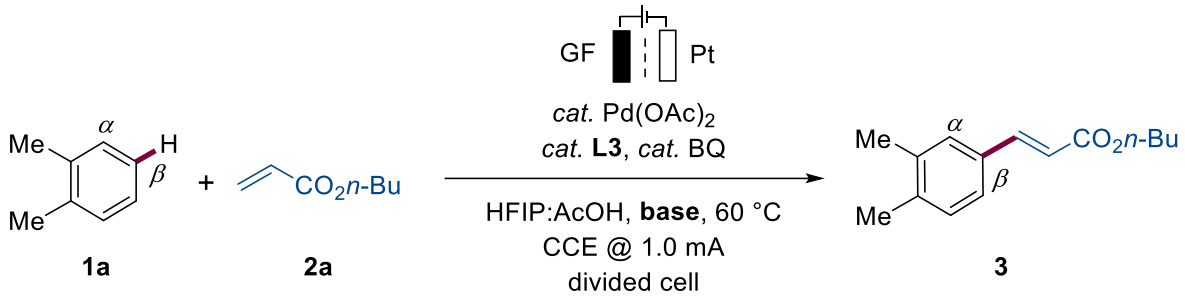
Table S2 Additive screening



Entry	Additive	Yield	*α:β*
1	None	37%	1:8
2	**1,4-benzoquinone**	**45%**	**1:6**
3	TBAI	<5%	---
4	Ferrocene	15%	1:8
5	2,5-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione	33%	1:6

Reaction conditions: divided cell, anodic chamber: **1a** (4.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L3** (20 mol %), NaOPiv (4.0 equiv), additive (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL), cathodic chamber: NaOPiv (4.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 20 h, graphite felt (GF) anode, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard.

Table S3 Base screening

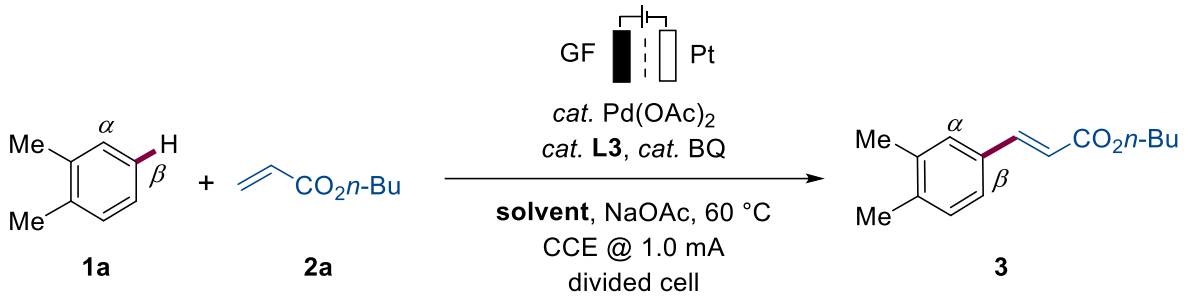


1a **2a** **3**

Entry	Base	Yield [%]	*α:β*
1	NaOPiv	76	1:6
2	**NaOAc**	**73**	**1:7**
3	KOAc	51	1:7
4	LiOAc	40	1:7
5	*n*-Bu_4NOAc	25	1:5

Reaction conditions: divided cell, anodic chamber: **1a** (4.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L3** (20 mol %), BQ (20 mol %), base (4.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL); cathodic chamber: BQ (20 mol %), base (4.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 20 h, graphite felt (GF) anode, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard.

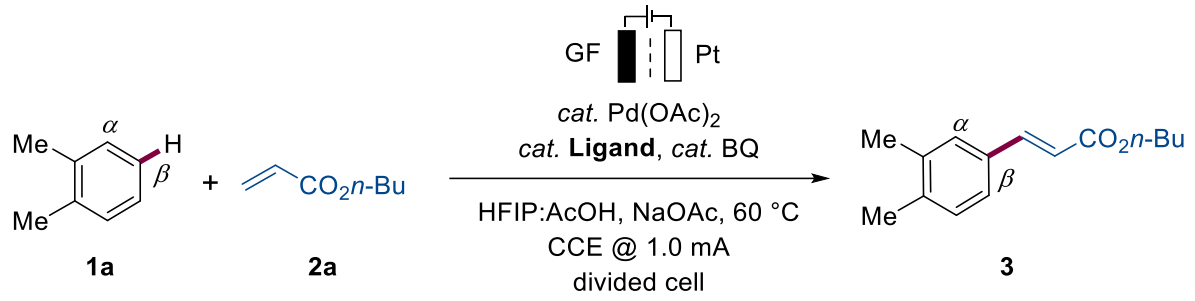
Table S4 Solvent screening

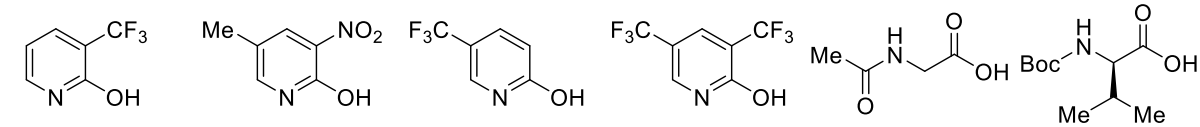


Entry	Solvent	Yield [%]	*α:β*
1	HFIP:AcOH (1:1)	63	1:8
2	**HFIP:AcOH (1:2)**	**76**	**1:6**
3	HFIP:AcOH (1:3)	60	1:6
4	HFIP:AcOH (1:4)	60	1:6
5	NMP:AcOH (1:2)	<5	---

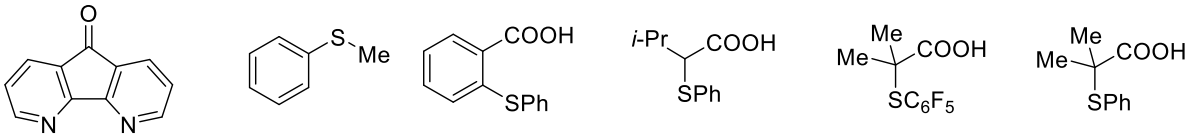
Reaction conditions: divided cell, anodic chamber: **1a** (4.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L3** (20 mol %), NaOPiv (4.0 equiv), BQ (20 mol %), solvent (4 mL); cathodic chamber: NaOPiv (4.0 equiv), BQ (20 mol %), solvent (4 mL), 60 °C, constant current at 1.0 mA, 20 h, graphite felt (GF) anode, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard.

Table S5 Ligand screening

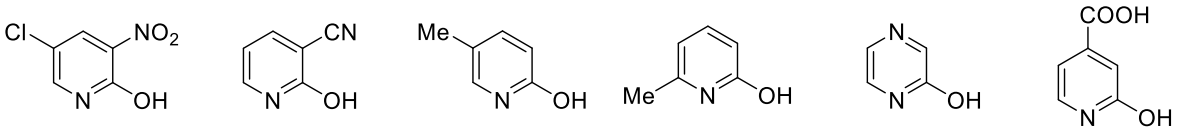




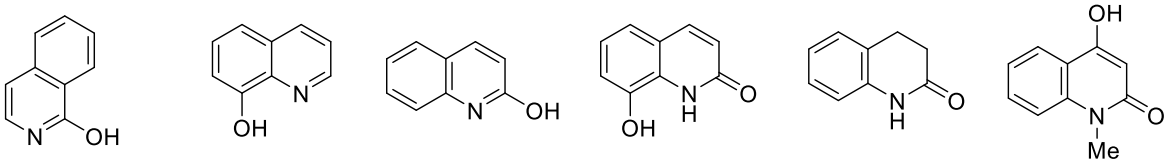
L1 28% (1:8) | **L2** 69% (1:13) | **L3** 73% (1:7) | **L4** 40% (1:7) | **L5** 37% (1:5) | **L6** 36% (1:5)



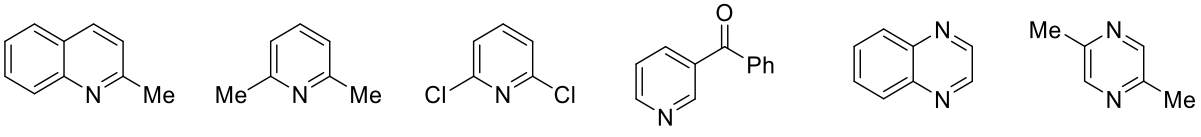
L7 15% (1:1.5) | **L8** 25% (1:4) | **L9** 63% (1:2) | **L10** 30% (1:2.3) | **L11** 72% (1:2.2) | **L12** 99% (1:1.6)



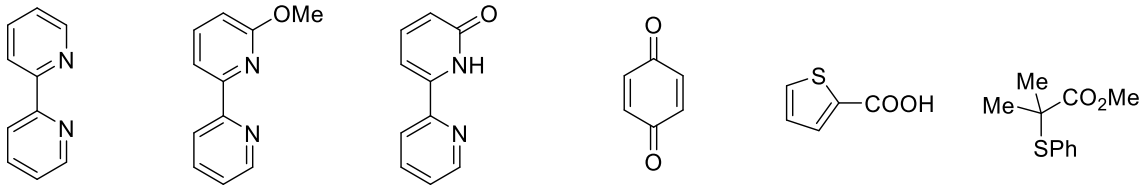
L13 47% (1:5) | **L14** 32% (1:6) | **L15** 32% (1:5) | **L16** 36% (1:5) | **L17** trace | **L18** 32% (1:10)



L19 26% (1:8) | **L20** trace | **L21** 51% (1:7) | **L22** 25% (1:8) | **L23** 52% (1:5) | **L24** 55% (1:6)



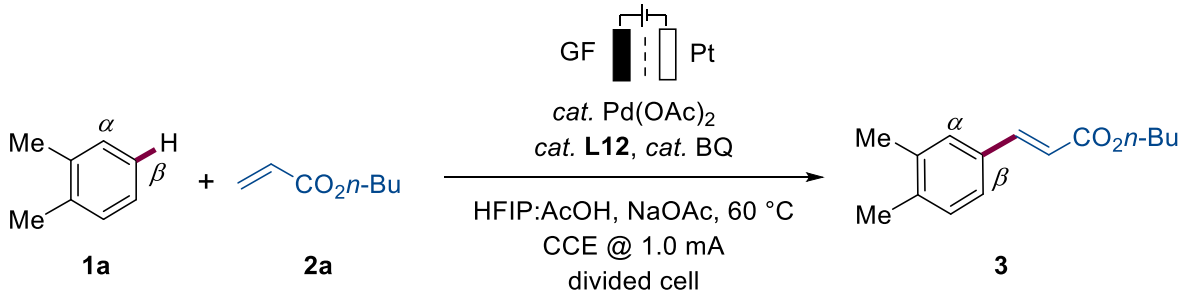
L25 44% (1:7) | **L26** 40% (1:9) | **L27** 44% (1:7) | **L28** 7% (1:6) | **L29** trace | **L30** 4% (1:10)



L31 n.r. | **L32** n.r. | **L33** n.r. | **L34** 36% (1:4)[a] | **L35** 47% (1:5) | **L36** 25% (1:1.8)

Reaction conditions: divided cell, anodic chamber: **1a** (4.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **Ligand** (20 mol %), NaOAc (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL), cathodic chamber: NaOAc (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 20 h, graphite felt (GF) anode, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard. α/β selectivities are given in the parentheses. [a] Without additional ligand.

Table S6 Different potentiostat

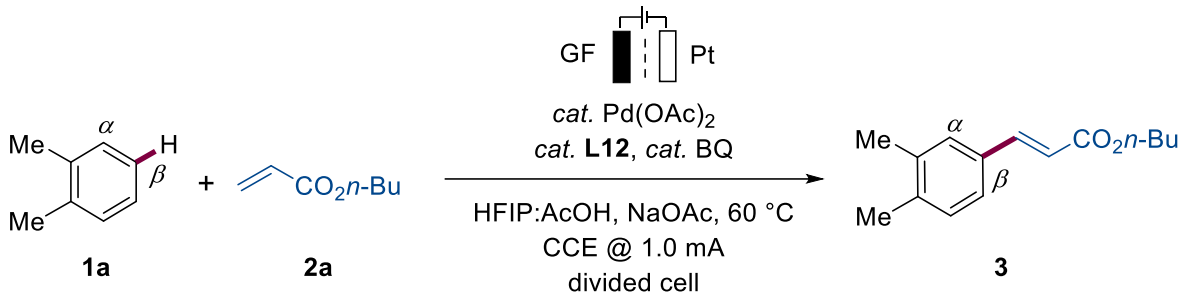


1a + **2a** → **3**

Entry	Potentiostat	Yield [%]	*α:β*
1	**S1**	**89**	**1:2**
2	**S2**	82	1:2

Reaction conditions: divided cell, anodic chamber: **1a** (1.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L12** (20 mol %), BQ (20 mol %), NaOAc (4.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL); cathodic chamber: BQ (20 mol %), NaOAc (4.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 20 h, graphite felt (GF) anode, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard.

Table S7 Supplemental control experiments deviated from standard condition



Entry	Deviations from standard condition	Yield [%]	*α:β*
1	**none**	**88**[a]	**1:2**
2	40 °C	5[b]	1:2
3	2.0 eq **1a**	35	1:2
4	2.0 eq **1a**	58[a,c]	1:2
5	2.5 eq **1a**	66[a,d]	1:2
6	No electricity	30%[b]	1:2

Reaction conditions: divided cell, anodic chamber: **1a** (1.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L12** (20 mol %), BQ (20 mol %), NaOAc (4.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL); cathodic chamber: BQ (20 mol %), NaOAc (4.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 20 h, graphite felt (GF) anode, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard. [a] isolated yield; [b] 20 eq. **1a**; [c] 100 °C; [d] anodic chamber: **1a** (1.0 mmol), **2a** (0.40 mmol), [Pd] (5 mol %), **L12** (10 mol %), BQ (10 mol %), NaOAc (2.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL); cathodic chamber: BQ (10 mol %), NaOAc (2.0 equiv), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 40 h. Entry 5 Emphasized the importance of **1a** concentration.

Cyclic voltammetric studies

CV measurements were conducted with a Metrohm Autolab PGSTAT204 potentiostat and Nova 2.1 software. A glassy carbon or platinum working electrode (disk, diameter: 3 mm), a coiled platinum wire counter electrode and a saturated calomel (SCE) reference electrode were employed. The voltammograms were recorded at room temperature in HFIP:AcOH (1.3 mL:2.6 mL) with 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte. The scan rate is 100 mV/s. Deviations from the general experimental conditions are indicated in the respective figures and descriptions.

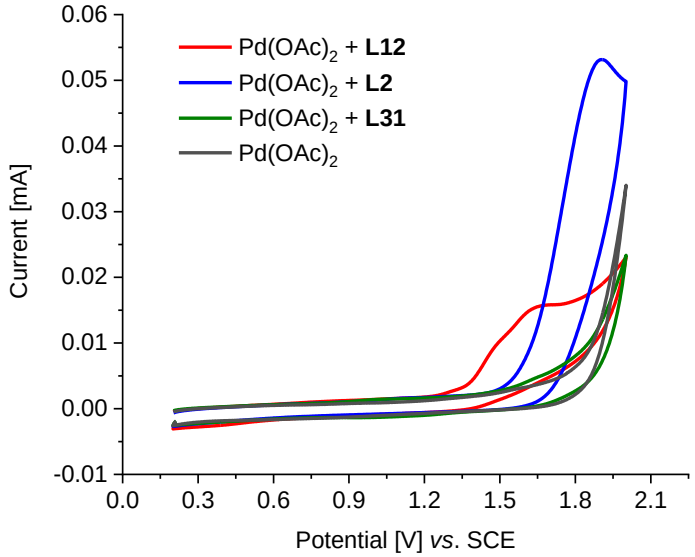


Figure S4 Cyclic voltammograms in HFIP:AcOH (1.3 mL:2.6 mL) with nBu$_4$NPF$_6$ (0.1 M) at 100 mV/s, Pd(OAc)$_2$ (5.0 mM), ligand (10 mM); the catalyst and ligand mixtures were pre-stirred overnight before CV measurement.

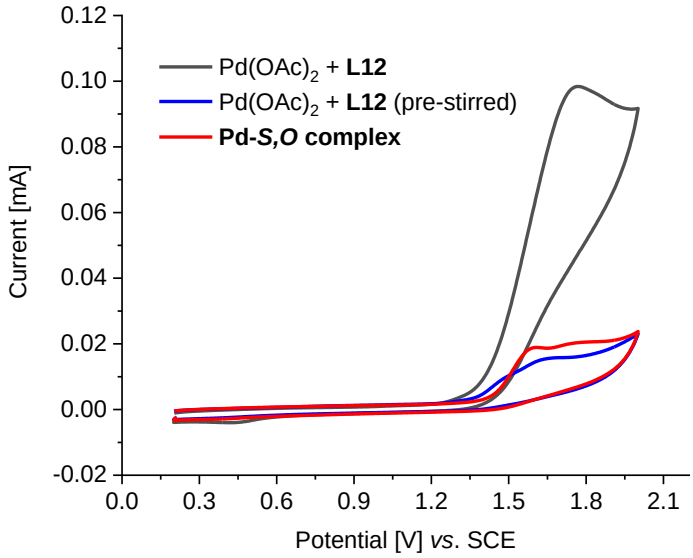
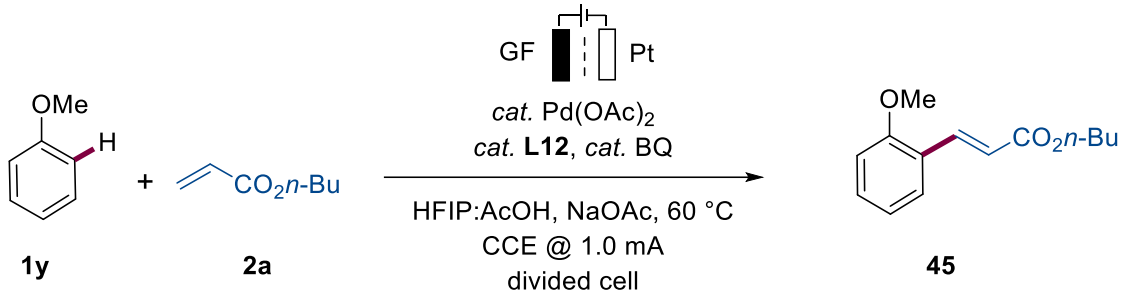


Figure S5 Cyclic voltammograms in HFIP:AcOH (1.3 mL:2.6 mL) with nBu$_4$NPF$_6$ (0.1 M) at 100 mV/s, Pd(OAc)$_2$ (5.0 mM), **L12** (10 mM), **Pd-*S,O* complex** (1.5 mM); the catalyst and ligand mixtures were pre-stirred overnight before CV measurement.

Mechanistic Investigation for High Site-selectivity

Table S8 Control experiment

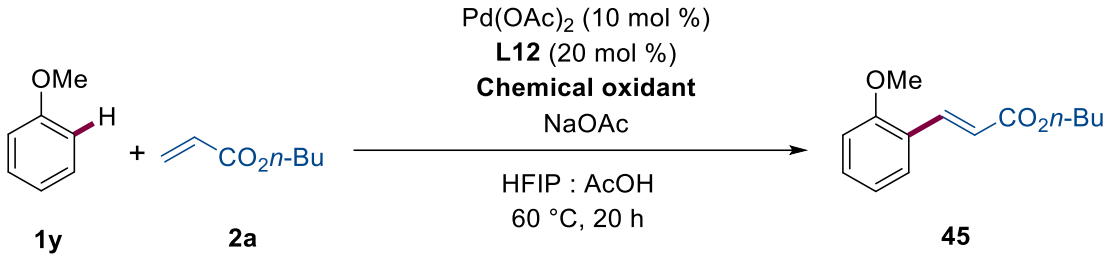


1y **2a** **45**

Entry	Deviations from standard condition	Yield [%]	*ortho*:*para*
1	None	52[a]	14:1
2	No electricity	37	2.6:1
3	Under N_2	54	2.6:1
4	No ligand	8	1:1
5	No BQ	56	11:1

Reaction conditions: divided cell, anodic chamber: **1y** (1.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L12** (20 mol %), NaOAc (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL); cathodic chamber: NaOAc (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 20 h, graphite felt (GF) anode, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard. [a] Isolated yield.

Table S9 Chemical oxidant

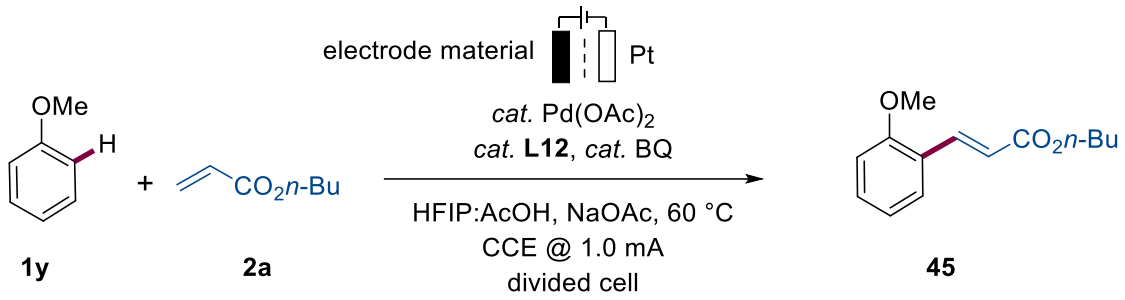


1y **2a** **45**

Entry	Oxidant	Amount	Yield [%]	*ortho*:*para*
1	*t*-BuCO$_3$Ph	1.0 equiv	59	2.5:1
2	BQ	1.0 equiv	47	2.1:1
3	AgOAc	2.0 equiv	74	2.7:1
4	O_2 (1 atm.)	---	30	2.3:1
5	$K_2S_2O_8$	1.0 equiv	22	2.7:1
6	PIDA	1.0 equiv	24	3:1

An oven-dried 10 mL Schlenk tube was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol %), **L12** (7.9 mg, 0.04 mmol, 20 mol %), NaOAc (66.0 mg, 0.8 mmol, 4.0 equiv), anisole **1y** (109.0 µL, 1 mmol, 5.0 equiv), *n*-butyl acrylate **2a** (28.8 µL, 0.2 mmol, 1.0 equiv), the corresponding oxidant, HFIP:AcOH (1.3 mL:2.6 mL). The tube was sealed with a septum and the reaction was placed in a 60 °C oil bath for 20 h. The mixture was filtered through a short pad of silica column and eluent with EtOAc (50 mL), the solvent was removed under reduced pressure. Yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard. PIDA = (Diacetoxyiodo)benzene.

Table S10 Effects of anode material

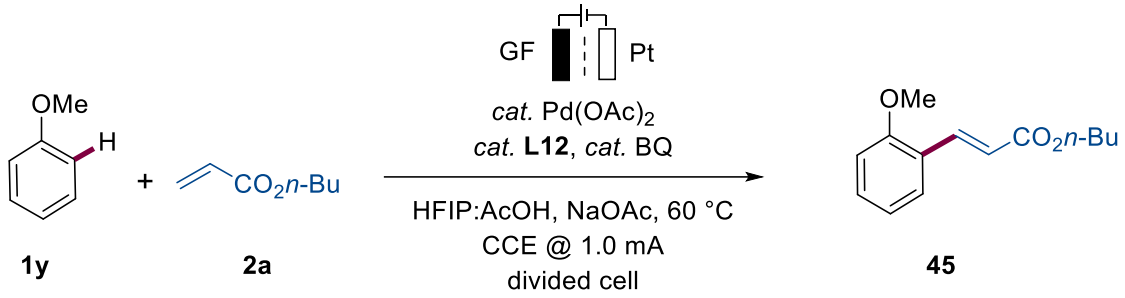


1y **2a** **45**

Entry	Anode material	Yield [%]	*ortho*:*para*
1	Carbon felt	52[a]	14:1
2	Glass carbon	66	7:1
3	BDD	49	16:1
4	RVC	49	14:1
5	Graphite rod	37	17:1
6	Pt	75	2.6:1
7	Ni foam	25	2.1:1
8	Stainless steel	5	2.0:1

Reaction conditions: divided cell, anodic chamber: **1y** (1.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L12** (20 mol %), NaOAc (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL); cathodic chamber: NaOAc (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, 20 h, Pt-plate cathode. Without special note, yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard. [a] Isolated yield. SS = Stainless steel. GC = Glass carbon. RVC = Reticulated vitreous carbon. GF = Graphite felt. BDD = Boron doped diamond. GR = Graphite rod.

Table S11 Variation of Selectivity and yield over time



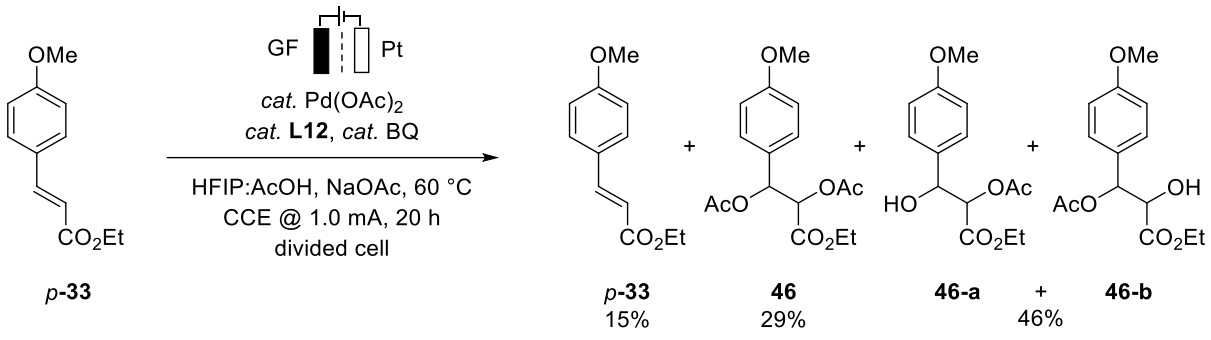
1y **2a** **45**

Entry	Time (h)	Yield [%]	*ortho*-Isomer [%]	*para*-Isomer [%]	*ortho*:*para*
1	2	33	23	10	2.3:1
2	4	50	36	14	2.5:1
3	6	59	42	17	2.4:1
4	8	66	46	20	2.1:1
5	10	74	54	20	2.7:1
6	12	87	62	25	2.5:1
7	14	74	59	15	4:1
8	16	68	68	8	7.5:1
9	20	66	62	4	14:1

Reaction conditions: divided cell, anodic chamber: **1y** (1.0 mmol), **2a** (0.20 mmol), [Pd] (10 mol %), **L12** (20 mol %), NaOAc (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL); cathodic chamber: NaOAc (4.0 equiv), BQ (20 mol %), HFIP:AcOH (1.3 mL:2.6 mL), 60 °C, constant current at 1.0 mA, graphite felt (GF) anode, Pt-plate cathode. Yields and isomer ratios were determined by crude ^{1}H-NMR by using CH_2Br_2 as internal standard.

Two-fold electrochemical oxidation

The experiment was carried out in a pre-dried divided cell, with a GF anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). (*E*)-Ethyl 3-(4-methoxyphenyl) acrylate **33** or **45** (0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), **L12** (20 mol %), 1,4-benzoquinone (4.3 mg, 20 mol %) and NaOAc (66.0 mg, 4.0 equiv) were placed in the anodic chamber and dissolved in AcOH (2.6 mL) and HFIP (1.3 mL); 1,4-benzoquinone (4.3 mg, 20 mol %) and NaOAc (66.0 mg, 4.0 equiv) were placed in the cathodic chamber and dissolved in AcOH (2.6 mL) and HFIP (1.3 mL). Electrocatalysis was performed at 60 °C at a constant current of 1.0 mA and a stirring rate of 500 rpm was maintained for 20 h. At ambient temperature, the GF anode was washed with EtOAc (3 × 10 mL) in an ultrasonic bath and the washings were added to the reaction mixture. The solvents were removed *in vacuo*. The residue was added in the sat. $NaHCO_3$ (30 mL), extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Then the crude mixture was dissolved with 4 mL DCM, then added with Et_3N (70 µL, 0.5 mmol, 2.5 equiv), acetyl chloride (18 µL, 0.25 mmol, 1.25 equiv) and stirred at RT for 1 hour. The solvents were removed *in vacuo*. The crude mixture was purified by flash column chromatography (*n*-hexane/EtOAc = 4:1) on silica gel to yield the products.



p-**33** | **46** | **46-a** + **46-b**
15% | 29% | 46%

Figure S6 Second fold oxidation

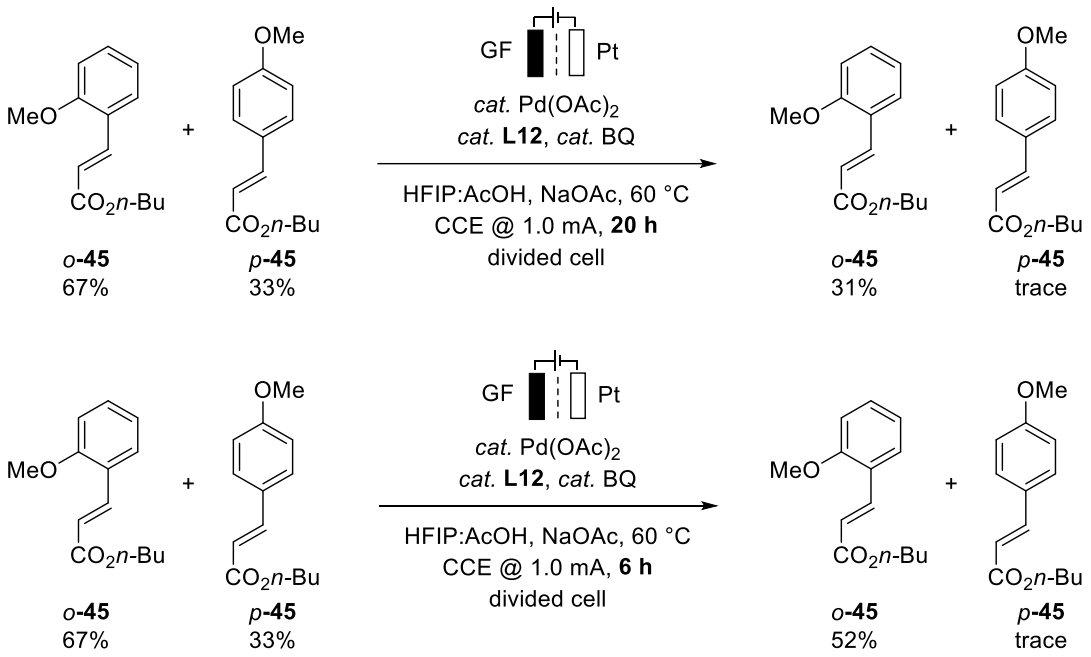
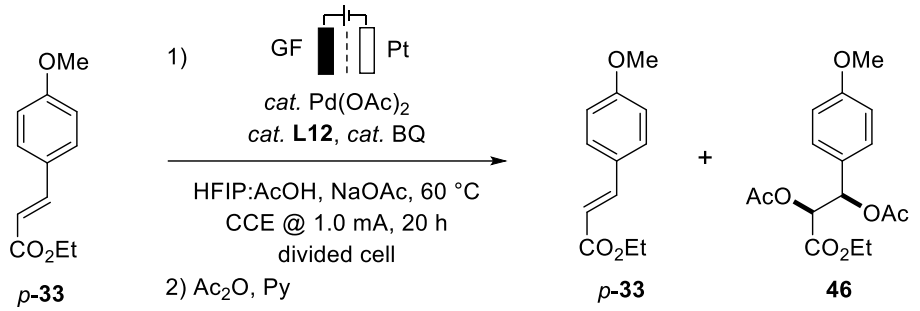


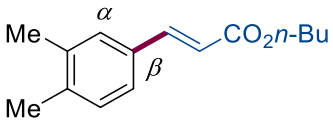
Figure S7 Selective oxidation of *p*-isomer

Table S12 Controlled experiment for second oxidation



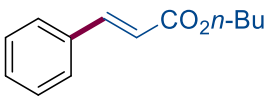
Entry	Deviation from the standard conditions	*p*-**33**	**46**
1	none	8%	67%
2	Pt as anode	24%	65%
3	No electricity	97%	---
4	No $Pd(OAc)_2$	16%	57%

Characterization Data of Products



(*E*)-*n*-Butyl-3-(2,3-dimethylphenyl)acrylate (*α*-3) & (*E*)-*n*-butyl-3-(3,4-dimethylphenyl)acrylate (*β*-3)

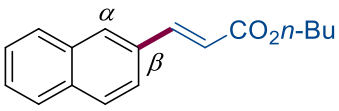
The general procedure **A** was followed using *o*-xylene (**1a**) (120.6 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **3** (40.9 mg, 88%) as a colorless oil. The *α* and *β*-olefinated products are known compounds[9] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *α* : *β* = 1 : 1.6. ^{1}H-NMR (600 MHz, $CDCl_3$): *δ* = 8.03 (d, *J* = 15.8 Hz, 1H$^{\alpha}$), 7.60 (d, *J* = 16.0 Hz, 1H$^{\beta}$), 7.39 – 6.99 (m, 3H$^{\alpha+\beta}$), 6.35 (d, *J* = 16.0 Hz, 1H$^{\beta}$), 6.27 (d, *J* = 15.8 Hz, 1H$^{\alpha}$), 4.25 – 4.10 (m, 2H$^{\alpha+\beta}$), 2.33 – 2.18 (m, 6H$^{\alpha+\beta}$), 1.74 – 1.59 (m, 2H$^{\alpha+\beta}$), 1.48 – 1.35 (m, 2H$^{\alpha+\beta}$), 0.98 – 0.89 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): *δ* = 167.3 (C_q), 167.2 (C_q), 144.7 (CH), 143.3 (CH), 139.3 (C_q), 137.3 (C_q), 137.0 (C_q), 136.0 (C_q), 133.8 (C_q), 132.1 (C_q), 131.4 (CH), 130.1 (CH), 129.2 (CH), 125.7 (CH), 125.6 (CH), 124.4 (CH), 119.7 (CH), 117.0 (CH), 64.3 (CH_2), 64.2 (CH_2), 30.8 (CH_2), 30.8 (CH_2), 20.5 (CH_3), 19.7 (CH_3), 19.7 (CH_3), 19.2 (CH_2), 15.4 (CH_3), 13.7 (CH_3). IR (ATR): 3060, 2957, 2933, 2872, 1711, 1455, 1312, 1236, 982, 817 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 255 (100) $[M + Na]^+$, 233 (100) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{15}H_{20}O_2 + H]^+$ 233.1536 found 233.1534.



***n*-Butyl cinnamate (4)**

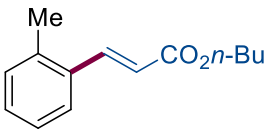
The general procedure **A** was followed using benzene (**1b**) (356.4 µL, 4.0 mmol, 20 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 20:1) yielded **4** (33.1 mg, 81%) as a colorless oil. The product is known compound.[10] ^{1}H-NMR (600 MHz, $CDCl_3$): *δ* = 7.68 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.40 – 7.37 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J*

= 6.7 Hz, 2H), 1.73 – 1.67 (m, 2H), 1.49 – 1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.1 (C_q), 144.5 (CH), 134.5 (C_q), 130.2 (CH), 128.8 (CH), 128.0 (CH), 118.3 (CH), 64.4 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3059, 2960, 2931, 2873, 2251, 1708, 1638, 1265, 909, 737 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 227 (100) [M + Na]$^+$, 205 (10) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{13}H_{16}O_2$ + Na]$^+$ 227.1043 found 227.1043.



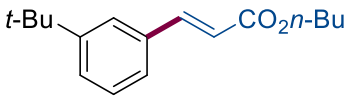
(*E*)-*n*-Butyl-3-(naphthalen-1-yl)acrylate (*α*-5) & (*E*)-*n*-butyl-3-(naphthalen-2-yl)acrylate (*β*-5)

The general procedure **A** was followed using naphthalene (**1c**) (128.2 mg, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **5** (37.1 mg, 73%) as a white solid. The *α* and *β*-olefinated products are known compounds[9] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *α* : *β* = 1 : 2.8 . ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.54 (d, J = 15.7 Hz, 1H$^{\beta}$), 8.20 (d, J = 8.5 Hz, 1H$^{\beta}$), 8.20 (s, 1H$^{\alpha}$), 7.91 – 7.81 (m, 4H$^{\alpha}$+2H$^{\beta}$), 7.76 (d, J = 7.2 Hz, 1H$^{\beta}$), 7.67 (dd, J = 8.6, 1.8 Hz, 1H$^{\alpha}$), 7.61 – 7.46 (m, 2H$^{\alpha}$+3H$^{\beta}$), 6.58 – 6.52 (m, 1H$^{\alpha+\beta}$), 4.39 – 4.19 (m, 2H$^{\alpha+\beta}$), 1.78 – 1.69 (m, 2H$^{\alpha+\beta}$), 1.53 – 1.43 (m, 2H$^{\alpha+\beta}$), 1.04 – 0.97 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.1 (C_q), 166.9 (C_q), 144.5 (CH), 141.5 (CH), 134.1 (C_q), 133.6 (C_q), 133.2 (C_q), 131.9 (C_q), 131.8 (C_q), 131.4 (C_q), 130.4 (CH), 129.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 127.7 (CH), 127.1 (CH), 126.8 (CH), 126.6 (CH), 126.2 (CH), 125.4 (CH), 124.9 (CH), 123.5 (CH), 123.3 (CH), 120.9 (CH), 118.4 (CH), 64.5 (CH_2), 64.4 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 19.2 (CH_2), 13.7 (CH_3), 13.7 (CH_3). IR (ATR): 3058, 2958, 2932, 2872, 1708, 1633, 1303, 1166, 977, 776 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 277 (100) [M + Na]$^+$, 255 (50) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{17}H_{18}O_2$ + Na]$^+$ 277.1199 found 277.1191.



(*E*)-*n*-Butyl-3-(*o*-tolyl)acrylate (*o*-6) & (*E*)-*n*-butyl-3-(*m*-tolyl)acrylate (*m*-6) & (*E*)-*n*-butyl-3-(*p*-tolyl)acrylate (*p*-6)

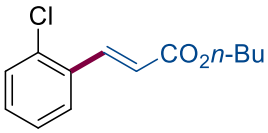
The general procedure **A** was followed using toluene (**1d**) (211.8 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **6** (34.1 mg, 78%) as a colorless oil. The *o*, *m*, and *p*-olefinated products are known compounds[9] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *m* : *p* = 2.1 : 1 : 1.1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 15.9 Hz, 1H^{o}), 7.66 (d, *J* = 16.0 Hz, 1H^{m+p}), 7.59 – 7.15 (m, 4H^{o+m+p}), 6.51 – 6.28 (m, 1H^{o+m+p}), 4.31 – 4.17 (m, 2H^{o+m+p}), 2.44 (s, 3H^{o}), 2.37 (s, 3H^{m+p}), 1.79 – 1.61 (m, 2H^{o+m+p}), 1.52 – 1.37 (m, 2H^{o+m+p}), 1.04 – 0.92 (m, 3H^{o+m+p}). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.3 (C_q), 167.1 (C_q), 144.7 (CH), 144.5 (CH), 142.2 (CH), 140.6 (C_q), 138.5 (C_q), 137.6 (C_q), 134.4 (C_q), 133.4 (C_q), 131.7 (C_q), 131.0 (CH), 130.7 (CH), 129.9 (CH), 129.6 (CH), 128.7 (CH), 128.7 (CH), 128.0 (CH), 126.4 (CH), 126.3 (CH), 125.2 (CH), 119.3 (CH), 118.0 (CH), 117.2 (CH), 64.4 (CH_2), 64.4 (CH_2), 64.3 (CH_2), 30.8 (CH_2), 30.8 (CH_2), 21.4 (CH_3), 21.3 (CH_3), 19.8 (CH_3), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3055, 2958, 2931, 2872, 1711, 1636, 1311, 1273, 1170, 982 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 241 (100) [M + Na]$^+$, 219 (10) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{14}H_{18}O_2$ + Na]$^+$ 241.1199 found 241.1201.



(*E*)-*n*-Butyl-3-(3-(*tert*-butyl)phenyl)acrylate (*m*-7) & (*E*)-*n*-butyl-3-(4-(*tert*-butyl)phenyl)acrylate (*p*-7)

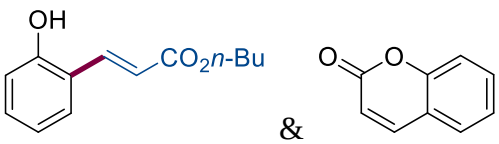
The general procedure **A** was followed using *tert*-butylbenzene (**1e**) (309.7 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **7** (34.4 mg, 66%) as a colorless oil. The *p*-olefinated product is known compound[11] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *m* : *p* = 0 : 1 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 16.0 Hz, 1H^{m}), 7.67 (d, *J* = 16.0 Hz, 1H^{p}), 7.55 – 7.30 (m, 4H^{m+p}), 6.45 (d, *J* = 16.0 Hz, 1H^{m}), 6.41 (d, *J* = 16.0 Hz, 1H^{p}), 4.25 – 4.17 (m, 2H^{m+p}), 1.73 – 1.66 (m, 2H^{m+p}), 1.50 – 1.40 (m, 2H^{m+p}), 1.37 – 1.29 (m, 9H^{m+p}), 1.00 – 0.94

(m, 3H^{m+p}). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.3 (C_q), 167.2 (C_q), 153.7 (C_q), 151.8 (C_q), 145.1 (CH), 144.4 (CH), 134.1 (C_q), 131.7 (C_q), 128.6 (CH), 127.9 (CH), 127.4 (CH), 125.8 (CH), 125.2 (CH), 125.1 (CH), 117.8 (CH), 117.3 (CH), 64.4 (CH_2), 64.3 (CH_2), 34.8 (C_q), 34.7 (C_q), 31.2 (CH_3), 31.1 (CH_3), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3061, 2959, 2871, 1711, 1636, 1308, 1166, 982, 828, 694 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 283 (30) [M + Na]$^+$, 261 (100) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{17}H_{24}O_2$ + H]$^+$ 261.1849 found 261.1849.



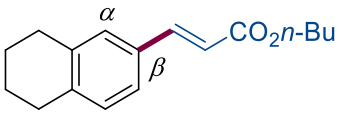
(*E*)-*n*-Butyl-3-(2-chlorophenyl)acrylate (*o*-8) & (*E*)-*n*-butyl-3-(3-chlorophenyl)acrylate (*m*-8) & (*E*)-*n*-butyl-3-(4-chlorophenyl)acrylate (*p*-8)

The general procedure **A** was followed using chlorobenzene (**1f**) (202.8 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 100 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **8** (17.2 mg, 36%) as a colorless oil. The *o*, *m* and *p*-olefinated products are known compounds[9] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *m* : *p* = 3.7 : 1.2 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 16.0 Hz, 1H^o), 7.64 – 7.26 (m, 4H^{o+m+p}), 6.46 – 6.39 (m, 1H^{o+m+p}), 4.32 – 4.14 (m, 2H^{o+m+p}), 1.74 – 1.65 (m, 2H^{o+m+p}), 1.48 – 1.39 (m, 2H^{o+m+p}), 1.01 – 0.93 (m, 3H^{o+m+p}). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 166.8 (C_q), 166.6 (C_q), 166.5 (C_q), 143.0 (CH), 142.9 (CH), 140.3 (CH), 136.3 (C_q), 136.1 (C_q), 134.9 (C_q), 134.9 (C_q), 132.9 (C_q), 132.7 (C_q), 130.9 (CH), 130.1 (CH), 130.1 (CH), 130.0 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 127.0 (CH), 126.2 (CH), 120.9 (CH), 119.8 (CH), 118.9 (CH), 64.6 (CH_2), 64.5 (CH_2), 30.7 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 19.2 (CH_2), 13.7 (CH_3), 13.7 (CH_3). IR (ATR): 3053, 2962, 2874, 1708, 1636, 1313, 1265, 1173, 907, 731 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 261 (100) [M + Na]$^+$, 239 (20) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{13}H_{15}O_2Cl$ + Na]$^+$ 261.0653 found 261.0650.



(*E*)-*n*-Butyl-3-(2-hydroxyphenyl)acrylate (*o*-9) & (*E*)-*n*-butyl-3-(4-hydroxyphenyl) acrylate (*p*-9) & 2*H*-chromen-2-one (*o*'-9)

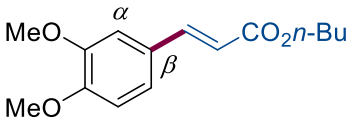
The general procedure **A** was followed using phenol (**1g**) (94.1 mg, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **9** (28.3 mg, 71%) as a white solid. The *o* and *p*-olefinated products are known compounds.[12] 2*H*-chromen-2-one was observed and isolated as well.[13] The ratio of the isomers was determined by the ^{1}H-NMR of crude mixture, *o* : *p* : *o*' = 2.0 : 1 : 1.2. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 16.1 Hz, $1H^{o}$), 7.63 (d, *J* = 16.0 Hz, $1H^{p}$), 7.47 (dd, *J* = 7.8, 1.7 Hz, $1H^{o}$), 7.43 – 7.39 (m, $2H^{p}$), 7.27 – 7.20 (m, $1H^{o}$), 6.93 – 6.89 (m, $1H^{o}$), 6.88 – 6.84 (m, $1H^{o}$+$2H^{p}$), 6.63 (d, *J* = 16.1 Hz, $1H^{o}$), 6.30 (d, *J* = 15.9 Hz, $1H^{p}$), 4.22 (m, $2H^{o+p}$), 1.74 – 1.64 (m, $2H^{o+p}$), 1.50 – 1.39 (m, $2H^{o+p}$), 1.00 – 0.92 (m, $3H^{o+p}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 168.6 (C_q), 167.9 (C_q), 158.0 (C_q), 155.4 (C_q), 144.6 (CH), 140.6 (CH), 131.4 (CH), 129.9 (CH), 129.2 (CH), 127.0 (C_q), 121.7 (C_q), 120.6 (CH), 118.4 (CH), 116.4 (CH), 115.9 (CH), 115.4 (CH), 64.6 (CH_2), 64.5 (CH_2), 30.8 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3335, 2959, 2933, 2873, 1705, 1586, 1453, 1167, 828, 751 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 243 (100) $[M + Na]^+$, 221 (50) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{13}H_{16}O_3 + Na]^+$ 243.0992 found 243.0985. For *o*'-**9**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.71 (dd, *J* = 9.5, 0.6 Hz, 1H), 7.54 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.34 (ddt, *J* = 8.3, 1.1, 0.5 Hz, 1H), 7.28 (td, *J* = 7.5, 1.1 Hz, 1H), 6.43 (d, *J* = 9.5 Hz, 1H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.8 (C_q), 154.1 (C_q), 143.4 (CH), 131.8 (CH), 127.8 (CH), 124.4 (CH), 118.8 (C_q), 116.9 (CH), 116.7 (CH). IR (ATR): 3069, 2933, 1627, 1320, 1256, 1227, 1063, 984, 599, 524 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 147 (100) $[M + Na]^+$, 169 (10) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_9H_6O_2 + H]^+$ 147.0441 found 147.0434.



(*E*)-*n*-Butyl-3-(5,6,7,8-tetrahydronaphthalen-1-yl)acrylate (*α*-10) & (*E*)-*n*-butyl-3-(5,6,7,8-tetrahydronaphthalen-2-yl)acrylate (*β*-10)

The general procedure **A** was followed using 1,2,3,4-tetrahydronaphthalene (**1h**) (136.3 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20

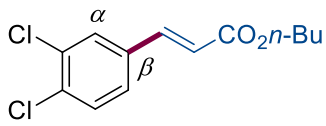
h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **10** (40.3 mg, 78%) as a colorless oil. The α-olefinated product is known compound[14] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, α : β = 1 : 1.4 . ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, J = 15.8 Hz, 1H$^{\alpha}$), 7.63 (d, J = 16.0 Hz, 1H$^{\beta}$), 7.40 – 7.03 (m, 3H$^{\alpha+\beta}$), 6.39 (d, J = 16.0 Hz, 1H$^{\beta}$), 6.32 (d, J = 15.8 Hz, 1H$^{\alpha}$), 4.25 – 4.16 (m, 2H$^{\alpha+\beta}$), 2.92 – 2.73 (m, 4H$^{\alpha+\beta}$), 1.92 – 1.76 (m, 4H$^{\alpha+\beta}$), 1.75 – 1.64 (m, 2H$^{\alpha+\beta}$), 1.49 – 1.40 (m, 2H$^{\alpha+\beta}$), 1.09 – 0.92 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.3 (C_q), 167.2 (C_q), 144.8 (CH), 142.4 (CH), 140.0 (C_q), 137.9 (C_q), 137.6 (C_q), 136.3 (C_q), 133.6 (C_q), 131.7 (C_q), 131.1 (CH), 129.6 (CH), 129.0 (CH), 125.5 (CH), 125.0 (CH), 124.0 (CH), 119.5 (CH), 116.9 (CH), 64.3 (CH_2), 64.3 (CH_2), 30.8 (CH_2), 30.8 (CH_2), 30.0 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.5 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 23.0 (CH_2), 22.5 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3379, 2955, 2931, 2864, 1711, 1634, 1309, 1222, 1171, 983 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 281 (100) $[M + Na]^+$, 259 (100) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{17}H_{22}O_2 + H]^+$ 259.1693 found 259.1688.



(*E*)-*n*-Butyl-3-(3,4-dimethoxyphenyl)acrylate (11)

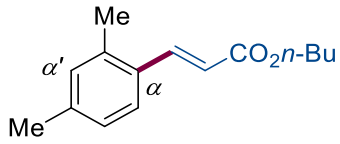
The general procedure **A** was followed using 1,2-dimethoxybenzene (**1i**) (127.5 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 10:1 to 5:1) yielded **11** (30.1 mg, 57%) as a colorless oil. The α and β-olefinated products are known compounds[9] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, β-olefinated product is sole product. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.61 (d, J = 15.9 Hz, 1H), 7.09 (dd, J = 8.6, 2.0 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.30 (d, J = 15.9 Hz, 1H), 4.19 (t, J = 6.7 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 1.71 – 1.63 (m, 2H), 1.47 – 1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.3 (C_q), 151.0 (C_q), 149.1 (C_q), 144.4 (CH), 127.4 (C_q), 122.5 (CH), 115.9 (CH), 111.0 (CH), 109.5 (CH), 64.2 (CH_2), 55.9 (CH_3), 55.8 (CH_3), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3000, 2957, 2932, 2871, 2834, 1704, 1633, 1512, 1257, 1025 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 287

(100) $[M + Na]^+$, 265 (50) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{15}H_{20}O_4 + Na]^+$ 287.1254 found 287.1252.



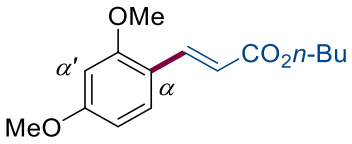
(*E*)-*n*-Butyl-3-(2,3-dichlorophenyl)acrylate (*α*-12) & (*E*)-*n*-butyl-3-(3,4-dichlorophenyl) acrylate (*β*-12)

The general procedure **A** was followed using 1,2-dichlorobenzene (**1j**) (225.1 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 100 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **12** (24.0 mg, 44%) as a colorless oil. The *α* and *β*-olefinated products are known compound[14] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, $\alpha : \beta$ = 1.5 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 15.9 Hz, 1H$^{\alpha}$), 7.59 (d, *J* = 2.1 Hz, 1H$^{\beta}$), 7.57 – 7.53 (d, *J* = 15.9 Hz, 1H$^{\beta}$), 7.51 (ddd, *J* = 7.9, 1.5, 0.5 Hz, 1H$^{\alpha}$), 7.47 (dd, *J* = 8.0, 1.5 Hz, 1H$^{\alpha}$), 7.45 (d, *J* = 8.3 Hz, 1H$^{\beta}$), 7.34 (ddd, *J* = 8.3, 2.1, 0.5 Hz, 1H$^{\beta}$), 7.21 (td, *J* = 7.9, 0.6 Hz, 1H$^{\alpha}$), 6.44 – 6.38 (m, 1H$^{\alpha+\beta}$), 4.26 – 4.17 (m, 2H$^{\alpha+\beta}$), 1.73 – 1.65 (m, 2H$^{\alpha+\beta}$), 1.48 – 1.39 (m, 2H$^{\alpha+\beta}$), 0.99 – 0.94 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 166.4 (C_q), 166.2 (C_q), 141.7 (CH), 140.2 (CH), 135.1 (C_q), 134.5 (C_q), 134.0 (C_q), 133.9 (C_q), 133.2 (C_q), 132.9 (C_q), 131.4 (CH), 130.8 (CH), 129.5 (CH), 127.3 (CH), 126.9 (CH), 125.7 (CH), 122.2 (CH), 120.1 (CH), 64.7 (CH_2), 64.6 (CH_2), 30.7 (CH_2), 19.1 (CH_2), 13.7 (CH_3), 13.7 (CH_3). IR (ATR): 3064, 2932, 2872, 1713, 1638, 1309, 1274, 1176, 979, 785 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 295 (100) $[M + Na]^+$, 273 (20) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{13}H_{14}O_2Cl_2 + Na]^+$ 295.0263 found 295.0255.



(*E*)-*n*-Butyl-3-(1,6-dimethylphenyl)acrylate (*α*'-13) & (*E*)-*n*-butyl-3-(2,4-dimethylphenyl)acrylate (*α*-13) & (*E*)-*n*-butyl-3-(3,5-dimethylphenyl)acrylate (*β*-13)

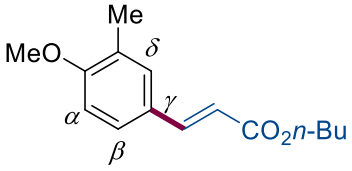
The general procedure **A** was followed using *m*-xylene (**1k**) (122.3 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **13** (38.1 mg, 82%) as a colorless oil. The α', α and β-olefinated products are known compounds[12] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, β : α : α' = 1 : 8.8 : 1.6. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, J = 15.9 Hz, 1H$^{\alpha}$), 7.85 (d, J = 16.4 Hz, 1H$^{\alpha'}$), 7.63 (d, J = 16.0 Hz, 1H$^{\beta}$), 7.47 (d, J = 8.4 Hz, 1H$^{\alpha}$), 7.19 – 6.98 (m, 3H$^{\alpha'+\beta}$ + 2H$^{\alpha}$), 6.42 (d, J = 16.0 Hz, 1H$^{\beta}$), 6.34 (d, J = 15.8 Hz, 1H$^{\alpha}$), 6.07 (d, J = 16.4 Hz, 1H$^{\alpha'}$), 4.22 (m, 2H$^{\alpha'+\alpha+\beta}$), 2.43 – 2.32 (m, 6H$^{\alpha'+\alpha+\beta}$), 1.86 – 1.61 (m, 2H$^{\alpha'+\alpha+\beta}$), 1.54 – 1.41 (m, 2H$^{\alpha'+\alpha+\beta}$), 1.08 – 0.89 (m, 3H$^{\alpha'+\alpha+\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.3 (C_q), 167.2 (C_q), 166.9 (C_q), 144.8 (CH), 143.2 (CH), 142.1 (CH), 140.2 (C_q), 138.3 (C_q), 137.6 (C_q), 136.6 (C_q), 134.4 (C_q), 134.0 (C_q), 132.0 (CH), 131.5 (CH), 130.5 (C_q), 128.2 (CH), 128.2 (CH), 127.1 (CH), 126.3 (CH), 125.9 (CH), 123.9 (CH), 118.1 (CH), 117.8 (CH), 64.5 (CH_2), 64.3 (CH_2), 30.8 (CH_2), 30.8 (CH_2), 30.7 (CH_2), 21.3 (CH_3), 21.1 (CH_3), 21.0 (CH_3), 19.7 (CH_3), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2958, 2930, 2872, 1711, 1633, 1610, 1310, 1274, 1159, 981 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 255 (95) $[M + Na]^+$, 233 (100) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{15}H_{20}O_2 + H]^+$ 233.1536 found 233.1532.



(*E*)-*n*-Butyl-3-(2,6-dimethoxyphenyl)acrylate (α'-14) & (*E*)-*n*-butyl-3-(2,4-dimethoxyphenyl)acrylate (α-14)

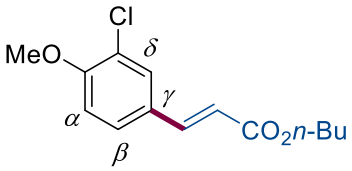
The general procedure **A** was followed using 1,3-dimethoxybenzene (**1l**) (143.2 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 10:1 to 5:1) yielded **14** (27.5 mg, 52%) as a colorless oil. The α', α and β-olefinated products are known compounds[9] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, α : α' = 4 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 16.3 Hz, 1H$^{\alpha'}$), 7.90 (d, J = 16.1 Hz, 1H$^{\alpha}$), 7.43 (d, J = 8.5 Hz, 1H$^{\alpha}$), 7.25 (t, J = 8.4 Hz, 1H$^{\alpha'}$), 6.87 (d, J = 16.3 Hz, 1H$^{\alpha'}$), 6.55 (d, J = 8.4 Hz, 2H$^{\alpha'}$), 6.49 (dd, J = 8.5, 2.4 Hz, 1H$^{\alpha}$), 6.46 – 6.40 (m, 2H$^{\alpha}$), 4.22 – 4.16 (m,

2H$^{\alpha'+\alpha}$), 3.90 – 3.81 (m, 6H$^{\alpha'+\alpha}$), 1.72 – 1.63 (m, 2H$^{\alpha'+\alpha}$), 1.49 – 1.37 (m, 2H$^{\alpha'+\alpha}$), 0.99 – 0.93 (m, 3H$^{\alpha'+\alpha}$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.7 (C_q), 168.0 (C_q), 162.6 (C_q), 160.0 (C_q), 159.8 (C_q), 139.9 (CH), 135.3 (CH), 131.1 (CH), 130.4 (CH), 120.7 (CH), 116.6 (C_q), 116.1 (CH), 112.3 (C_q), 105.1 (CH), 103.6 (CH), 98.4 (CH), 64.1 (CH_2), 64.0 (CH_2), 55.7 (CH_3), 55.4 (CH_3), 30.9 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3003, 2958, 2934, 2872, 2838, 1703, 1604, 1300, 1255, 1210 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 287 (50) [M + Na]$^+$, 265 (100) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{15}H_{20}O_4$ + H]$^+$ 265.1434 found 265.1430.



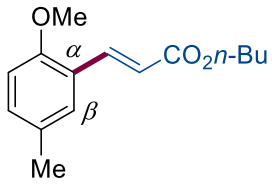
(*E*)-butyl-3-(3-methyl-2-methoxyphenyl)acrylate (*α*-15) & (*E*)-butyl-3-(4-methyl-3-methoxyphenyl)acrylate (*β*-15) & (*E*)-butyl-3-(3-methyl-4-methoxyphenyl)acrylate (*γ*-15) & (*E*)-butyl-3-(2-methyl-3-methoxyphenyl)acrylate (*δ*-15)

The general procedure **A** was followed using 1-methoxy-2-methylbenzene (**1m**) (124.7 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **15** (31.6 mg, 76%). The site selectivity was determined by ^{1}H-NMR and NOESY NMR, *γ : others* = 3 : 1. For *γ*-**15**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 15.9 Hz, 1H), 7.35 – 7.32 (m, 2H), 6.81 (d, *J* = 9.0 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 2.22 (s, 3H), 1.72 – 1.65 (m, 2H), 1.48 – 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.5 (C_q), 159.6 (C_q), 144.5 (CH), 130.0 (CH), 127.8 (CH), 127.2 (C_q), 126.7 (C_q), 115.4 (CH), 109.9 (CH), 64.2 (CH_2), 55.4 (CH_3), 30.8 (CH_2), 19.2 (CH_2), 16.2 (CH_3), 13.8 (CH_3). IR (ATR): 2959, 2933, 2252, 1702, 1604, 1502, 1254, 1175, 1132, 909 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 271 (100) [M + Na]$^+$, 249 (0) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{15}H_{20}O_3$ + Na]$^+$ 271.1305 found 271.1304.



(*E*)-butyl-3-(3-chloro-2-methoxyphenyl)acrylate (*α*-16) & (*E*)-butyl-3-(4-chloro-3-methoxyphenyl)acrylate (*β*-16) & (*E*)-butyl-3-(3-chloro-4-methoxyphenyl)acrylate (*γ*-16) & (*E*)-butyl-3-(2-chloro-3-methoxyphenyl)acrylate (*δ*-16)

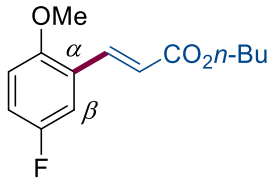
The general procedure **A** was followed using 1-chloro-2-methoxybenzene (**1n**) (228.5 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **16** (27.5 mg, 53%). The site selectivity was determined by ^{1}H-NMR and NOESY NMR, *α : γ : others* = 1 : 4 : 3. For *α*-**16**, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 16.2 Hz, 1H), 7.46 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.51 (d, *J* = 16.2 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 1.74 – 1.65 (m, 2H), 1.50 – 1.38 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.9 (C_q), 155.1 (C_q), 138.5 (CH), 132.0 (CH), 130.1 (C_q), 128.9 (C_q), 126.4 (CH), 125.0 (CH), 120.8 (CH), 64.6 (CH_2), 61.6 (CH_3), 30.8 (CH_2), 19.2 (CH_2), 13.8 (CH_3). For *γ*-**16**, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 15.9 Hz, 1H), 7.39 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.93 (s, 3H), 1.75 – 1.62 (m, 2H), 1.50 – 1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.1 (C_q), 156.5 (C_q), 142.8 (CH), 129.5 (CH), 128.2 (CH), 128.1 (C_q), 123.2 (C_q), 117.3 (CH), 112.0 (CH), 64.5 (CH_2), 56.3 (CH_3), 30.80 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2959, 2934, 2873, 1710, 1637, 1572, 1471, 1268, 1172, 1064 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 291 (100) $[M + Na]^+$, 269 (0) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{14}H_{17}ClO_3 + Na]^+$ 291.0758 found 291.0751.



(*E*)-*n*-Butyl-3-(2-methoxy-5-methylphenyl)acrylate (*α*-17) & (*E*)-*n*-butyl-3-(5-methoxy-2-methylphenyl)acrylate (*β*-17)

The general procedure **A** was followed using 1-methoxy-4-methylbenzene (**1o**) (126.1 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1)

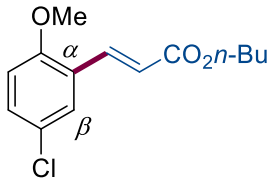
yielded **17** (47.2 mg, 95%) as a colorless oil. The site selectivity was determined by NOESY NMR and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, α : β = 12.6 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ^{α} = 7.96 (d, *J* = 16.2 Hz, 1H), 7.31 (d, *J* = 2.2 Hz, 1H), 7.13 (ddd, *J* = 8.4, 2.3, 0.8 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 16.1 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.85 (s, 3H), 2.29 (s, 3H), 1.76 – 1.63 (m, 2H), 1.49 – 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ^{α} = 167.6 (C_q), 156.3 (C_q), 140.0 (CH), 131.8 (CH), 129.7 (C_q), 129.3 (CH), 123.1 (C_q), 118.5 (CH), 111.1 (CH), 64.2 (CH_2), 55.5 (CH_3), 30.8 (CH_2), 20.3 (CH_3), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2959, 2933, 2872, 2252, 1702, 1631, 1250, 1031, 908, 731 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 271 (100) $[M + Na]^+$, 249 (95) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{15}H_{20}O_3 + H]^+$ 249.1485 found 249.1483.



(*E*)-*n*-Butyl-3-(5-fluoro-2-methoxyphenyl)acrylate (*α*-18) & (*E*)-*n*-butyl-3-(2-fluoro-5-methoxyphenyl)acrylate (*β*-18)

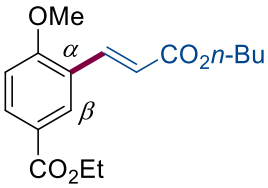
The general procedure **A** was followed using 1-fluoro-4-methoxybenzene (**1p**) (227.1 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **18** (38.9 mg, 77%) as a white solid. The site-selectivity was determined by ^{13}C NMR and the ratio of the isomers was determined by the ^{1}H-NMR of crude mixture, α : β = 3.6 : 1. For *α*-**18**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.93 (dd, *J* = 16.4, 1.1 Hz, 1H), 7.20 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.03 (ddd, *J* = 9.1, 7.7, 3.1 Hz, 1H), 6.84 (dd, *J* = 9.1, 4.4 Hz, 1H), 6.47 (d, *J* = 16.2 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 1.73 – 1.65 (m, 2H), 1.47 – 1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.1 (C_q), 156.8 (d, *J* = 239.0 Hz, C_q), 154.4 (d, *J* = 1.9 Hz, C_q), 138.6 (d, *J* = 2.3 Hz, CH), 124.6 (d, *J* = 7.4 Hz, C_q), 119.9 (CH), 117.4 (d, *J* = 23.1 Hz, CH), 114.5 (d, *J* = 23.4 Hz, CH), 112.2 (d, *J* = 8.1 Hz, CH), 64.4 (CH_2), 56.0 (CH_3), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = -123.67 (td, *J* = 8.4, 4.4 Hz). IR (ATR): 2959, 2931, 2873, 1709, 1633, 1492, 1251, 1170, 1029, 861 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 275 (100) $[M + Na]^+$, 253 (50) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{14}H_{17}O_3F + Na]^+$ 275.1054 found 275.1051. For *β*-**18**, ^{1}H-NMR (600 MHz, $CDCl_3$):

δ = 7.77 (d, J = 16.2 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.88 (m, 1H), 6.51 (d, J = 16.2 Hz, 1H), 4.22 (t, J = 6.7 Hz, 2H), 3.80 (s, 3H), 1.74 – 1.64 (m, 2H), 1.48 – 1.40 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 166.8 (C_q), 155.9 (d, J = 246.8 Hz, C_q), 155.7 (d, J = 2.1 Hz, C_q), 137.2 (d, J = 2.7 Hz, CH), 122.8 (d, J = 13.3 Hz, C_q), 120.9 (d, J = 6.4 Hz, CH), 117.3 (d, J = 8.3 Hz, CH), 116.8 (d, J = 24.1 Hz, CH), 112.6 (d, J = 3.0 Hz, CH), 64.6 (CH_2), 55.8 (CH_3), 30.7 (CH_2), 19.2 (CH_2), 13.7 (CH_3). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = -125.08 (ddd, J = 9.9, 5.8, 4.1 Hz). IR (ATR): 2959, 2931, 2873, 1709, 1633, 1492, 1251, 1170, 981, 807 cm^{-1}. MS (ESI) m/z (relative intensity): 275 (100) $[M + Na]^+$, 253 (50) $[M + H]^+$. HR-MS (ESI): m/z calcd. for $[C_{14}H_{17}O_3F + Na]^+$ 275.1054 found 275.1051.



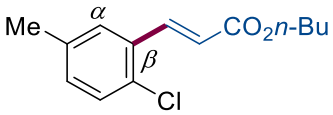
(*E*)-*n*-Butyl-3-(5-chloro-2-methoxyphenyl)acrylate (α-19) & (*E*)-*n*-butyl-3-(2-chloro-5-methoxyphenyl)acrylate (β-19)

The general procedure **A** was followed using 1-chloro-4-methoxybenzene (**1q**) (250.8 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **19** (36.0 mg, 67%) as a colorless oil. The site selectivity was determined by NOESY NMR and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, α : β = 6.6 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 16.0 Hz, 1H$^{\beta}$), 7.84 (d, J = 16.2 Hz, 1H$^{\alpha}$), 7.41 (d, J = 2.6 Hz, 1H$^{\alpha}$), 7.25 – 7.20 (m, 1H$^{\alpha+\beta}$), 7.06 (d, J = 2.9 Hz, 1H$^{\beta}$), 6.84 – 6.75 (m, 1H$^{\alpha+\beta}$), 6.44 (d, J = 16.1 Hz, 1H$^{\alpha}$), 6.36 (d, J = 15.9 Hz, 1H$^{\beta}$), 4.20 – 4.13 (m, 2H$^{\alpha+\beta}$), 3.82 (s, 3H$^{\alpha}$), 3.76 (s, 3H$^{\beta}$), 1.69 – 1.58 (m, 2H$^{\alpha+\beta}$), 1.46 – 1.31 (m, 2H$^{\alpha+\beta}$), 0.96 – 0.88 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.1 (C_q), 166.5 (C_q), 158.3 (C_q), 156.7 (C_q), 140.4 (CH), 138.4 (CH), 133.3 (C_q), 130.7 (CH), 130.7 (CH), 128.2 (CH), 126.5 (C_q), 125.7 (C_q), 124.9 (C_q), 120.9 (CH), 120.0 (CH), 117.3 (CH), 112.4 (CH), 112.1 (CH), 64.6 (CH_2), 64.4 (CH_2), 55.8 (CH_3), 55.5 (CH_3), 30.7 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2958, 2934, 2872, 2840, 1709, 1633, 1484, 1252, 1171, 1026 cm^{-1}. MS (ESI) m/z (relative intensity): 291 (100) $[M + Na]^+$, 269 (70) $[M + H]^+$. HR-MS (ESI): m/z calcd. for $[C_{14}H_{17}O_3Cl + Na]^+$ 291.0758 found 291.0753.



(*E*)-Ethyl-3-(3-butoxy-3-oxoprop-1-en-1-yl)-4-methoxybenzoate (20)

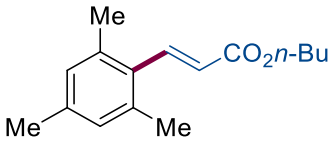
The general procedure **A** was followed using ethyl 4-methoxybenzoate (**1r**) (325.9 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 10:1 to 5:1) yielded **20** (37.4 mg, 61%) as a colorless oil. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.18 (d, J = 2.2 Hz, 1H), 8.01 (dd, J = 8.7, 2.2 Hz, 1H), 7.93 (dd, J = 16.2, 0.5 Hz, 1H), 6.91 (d, J = 8.7 Hz, 1H), 6.56 (d, J = 16.2 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 4.19 (t, J = 6.7 Hz, 2H), 3.92 (s, 3H), 1.70 – 1.62 (m, 2H), 1.45 – 1.39 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.2 (C_q), 165.9 (C_q), 161.4 (C_q), 138.9 (CH), 132.9 (CH), 130.3 (CH), 123.3 (C_q), 123.0 (C_q), 119.9 (CH), 110.6 (CH), 64.36 (CH_2), 60.9 (CH_2), 55.8 (CH_3), 30.8 (CH_2), 19.2 (CH_2), 14.3 (CH_3), 13.7 (CH_3). IR (ATR): 2958, 2933, 2872, 1710, 1632, 1605, 1459, 1306, 1122, 1025 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 329 (100) $[M + Na]^+$, 307 (50) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{17}H_{22}O_5 + Na]^+$ 329.1359 found 329.1355.



(*E*)-*n*-Butyl-3-(5-chloro-2-methylphenyl)acrylate (α-21) & (*E*)-*n*-butyl-3-(2-chloro-5-methylphenyl)acrylate (β-21)

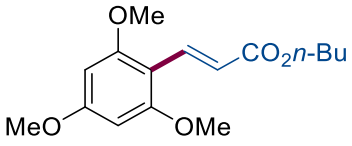
The general procedure **A** was followed using 1-chloro-4-methylbenzene (**1s**) (236.7 µL, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 30:1) yielded **21** (39.2 mg, 78%) as a colorless oil. The site selectivity was determined by NOESY NMR and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, α : β = 1 : 2.3. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 16.2 Hz, 1H$^{\beta}$), 7.86 (d, J = 15.9 Hz, 1H$^{\alpha}$), 7.50 (d, J = 2.3 Hz, 1H$^{\alpha}$), 7.41 (d, J = 1.7 Hz, 1H$^{\beta}$), 7.27 (d, J = 8.1 Hz, 1H$^{\beta}$), 7.21 (dd,

J = 8.2, 2.3 Hz, 1H$^{\alpha}$), 7.14 – 7.07 (m, 1H$^{\alpha+\beta}$), 6.41 (d, J = 16.0 Hz, 1H$^{\beta}$), 6.34 (d, J = 15.9 Hz, 1H$^{\alpha}$), 4.26 – 4.16 (m, 2H$^{\alpha+\beta}$), 2.38 (s, 3H$^{\alpha}$), 2.33 (s, 3H$^{\beta}$), 1.75 – 1.64 (m, 2H$^{\alpha+\beta}$), 1.52 – 1.37 (m, 2H$^{\alpha+\beta}$), 1.01 – 0.91 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7 (C_q), 166.6 (C_q), 140.8 (CH), 140.4 (CH), 136.8 (C_q), 135.8 (C_q), 135.0 (C_q), 132.2 (C_q), 132.0 (C_q), 132.0 (CH), 131.9 (C_q), 131.8 (CH), 129.8 (CH), 129.6 (CH), 128.0 (CH), 126.1 (CH), 120.5 (CH), 64.5 (CH_2), 64.5 (CH_2), 30.7 (CH_2), 20.8 (CH_3), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2959, 2932, 2874, 1714, 1637, 1472, 1314, 1173, 979, 811 cm^{-1}. MS (ESI) m/z (relative intensity): 275 (100) [M + Na]$^+$, 253 (40) [M + H]$^+$. HR-MS (ESI): m/z calcd. for [$C_{14}H_{17}O_2Cl$ + Na]$^+$ 275.0809 found 275.0804.



(*E*)-*n*-Butyl-3-mesitylacrylate (22)

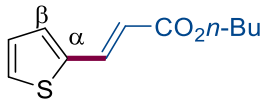
The general procedure **A** was followed using mesitylene (**1t**) (139.2 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 20:1) yielded **22** (25.1 mg, 51%) as a colorless oil. The product is known compound.[15] ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 16.3 Hz, 1H), 6.90 (s, 2H), 6.06 (d, J = 16.3 Hz, 1H), 4.22 (t, J = 6.7 Hz, 2H), 2.34 (s, 6H), 2.29 (s, 3H), 1.71 (p, J = 7.0 Hz, 2H), 1.51 – 1.39 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.1 (C_q), 143.1 (CH), 138.3 (C_q), 136.8 (C_q), 131.0 (C_q), 129.1 (CH), 123.2 (CH), 64.4 (CH_2), 30.8 (CH_2), 21.1 (CH_3), 21.1 (CH_3), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2961, 2931, 2872, 1708, 1636, 1459, 1305, 1265, 1173, 728 cm^{-1}. MS (ESI) m/z (relative intensity): 269 (100) [M + Na]$^+$, 247 (20) [M + H]$^+$. HR-MS (ESI): m/z calcd. for [$C_{16}H_{22}O_2$ + Na]$^+$ 269.1512 found 269.1508.



(*E*)-*n*-Butyl-3-(2,4,6-trimethoxyphenyl)acrylate (23)

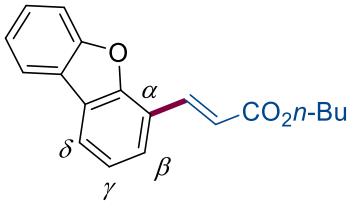
The general procedure **A** was followed using 1,3,5-trimethoxybenzene (**1u**) (168.2 mg, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h.

L12 was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 15:1) yielded **23** (51.9 mg, 88%) as a white solid. The product is known compound.[16] ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.08 (d, J = 16.2 Hz, 1H), 6.74 (d, J = 16.2 Hz, 1H), 6.10 (s, 2H), 4.18 (t, J = 6.8 Hz, 2H), 3.86 (s, 6H), 3.83 (s, 3H), 1.73 – 1.61 (m, 2H), 1.47 – 1.34 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 169.1 (C_q), 162.7 (C_q), 161.2 (C_q), 135.4 (CH), 117.6 (CH), 105.9 (C_q), 90.4 (CH), 63.9 (CH_2), 55.7 (CH_3), 55.3 (CH_3), 30.9 (CH_2), 19.2 (CH_2), 13.8 (CH_3). IR (ATR): 2957, 2893, 2841, 1697 ,1599, 1454, 1415, 1293, 1148, 1119 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 295 (100) $[M + H]^+$, 317 (51) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{16}H_{22}O_5 + H]^+$ 295.1540 found 295.1534.



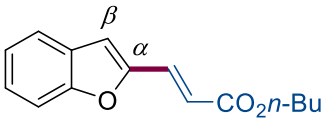
(*E*)-*n*-Butyl-3-(thiophen-3-yl)acrylate (24-1) & (*E*)-*n*-butyl-3-(thiophen-2-yl)acrylate (24-2)

The general procedure **A** was followed using thiophene (**1v**) (316.0 µL, 4.0 mmol, 20 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 30:1) yielded **24** (21.9 mg, 52%) as a yellow oil. The 1 and 2-olefinated products are known compounds[17] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, β : α = 1 : 7.2. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 15.7 Hz, 1H$^{\alpha}$), 7.66 (d, J = 15.9 Hz, 1H$^{\beta}$), 7.52 – 7.46 (m, 1H$^{\beta}$), 7.36 (d, J = 5.1 Hz, 1H$^{\alpha}$), 7.36 – 7.30 (m, 1H$^{\beta}$), 7.30 – 7.26 (m, 1H$^{\beta}$), 7.24 (d, J = 3.5 Hz, 1H$^{\alpha}$), 7.04 (dd, J = 5.1, 3.6 Hz, 1H$^{\alpha}$), 6.26 (d, J = 15.7 Hz, 1H$^{\beta}$), 6.24 (d, J = 15.7 Hz, 1H$^{\alpha}$), 4.23 – 4.15 (m, 2H$^{\alpha+\beta}$), 1.73 – 1.62 (m, 2H$^{\alpha+\beta}$), 1.49 – 1.36 (m, 2H$^{\alpha+\beta}$), 1.00 – 0.92 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ^{α} = 166.9 (C_q), 139.6 (C_q), 136.9 (CH), 130.8 (CH), 128.3 (CH), 128.0 (CH), 117.0 (CH), 64.4 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2958, 2933, 2872, 1704, 1625, 1464, 1303, 1201, 1159, 1024 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 233 (100) $[M + Na]^+$, 211 (25) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{11}H_{14}O_2S + Na]^+$ 233.0607 found 233.0600.



(*E*)-*n*-butyl-4-(dibenzo[*b,d*]furan-4-yl)acrylate (*α*-25) & (*E*)-*n*-butyl-3-(dibenzo[*b,d*]furan-3-yl)acrylate (*β*-25) & (*E*)-*n*-butyl-3-(dibenzo[*b,d*]furan-2-yl)acrylate (*γ*-25) & (*E*)-*n*-Butyl-3-(dibenzo[*b,d*]furan-1-yl)acrylate (*δ*-25)

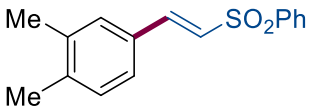
The general procedure **A** was followed using dibenzo[*b,d*]furan (**1w**) (168.2 mg, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 20:1 to 10:1) yielded **25** (44.1 mg, 75%) as a colorless oil. The site selectivity was determined by HMBC and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, α : others = 1 : 1. For *α*-**25**, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.01 – 7.94 (m, 3H), 7.67 (d, J = 8.3 Hz, 1H), 7.57 (dd, J = 7.6, 1.3 Hz, 1H), 7.51 (ddd, J = 8.4, 7.3, 1.4 Hz, 1H), 7.43 – 7.32 (m, 2H), 7.09 (d, J = 16.1 Hz, 1H), 4.28 (t, J = 6.7 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.54 – 1.44 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.5 (C_q), 156.2 (C_q), 154.4 (C_q), 139.3 (CH), 128.3 (CH), 127.6 (CH), 125.1 (C_q), 123.6 (C_q), 123.2 (CH), 123.1 (CH), 122.3 (CH), 121.6 (CH), 120.8 (CH), 119.80 (C_q), 112.00 (CH), 64.58 (CH_2), 30.88 (CH_2), 19.28 (CH_2), 13.83 (CH_3). IR (ATR): 2933, 2871, 1711, 1600, 1451, 1190, 1172, 1022, 959, 749 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 317 (40) $[M + Na]^+$, 295 (100) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{19}H_{18}O_3 + H]^+$ 295.1329 found 295.1320.



(*E*)-*n*-butyl-3-(benzofuran-2-yl)acrylate (*α*-26) & (*E*)-*n*-Butyl-3-(benzofuran-3-yl)acrylate (*β*-26)

The general procedure **A** was followed using benzofuran (**1x**) (108.2 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 20:1) yielded **26** (29.2 mg, 60%) as a colorless oil. The 1 and 2-olefinated products are known compounds[9] and the

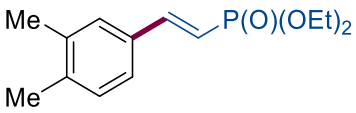
ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, $\beta : \alpha$ = 1 : 2.3. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H$^{\beta}$), 7.87 – 7.84 (m, 1H$^{\beta}$), 7.79 (d, J = 16.1 Hz, 1H$^{\beta}$), 7.58 (d, J = 7.6 Hz, 1H$^{\alpha}$), 7.56 – 7.52 (m, 1H$^{\alpha+\beta}$), 7.48 (dd, J = 8.3, 0.9 Hz, 1H^{2}), 7.39 – 7.32 (m, 1H$^{\alpha}$+2H$^{\beta}$), 7.28 – 7.19 (m, 1H$^{\alpha}$), 6.93 (s, 1H$^{\alpha}$), 6.62 – 6.53 (m, 1H$^{\alpha+\beta}$), 4.26 – 4.20 (m, 2H$^{\alpha+\beta}$), 1.74 – 1.66 (m, 2H$^{\alpha+\beta}$), 1.50 – 1.40 (m, 2H$^{\alpha+\beta}$), 1.01 – 0.94 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.2 (C_q), 166.7 (C_q), 156.1 (C_q), 155.5 (C_q), 152.4 (C_q), 147.7 (CH), 134.3 (CH), 131.1 (CH), 128.3 (C_q), 126.4 (CH), 125.3 (CH), 124.8 (C_q), 123.7 (CH), 123.3 (CH), 121.7 (CH), 121.0 (CH), 119.0 (CH), 118.4 (CH), 117.9 (C_q), 112.0 (CH), 111.4 (CH), 110.9 (CH), 64.6 (CH_2), 64.4 (CH_2), 30.8 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 19.2 (CH_2), 13.7 (CH_3), 13.7 (CH_3). IR (ATR): 2960, 2934, 2874, 1711, 1638, 1451, 1300, 1263, 1169, 750 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 267 (100) $[M + Na]^+$, 245 (30) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{15}H_{16}O_3 + Na]^+$ 267.0992 found 267.0995.



(*E*)-1,2-Dimethyl-3-(2-(phenylsulfonyl)vinyl)benzene (*α*-27) & (*E*)-1,2-dimethyl-4-(2-(phenylsulfonyl)vinyl)benzene (*β*-27)

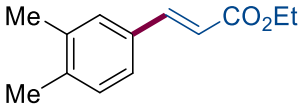
The general procedure **A** was followed using *o*-xylene (**1a**) (120.6 µL, 1.0 mmol, 5.0 equiv) and (vinylsulfonyl)benzene (**2b**) (33.6 mg, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **27** (30.0 mg, 55%) as a colorless oil. The *β*-olefinated product is known compound[18] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, $\alpha : \beta$ = 1 : 2.1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 15.2 Hz, 1H$^{\alpha}$), 7.98 – 7.91 (m, 2H$^{\alpha+\beta}$), 7.67 – 7.48 (m, 3H$^{\alpha}$+4H$^{\beta}$), 7.29 – 7.23 (m, 1H$^{\alpha+\beta}$), 7.23 – 7.17 (m, 1H$^{\alpha+\beta}$), 7.14 (d, J = 7.8 Hz, 1H$^{\beta}$), 7.08 (t, J = 7.7 Hz, 1H$^{\alpha}$), 6.80 (d, J = 15.4 Hz, 1H$^{\beta}$), 6.74 (d, J = 15.2 Hz, 1H$^{\alpha}$), 2.37 – 2.16 (m, 6H$^{\alpha+\beta}$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 142.7 (CH), 141.1 (CH), 140.9 (C_q), 140.7 (C_q), 140.6 (C_q), 137.7 (C_q), 137.4 (C_q), 136.6 (C_q), 133.3 (CH), 133.2 (CH), 132.4 (CH), 131.5 (C_q), 130.3 (CH), 129.9 (C_q), 129.6 (CH), 129.3 (CH), 129.2 (CH), 128.4 (CH), 127.6 (CH), 127.5 (CH), 126.2 (CH), 125.9 (CH), 125.7 (CH), 124.7 (CH), 20.5 (CH_3), 19.1 (CH_3), 19.6 (CH_3), 15.4 (CH_3). IR (ATR): 3056, 2942, 2858, 1608, 1501, 1446, 1304, 1143, 1084, 975 cm^{-1}. MS (ESI) *m*/*z*

(relative intensity): 273 (100) $[M + H]^+$, 290 (48) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{16}H_{16}O_2S + H]^+$ 273.0944 found 273.0947.



(*E*)-Diethyl-(2,3-dimethylstyryl)phosphonate (*α*-28) & (*E*)-diethyl-(3,4-dimethylstyryl)phosphonate (*β*-28)

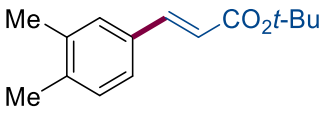
The general procedure **A** was followed using *o*-xylene (**1a**) (120.6 µL, 1.0 mmol, 5.0 equiv) and diethyl vinylphosphonate (**2c**) (30.7 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 1:1) yielded **28** (30.0 mg, 56%) as a colorless oil. The *β*-olefinated products is known compound[18] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, $\alpha : \beta = 1 : 1.8$. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 22.6, 17.3 Hz, 1H$^{\alpha}$), 7.44 (dd, *J* = 22.6, 17.5 Hz, 1H$^{\beta}$), 7.35 (dd, *J* = 7.7, 1.4 Hz, 1H$^{\alpha}$), 7.26 (d, *J* = 1.2 Hz, 1H$^{\beta}$), 7.23 (dd, *J* = 7.8, 1.9 Hz, 1H$^{\beta}$), 7.18 – 7.02 (m, 2H$^{\alpha}$+1H$^{\beta}$), 6.31 – 5.97 (m, 1H$^{\alpha+\beta}$), 4.33 – 3.89 (m, 4H$^{\alpha+\beta}$), 2.40 – 2.09 (m, 6H$^{\alpha+\beta}$), 1.44 – 1.17 (m, 6H$^{\alpha+\beta}$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 148.9 (d, *J* = 6.7 Hz, CH), 147.5 (d, *J* = 7.1 Hz, CH), 139.3 (C_q), 137.3 (d, *J* = 1.1 Hz, C_q), 137.0 (C_q), 135.5 (C_q), 134.4 (d, *J* = 22.4 Hz, C_q), 132.5 (d, *J* = 23.0 Hz, C_q), 131.4 (CH), 130.0 (CH), 128.8 (CH), 125.7 (CH), 125.3 (CH), 124.1 (d, *J* = 1.6 Hz, CH), 115.6 (d, *J* = 189.8 Hz, CH), 112.2 (d, *J* = 191.9 Hz, CH), 62.6 – 61.1 (m, CH_2), 20.5 (CH_3), 19.7 – 19.6 (m, CH_3), 16.5 – 16.3 (m, CH_3), 15.3 (CH_3). ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 20.2, 19.5. IR (ATR): 2979, 2930, 2906, 1615, 1446, 1390, 1242, 1050, 1022, 956 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 269 (100) $[M + H]^+$, 291 (19) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{14}H_{21}O_3P + H]^+$ 269.1301 found 269.1306.



(*E*)-*n*-Butyl-3-(2,3-dimethylphenyl)acrylate (*α*-29) & (*E*)-*n*-butyl-3-(3,4-dimethylphenyl)acrylate (*β*-29)

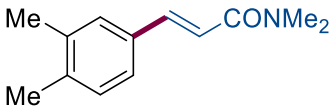
The general procedure **A** was followed using *o*-xylene (**1a**) (482.6 µL, 4.0 mmol, 20 equiv) and ethyl acrylate (**2d**) (21.7 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L3** was used as

ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **29** (28.4 mg, 69%) as a colorless oil. The α and β-olefinated products are known compounds[18] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, $\alpha : \beta = 1 : 8$. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.07 (d, J = 15.8 Hz, 1H$^{\alpha}$), 7.65 (d, J = 16.0 Hz, 1H$^{\beta}$), 7.39 (d, J = 7.7 Hz, 1H$^{\alpha}$), 7.30 (d, J = 1.9 Hz, 1H$^{\beta}$), 7.27 (dd, J = 7.8, 2.0 Hz, 1H$^{\beta}$), 7.19 – 7.14 (m, 2H$^{\alpha}$+1H$^{\beta}$), 6.39 (d, J = 16.0 Hz, 1H$^{\beta}$), 6.31 (d, J = 15.8 Hz, 1H$^{\alpha}$), 4.37 – 4.21 (m, 2H$^{\alpha+\beta}$), 2.40 – 2.26 (m, 6H$^{\alpha+\beta}$), 1.40 – 1.29 (m, 3H$^{\alpha+\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.2 (C_q), 144.7 (CH), 139.3 (C_q), 137.0 (C_q), 132.1 (C_q), 130.1 (CH), 129.2 (CH), 125.6 (CH), 116.9 (CH), 60.3 (CH_2), 19.8 (CH_3), 19.7 (CH_3), 14.3 (CH_3). IR (ATR): 2978, 2938, 2921, 1707, 1638, 1449, 1365, 1313, 1262, 1174 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 227 (100) [M + Na]$^+$, 205 (58) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{13}H_{16}O$ + H]$^+$ 205.1223 found 205.1221.



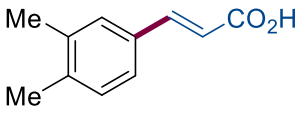
(*E*)-*tert*-Butyl-3-(2,3-dimethylphenyl)acrylate (α-30) & (*E*)-*tert*-butyl-3-(3,4-dimethylphenyl)acrylate (β-30)

The general procedure **A** was followed using *o*-xylene (**1a**) (482.6 µL, 4.0 mmol, 20 equiv) and *tert*-butyl acrylate (**2e**) (29.1 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L3** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 20:1) yielded **30** (26.0 mg, 56%) as a colorless oil. The α and β-olefinated products are known compounds[19] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, $\alpha : \beta = 1 : 8.1$. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, J = 15.7 Hz, 1H$^{\alpha}$), 7.55 (d, J = 16.0 Hz, 1H$^{\beta}$), 7.38 (dd, J = 7.9, 1.4 Hz, 1H$^{\alpha}$), 7.31 – 7.27 (s, 1H$^{\beta}$), 7.27 – 7.24 (m, 1H$^{\beta}$), 7.19 – 7.09 (m, 2H$^{\alpha}$+1H$^{\beta}$), 6.33 (d, J = 15.9 Hz, 1H$^{\beta}$), 6.25 (d, J = 15.7 Hz, 1H$^{\alpha}$), 2.37 – 2.21 (m, 6H$^{\alpha+\beta}$), 1.55 (s, 9H$^{\alpha}$), 1.54 (s, 9H$^{\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 166.5 (C_q), 143.7 (CH), 139.0 (C_q), 137.0 (C_q), 132.3 (C_q), 130.0 (CH), 129.1 (CH), 125.5 (CH), 118.9 (CH), 80.2 (C_q), 28.2 (CH_3), 19.7 (CH_3), 19.7 (CH_3). IR (ATR): 3004, 2976, 2923, 1703, 1633, 1454, 1366, 1319, 1236, 1146 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 255 (100) [M + Na]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{15}H_{20}O_2$ + Na]$^+$ 255.1356 found 255.1357.



(*E*)-3-(2,3-Dimethylphenyl)-*N*,*N*-dimethylacrylamide (*α*-31) & (*E*)-3-(3,4-dimethylphenyl)-*N*,*N*-dimethylacrylamide (*β*-31)

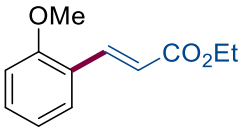
The general procedure **A** was followed using *o*-xylene (**1a**) (482.6 µL, 4.0 mmol, 20 equiv) and *N*,*N*-dimethylacrylamide (**2f**) (20.6 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L3** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 2:1) yielded **31** (23.2 mg, 57%) as a white solid. The *β*-olefinated products is known compound[20] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *α* : *β* = 1 : 4.4. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 15.2 Hz, 1H$^{\alpha}$), 7.62 (d, *J* = 15.4 Hz, 1H$^{\beta}$), 7.35 (dd, *J* = 7.7, 1.4 Hz, 1H$^{\alpha}$), 7.30 – 7.21 (m, 2H$^{\beta}$), 7.18 – 7.03 (m, 2H$^{\alpha}$+1H$^{\beta}$), 6.83 (d, *J* = 15.4 Hz, 1H$^{\beta}$), 6.72 (d, *J* = 15.2 Hz, 1H$^{\alpha}$), 3.19 – 3.12 (m, 3H$^{\alpha+\beta}$), 3.09 – 3.02 (m, 3H$^{\alpha+\beta}$), 2.34 – 2.20 (m, 6H$^{\alpha+\beta}$). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 166.9 (C_q), 166.8 (C_q), 142.5 (CH), 141.3 (CH), 138.5 (C_q), 137.2 (C_q), 136.9 (C_q), 135.8 (C_q), 134.9 (C_q), 133.0 (C_q), 130.8 (CH), 130.0 (CH), 128.9 (CH), 125.5 (CH), 125.3 (CH), 124.2 (CH), 119.2 (CH), 116.1 (CH), 37.4 (CH_3), 35.9 (CH_3), 20.5 (CH_3), 19.7 (CH_3), 19.7 (CH_3), 15.5 (CH_3). IR (ATR): 3058, 2930, 2858, 1725, 1649, 1611, 1489, 1392, 1260, 1139 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 204 (100) $[M + H]^+$, 226 (52) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{13}H_{17}NO + H]^+$ 204.1383 found 204.1386.



(*E*)-3-(2,3-Dimethylphenyl)acrylic acid (*α*-32) & (*E*)-3-(3,4-dimethylphenyl)acrylic acid (*β*-32)

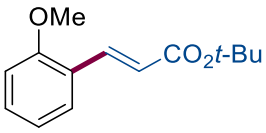
The general procedure **A** was followed using *o*-xylene (**1a**) (482.6 µL, 4.0 mmol, 20 equiv) and acrylic acid (**2g**) (13.7 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L3** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **32** (21.9 mg, 62%) as a white solid. The *α* and *β*-olefinated products are known compounds[21] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *α* : *β* = 1 : 6.7. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 15.7 Hz, 1H$^{\alpha}$), 7.75 (d, *J* = 16.0 Hz, 1H$^{\beta}$), 7.43 (dd, *J* = 7.8, 1.4 Hz, 1H$^{\alpha}$), 7.33 (s, 1H$^{\beta}$), 7.30 (dd, *J* = 7.8, 1.9 Hz, 1H$^{\beta}$), 7.23 – 7.09 (m, 2H$^{\alpha}$+1H$^{\beta}$), 6.40

(d, J = 15.9 Hz, 1H$^{\beta}$), 6.34 (d, J = 15.7 Hz, 1H$^{\alpha}$), 2.46 – 2.21 (m, 6H$^{\alpha+\beta}$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.7 (C_q), 147.3 (CH), 140.0 (C_q), 137.2 (C_q), 131.7 (C_q), 130.2 (CH), 129.5 (CH), 126.0 (CH), 115.9 (CH), 19.8 (CH_3), 19.7 (CH_3). IR (ATR): 3020, 2921, 2855, 1681, 1618, 1503, 1418, 1281, 1235, 1214 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 177 (100) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{11}H_{12}O_2$ + H]$^+$ 177.0910 found 177.0905.



(*E*)-Ethyl-3-(2-methoxyphenyl)acrylate (*o*-33) & (*E*)-ethyl-3-(4-methoxyphenyl)acrylate (*p*-33)

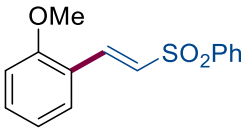
The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and ethyl acrylate (**2d**) (21.7 µL, 0.20 mmol, 1.0 equiv). **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **33** (22.2 mg, 54%) as a colorless oil. The *o* and *p*-olefinated products are known compounds[22] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 11.5 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ^o = 7.99 (d, J = 16.2 Hz, 1H), 7.50 (dd, J = 7.6, 1.8 Hz, 1H), 7.34 (ddd, J = 8.2, 7.4, 1.7 Hz, 1H), 7.00 – 6.91 (m, 1H), 6.91 (dd, J = 8.4, 1.0 Hz, 1H), 6.53 (d, J = 16.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.5 (C_q), 158.3 (C_q), 140.0 (CH), 131.3 (CH), 129.6 (CH), 128.9 (CH), 123.4 (C_q), 120.6 (CH), 118.8 (CH), 114.3 (CH), 111.1 (CH), 60.3 (CH_2), 55.4 (CH_3), 14.3 (CH_3). IR (ATR): 2976, 2938, 2839, 1709, 1632, 1465, 1249, 1172, 1029, 753 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 229 (100) [M + Na]$^+$, 207 (10) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{12}H_{14}O_3$ + Na]$^+$ 229.0835 found 229.0831.



(*E*)-*t*-Butyl-3-(2-methoxyphenyl)acrylate (*o*-34) & (*E*)-*t*-butyl-3-(4-methoxyphenyl)acrylate (*p*-34)

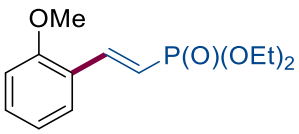
The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and *tert*-butyl acrylate (**2e**) (29.1 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as

ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **34** (23.4 mg, 50%) as a colorless oil. The *o* and *p*-olefinated products are known compounds[23] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = >20 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ^o = 7.91 (d, *J* = 16.1 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.32 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.90 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.44 (d, *J* = 16.1 Hz, 1H), 3.87 (s, 3H), 1.53 (s, 9H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ^o = 166.8 (C_q), 158.2 (C_q), 138.9 (CH), 131.1 (CH), 128.7 (CH), 123.6 (C_q), 120.6 (CH), 120.6 (CH), 111.0 (CH), 80.2 (C_q), 55.4 (CH_3), 28.2 (CH_3). IR (ATR): 3003, 2977, 2930, 2839, 1704, 1598, 1489, 1322, 1148, 987 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 257 (100) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{14}H_{18}O_3 + Na]^+$ 257.1148 found 257.1141.



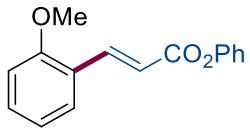
(*E*)-1-Methoxy-2-(2-(phenylsulfonyl)vinyl)benzene (35)

The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and (vinylsulfonyl)benzene (**2b**) (33.6 mg, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **35** (25.8 mg, 47%) as a colorless oil. The product is known compound.[24] The ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* > 20 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 6.9 Hz, 2H), 7.89 (d, *J* = 15.4 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.56 – 7.49 (m, 2H), 7.44 – 7.34 (m, 2H), 7.08 (d, *J* = 15.5 Hz, 1H), 6.96 (td, *J* = 7.5, 1.1 Hz, 1H), 6.92 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.88 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.8 (C_q), 141.2 (C_q), 138.5 (CH), 133.1 (CH), 132.5 (CH), 130.8 (CH), 129.2 (CH), 127.8 (CH), 127.6 (CH), 121.2 (C_q), 120.8 (CH), 111.2 (CH), 55.5 (CH_3). IR (ATR): 3062, 2973, 2944, 2843, 1597, 1483, 1306, 1249, 1141, 1081 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 297 (100) $[M + Na]^+$, 275 (60) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{15}H_{14}O_3S + Na]^+$ 297.0556 found 297.0553.



(*E*)-Diethyl-(2-methoxystyryl)phosphonate (36)

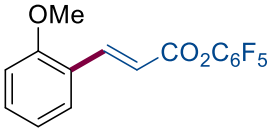
The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and diethyl vinylphosphonate (**2c**) (30.7 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 1:1) yielded **36** (24.9 mg, 46%) as a colorless oil. The product is known compound.[25] The ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* > 20 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, *J* = 23.6, 17.7 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.32 (ddd, *J* = 8.8, 7.3, 1.7 Hz, 1H), 6.94 (td, *J* = 7.5, 1.1 Hz, 1H), 6.89 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.31 (dd, *J* = 19.6, 17.7 Hz, 1H), 4.17 – 4.06 (m, 4H), 3.85 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.0 (C_q), 144.0 (d, *J* = 7.8 Hz, CH), 131.3 (CH), 128.4 (CH), 123.7 (d, *J* = 23.3 Hz, C_q), 120.5 (CH), 114.2 (d, *J* = 190 Hz, CH), 111.1 (CH), 61.7 (s, CH_2), 61.6 (s, CH_2), 55.4 (CH_3), 16.4 (s, CH_3), 16.3 (s, CH_3). ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 20.5. IR (ATR): 2981, 2938, 2904, 1598, 1487, 1464, 1292, 1243, 1163, 1018 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 271 (100) $[M + H]^+$, 293 (30) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{13}H_{19}O_4P + H]^+$ 271.1094 found 271.1096.



(*E*)-Phenyl-3-(2-methoxyphenyl)acrylate (*o*-37) & (*E*)-phenyl-3-(4-methoxyphenyl)acrylate (*p*-37)

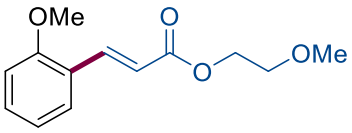
The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and phenyl acrylate (**2h**) (27.5 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1) yielded **37** (30.0 mg, 59%) as a yellow oil. The *p*-olefinated product is known compound[26] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 2 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 16.2 Hz, 1H^{o}), 7.84 (d, *J* = 15.9 Hz, 1H^{p}), 7.61 – 7.52 (m, 1H^{o}+2H^{p}), 7.46 – 7.35 (m, 3H^{o}+2H^{p}), 7.29 – 7.21 (m, 1H^{o+p}), 7.06 – 7.12 (m, 2H^{o+p}), 6.91 – 7.04 (m, 2H^{o+p}), 6.75 (d, *J* = 16.1 Hz, 1H^{o}), 6.51 (d, *J* = 15.9 Hz, 1H^{p}), 3.92 (s, 3H^{o}), 3.86 (s, 3H^{p}). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.9 (C_q), 165.7 (C_q), 161.7 (C_q), 158.5 (C_q), 150.9 (C_q), 150.9 (C_q), 146.2 (CH), 142.0 (CH), 131.9 (CH), 130.0 (CH), 129.4 (CH), 129.3 (CH), 129.3 (CH), 126.9 (C_q), 125.6 (CH), 125.6 (CH), 123.1 (C_q), 121.7 (CH), 121.6 (CH), 120.7 (CH), 117.8 (CH), 114.6 (CH), 114.4 (CH), 111.2 (CH), 55.5 (CH_3), 55.4 (CH_3). IR (ATR): 3072, 2937, 2838, 1720, 1630, 1598, 1488, 1309, 1194, 1134 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 277 (100)

[M + Na]$^+$, 255 (64) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{16}H_{14}O_3$ + Na]$^+$ 277.0835 found 277.0833.



(*E*)-perfluorophenyl-3-(2-methoxyphenyl)acrylate (*o*-38) & (*E*)-perfluorophenyl-3-(4-methoxyphenyl)acrylate (*p*-38)

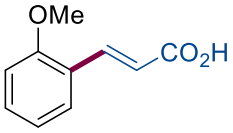
The general procedure **A** was followed using anisole (**1y**) (108.7 µL, 1.0 mmol, 5.0 equiv) and perfluorophenyl acrylate (**2i**) (32.0 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **38** (45.5 mg, 72%). The site selectivity was determined by ^{1}H-NMR, ***p*-38** was known compound,[27] *o* : *p* = 2 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 16.1 Hz, 1H^o), 7.90 (d, *J* = 15.9 Hz, 1H^p), 7.58 – 7.54 (m, 1H^o+2H^p), 7.43 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H^o), 7.01 (td, *J* = 7.5, 1.1 Hz, 1H^o), 6.98 – 6.93 (m, 1H^o+2H^p), 6.77 (d, *J* = 16.1 Hz, 1H^o), 6.51 (d, *J* = 15.9 Hz, 1H^p), 3.93 (s, 3H^o), 3.87 (s, 3H^p). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 163.2 (C_q), 163.0 (C_q), 162.4 (C_q), 158.9 (C_q), 149.1 (CH), 145.0 (CH), 142.83 – 142.15 (m, C_q), 140.7 – 140.2 (m, C_q), 139.2 – 138.6 (m, C_q), 138.6 – 138.1 (m, C_q), 137.1 – 136.7 (m, C_q), 132.8 (CH), 130.5 (CH), 129.8 (CH), 126.3 (C_q), 125.7 – 125.2 (m, C_q), 122.5 (C_q), 120.8 (CH), 114.6 (CH), 114.6 (CH), 111.3 (CH), 111.3 (CH), 55.5 (CH_3), 55.4 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ -152.37 – -152.77 (m), -158.41 – -158.80 (m), -162.49 – -162.98 (m). IR (ATR): 2964, 2843, 2666, 1748, 1625, 1599, 1516, 1251, 1101, 995 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 367 (100) [M + Na]$^+$, 345 (0) [M + H]$^+$. HR-MS (ESI): *m*/*z* calcd. for [$C_{16}H_9F_5O_3$ + Na]$^+$ 367.0364 found 367.0369.



(*E*)-2-Methoxyethyl-3-(2-methoxyphenyl)acrylate (39)

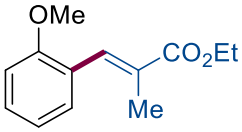
The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and 2-methoxyethyl acrylate (**2j**) (25.7 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 50:1 to 10:1) yielded **39**

(31.2 mg, 66%) as a colorless oil. The ratio of the isomers was determined by the crude ^{1}H-NMR, *o* : *p* = 5 : 1. The *o*-product was isolated. ^{1}H-NMR (600 MHz, $CDCl_3$): δ^o = 8.01 (d, *J* = 16.1 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.34 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 6.96 – 6.93 (m, 1H), 6.90 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.59 (d, *J* = 16.1 Hz, 1H), 4.41 – 4.31 (m, 2H), 3.87 (s, 3H), 3.69 – 3.63 (m, 2H), 3.42 (s, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ^o = 167.5 (C_q), 158.4 (C_q), 140.6 (CH), 131.5 (CH), 129.1 (CH), 123.3 (C_q), 120.7 (CH), 118.3 (CH), 111.1 (CH), 70.6 (CH_2), 63.4 (CH_2), 59.0 (CH_3), 55.4 (CH_3). IR (ATR): 2939, 2887, 2838, 1708, 1630, 1598, 1438, 1267, 1161, 1124 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 259 (100) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{13}H_{16}O_4 + Na]^+$ 259.0941 found 259.0938.



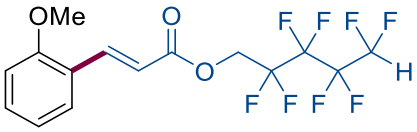
(*E*)-3-(2-Methoxyphenyl)acrylic acid (40)

The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5equiv) and acrylic acid (**2g**) (13.7 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 5:1) yielded **40** (21.0 mg, 59%) as a white solid. The product is known compound.[28] The ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* > 20 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 16.1 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.42 – 7.34 (m, 1H), 6.98 (td, *J* = 7.6, 1.1 Hz, 1H), 6.93 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.55 (d, *J* = 16.1 Hz, 1H), 3.90 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.6 (C_q), 158.6 (C_q), 142.5 (CH), 132.0 (CH), 129.3 (CH), 123.0 (C_q), 120.7 (CH), 117.6 (CH), 111.2 (CH), 55.5 (CH_3). IR (ATR): 2970, 2936, 2839, 1686, 1599, 1488, 1464, 1248, 1163, 1026 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 201 (30) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{10}H_{10}O_3 + Na]^+$ 201.0522 found 201.0519.



(*E*)-Ethyl-3-(2-methoxyphenyl)-2-methylacrylate (*o*-41) & (*E*)-ethyl-3-(4-methoxyphenyl)-2-methylacrylate (*p*-41)

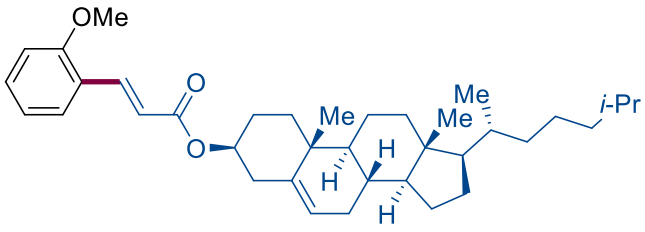
The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and ethyl methacrylate (**2k**) (24.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 15:1 to 10:1) yielded **41** (18.9 mg, 43%) as a yellow oil. The ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 7 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1H^{o}), 7.64 (d, *J* = 1.6 Hz, 1H^{p}), 7.42 – 7.27 (m, 2H^{o+p}), 7.01 – 6.87 (m, 2H^{o+p}), 4.31 – 4.23 (m, 2H^{o+p}), 3.86 (s, 3H^{o}), 3.84 (s, 3H^{p}), 2.13 (d, *J* = 1.5 Hz, 3H^{p}), 2.05 (d, *J* = 1.5 Hz, 3H^{o}), 1.40 – 1.31 (m, 3H^{o+p}). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.6 (C_q), 157.5 (C_q), 134.6 (CH), 130.2 (CH), 129.7 (CH), 128.7 (C_q), 124.9 (C_q), 120.0 (CH), 110.4 (CH), 60.7 (CH_2), 55.4 (CH_3), 14.3 (CH_3), 14.2 (CH_3). IR (ATR): 2980, 2935, 2837, 1703, 1597, 1487, 1366, 1241, 1104, 1027 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 243 (100) $[M + Na]^+$, 221 (30) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{13}H_{16}O_3 + Na]^+$ 243.0992 found 243.0989.



(*E*)-2,2,3,3,4,4,5,5-Octafluoropentyl-3-(2-methoxyphenyl)acrylate (*o*-42) & (*E*)-2,2,3,3,4,4,5,5-octafluoropentyl-3-(4-methoxyphenyl)acrylate (*p*-42)

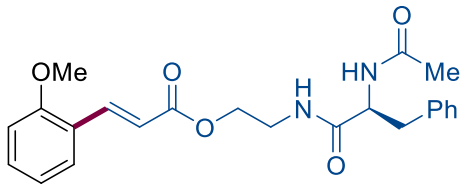
The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol 5.0 equiv) and 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (**2l**) (40.7 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 24 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **42** (50.2 mg, 64%) as a white solid. The site selectivity was determined by NOESY NMR and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 4.6 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 16.2 Hz, 1H^{o}), 7.74 (d, *J* = 16.0 Hz, 1H^{p}), 7.56 – 7.47 (m, 1H^{o}+2H^{p}), 7.38 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H^{o}), 7.03 – 6.88 (m, 2H^{o+p}), 6.58 (d, *J* = 16.1 Hz, 1H^{o}), 6.34 (d, *J* = 15.9 Hz, 1H^{p}), 6.07 (tt, *J* = 51.9, 5.4 Hz, 1H^{o+p}), 4.74 – 4.64 (m, 2H^{o+p}), 3.90 (s, 3H^{o}), 3.85 (s, 3H^{p}). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.8 (C_q), 165.5 (C_q), 161.9 (C_q), 158.6 (C_q), 146.9 (CH), 142.8 (CH), 132.1 (CH), 130.1 (CH), 129.4 (CH), 126.6 (C_q), 122.8 (C_q), 120.7 (CH), 116.2 (CH), 114.7 (t, *J* = 31.0 Hz, C_q), 114.4 (CH), 113.2 (CH), 111.2 (CH), 110.29 – 109.63 (m, C_q), 107.58 (t, *J* = 30.8 Hz, C_q), 105.06 (t, *J* = 31.2 Hz, C_q), 59.34 (t, *J* = 26.6 Hz, CH_2), 55.5 (CH_3), 55.4 (CH_3). ^{19}F-NMR (282 MHz, $CDCl_3$): δ = -119.35 – -120.70 (m), -125.22 – -126.43 (m), -130.06 – -130.94 (m), -137.52 – -

138.99 (m). IR (ATR): 3016, 2968, 2843, 1731, 1630, 1601, 1490, 1251, 1169, 1028 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 415 (100) $[M + Na]^+$, 393 (30) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{15}H_{12}O_3F_8 + Na]^+$ 415.0551 found 415.0556.



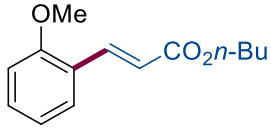
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-[(*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl (*E*)-3-(2-methoxyphenyl)acrylate (*o*-43) & (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-[(*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl (*E*)-3-(4-methoxyphenyl)acrylate (*p*-43)

The general procedure **A** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-[(*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl acrylate (**2m**) (88.1 mg, 0.20 mmol, 1.0 equiv) at 60 °C for 30 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **43** (47.0 mg, 43%) as a white solid. The *o* and *p*-olefinated products are known compounds[29] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 13.4 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ^o = 7.97 (d, *J* = 16.1 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.34 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.91 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 5.40 (d, *J* = 5.6 Hz, 1H), 4.79 – 4.72 (m, 1H), 3.89 (s, 3H), 2.44 – 2.39 (m, 2H), 2.04 – 1.79 (m, 5H), 1.72 – 0.97 (m, 24H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.7 Hz, 6H), 0.69 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ^o = 166.9 (C_q), 158.3 (C_q), 139.8 (CH), 139.8 (C_q), 131.3 (CH), 128.9 (CH), 123.5 (C_q), 122.6 (CH), 120.6 (CH), 119.2 (CH), 111.1 (CH), 73.9 (CH), 56.7 (CH), 56.1 (CH), 55.4 (CH_3), 50.0 (CH), 42.3 (C_q), 39.7 (CH_2), 39.5 (CH_2), 38.2 (CH_2), 37.0 (CH_2), 36.6 (C_q), 36.2 (CH_2), 35.8 (CH), 31.9 (CH_2), 31.9 (CH), 28.2 (CH_2), 28.0 (CH), 27.9 (CH_2), 24.3 (CH_2), 23.8 (CH_2), 22.8 (CH_3), 22.6 (CH_3), 21.0 (CH_2), 19.4 (CH_3), 18.7 (CH_3), 11.9 (CH_3). IR (ATR): 2946, 2868, 2152, 1710, 1631, 1438, 1321, 1248, 1167, 1014 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 569 (100) $[M + Na]^+$, 547 (30) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{37}H_{54}O_3 + H]^+$ 569.3965 found 569.3955.



(*S,E*)-2-(2-Acetamido-3-phenylpropanamido)ethyl-3-(2-methoxyphenyl)acrylate (*o*-44) & (*S,E*)-2-(2-acetamido-3-phenylpropanamido)ethyl-3-(4-methoxyphenyl)acrylate (*p*-44)

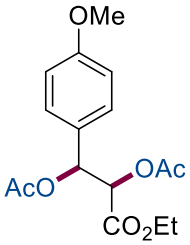
The general procedure **B** was followed using anisole (**1y**) (108.6 µL, 1.0 mmol, 5.0 equiv) and (*S*)-2-(2-acetamido-3-phenylpropanamido)ethyl acrylate (**2n**) (60.9 mg, 0.20 mmol, 1.0 equiv) at 60 °C for 24 h. **L12** was used as ligand. Isolation by column chromatography (DCM/MeOH = 20:1) yielded **44** (43.5 mg, 53%) as a white solid. The site selectivity was determined by ^{1}H-NMR and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 11.5 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ^o = 7.96 (d, *J* = 16.1 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.35 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.22 – 7.16 (m, 3H), 6.96 (td, *J* = 7.5, 1.0 Hz, 1H), 6.91 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.50 – 6.39 (m, 1H), 4.68 (td, *J* = 8.0, 6.3 Hz, 1H), 4.21 – 4.01 (m, 2H), 3.87 (s, 3H), 3.59 – 3.35 (m, 2H), 3.13 – 2.97 (m, 2H), 1.96 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ^o = 171.1 (C_q), 170.0 (C_q), 167.3 (C_q), 158.3 (C_q), 140.9 (CH), 136.6 (C_q), 131.7 (CH), 129.1 (CH), 129.0 (CH), 128.6 (CH), 127.0 (CH), 123.1 (C_q), 120.7 (CH), 117.8 (CH), 111.1 (CH), 62.7 (CH_2), 55.4 (CH_3), 54.6 (CH), 38.7 (CH_2), 38.6 (CH_2), 23.1 (CH_3). IR (ATR): 3280, 3070, 3030, 2925, 2837, 1711, 1320, 1247, 1159, 698 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 433 (100) $[M + Na]^+$, 411 (40) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{23}H_{26}N_2O_5 + Na]^+$ 433.1734 found 433.1715.



(*E*)-*n*-Butyl-3-(2-methoxyphenyl)acrylate (*o*-45) & (*E*)-*n*-butyl-3-(4-methoxyphenyl)acrylate (*p*-45)

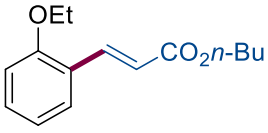
The general procedure **A** was followed using anisole (**1y**) (108.7 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand.

Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **45** (24.4 mg, 52%) as a colorless oil. The *o* and *p*-olefinated products are known compounds[9] and the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 16.3 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ^o = 7.99 (d, *J* = 16.2 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.34 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 6.97 – 6.93 (m, 1H), 6.91 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.53 (d, J = 16.1 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.88 (s, 3H), 1.74 – 1.64 (m, 2H), 1.50 – 1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ^o = 167.6 (C_q), 158.3 (C_q), 139.9 (CH), 131.3 (CH), 128.9 (CH), 123.4 (C_q), 120.6 (CH), 118.8 (CH), 111.1 (CH), 64.2 (CH_2), 55.4 (CH_3), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3060, 2959, 2934, 2872, 1708, 1634, 1304, 1165, 978, 775 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 257 (100) $[M + Na]^+$, 235 (20) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{14}H_{18}O_3 + Na]^+$ 257.1148 found 257.1152.



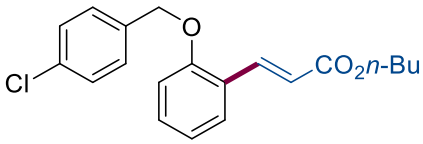
3-Ethoxy-1-(4-methoxyphenyl)-3-oxopropane-1,2-diyl diacetate (46)

The product is known compound.[30] ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.27 (m, 2H), 6.89 – 6.84 (m, 2H), 6.18 (dd, *J* = 24.8, 4.9 Hz, 1H), 5.46 – 5.25 (m, 1H), 4.21 – 4.07 (m, 2H), 3.79 (d, *J* = 1.4 Hz, 3H), 2.13 – 2.05 (m, 6H), 1.27 – 1.10 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.9 (C_q), 169.8 (C_q), 169.4 (C_q), 169.4 (C_q), 167.0 (C_q), 166.9 (C_q), 159.8 (C_q), 159.8 (C_q), 128.9 (CH), 128.3 (CH), 127.5 (C_q), 127.3 (C_q), 113.8 (CH), 113.7 (CH), 74.3 (CH), 73.5 (CH), 73.5 (CH), 73.1 (CH), 61.7 (CH_2), 61.7 (CH_2), 55.2 (CH_3), 55.2 (CH_3), 20.9 (CH_3), 20.8 (CH_3), 20.5 (CH_3), 20.4 (CH_3), 14.0 (CH_3), 13.9 (CH_3). IR (ATR): 3012, 2977, 2200, 2041, 1710, 1614, 1516, 1372, 1219, 1033 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 347 (100) $[M + Na]^+$, 363 (20) $[M + K]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{16}H_{20}O_7 + Na]^+$ 347.1101 found 347.1097.



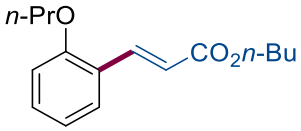
(*E*)-*n*-Butyl-3-(2-ethoxyphenyl)acrylate (47)

The general procedure **A** was followed using ethoxybenzene (**1z**) (126.3 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **47** (27.3 mg, 55%) as a colorless oil. The ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 20 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ^o = 8.02 (d, *J* = 16.2 Hz, 1H), 7.51 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.31 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 6.94 (td, *J* = 7.4, 0.6 Hz, 1H), 6.89 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 1.76 – 1.62 (m, 2H), 1.51 – 1.40 (m, 5H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.7 (C_q), 157.7 (C_q), 140.1 (CH), 131.3 (CH), 128.8 (CH), 123.5 (C_q), 120.5 (CH), 118.6 (CH), 112.1 (CH), 64.2 (CH_2), 64.0 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 14.8 (CH_3), 13.8 (CH_3). IR (ATR): 2960, 2933, 2252, 1702, 1631, 1317, 1173, 908, 733, 650 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 249 (40) $[M + H]^+$, 271 (100) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{15}H_{20}O_3 + Na]^+$ 271.1305 found 271.1299.



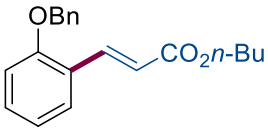
(*E*)-*n*-Butyl-3-(2-((4-chlorobenzyl)oxy)phenyl)acrylate (48)

The general procedure **A** was followed using 1-chloro-4-(phenoxymethyl)benzene (**1a'**) (218.7 mg, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 24 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **48** (36.2 mg, 52%) as a colorless oil. The ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 9 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ^o = 8.06 (d, *J* = 16.2 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.38 – 7.35 (m, 4H), 7.31 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 6.98 (td, *J* = 7.7, 1.1 Hz, 1H), 6.92 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.52 (d, *J* = 16.1 Hz, 1H), 5.12 (s, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 1.74 – 1.64 (m, 2H), 1.50 – 1.38 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.4 (C_q), 157.0 (C_q), 139.5 (CH), 135.1 (C_q), 133.8 (C_q), 131.3 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 123.9 (C_q), 121.2 (CH), 119.0 (CH), 112.6 (CH), 69.6 (CH_2), 64.2 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2960, 2933, 2252, 1703, 1632, 1599, 1271, 1172, 909, 736 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 345 (40) $[M + H]^+$, 367 (100) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{20}H_{21}O_3Cl + Na]^+$ 367.1071 found 367.1073.



(*E*)-*n*-Butyl-3-(2-propoxyphenyl)acrylate (49)

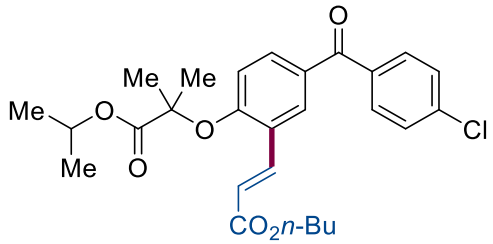
The general procedure **A** was followed using propoxybenzene (**1b'**) (140.5 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **49** (21.6 mg, 41%) as a colorless oil. The ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 20 : 1. ^{1}H-NMR (600 MHz, $CDCl_3$): δ^o = 8.02 (d, *J* = 16.2 Hz, 1H), 7.51 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.31 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 6.94 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.73 – 1.65 (m, 2H), 1.50 – 1.39 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 167.6 (C_q), 157.8 (C_q), 140.0 (CH), 131.3 (CH), 128.7 (CH), 123.5 (C_q), 120.4 (CH), 118.5 (CH), 112.0 (CH), 69.9 (CH_2), 64.1 (CH_2), 30.8 (CH_2), 22.5 (CH_2), 19.2 (CH_2), 13.7 (CH_3), 10.6 (CH_3). IR (ATR): 2963, 2876, 2252, 1702, 1631, 1270, 1173, 906, 729, 649 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 263 (10) $[M + H]^+$, 285 (100) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{16}H_{22}O_3 + Na]^+$ 285.1461 found 285.1460.



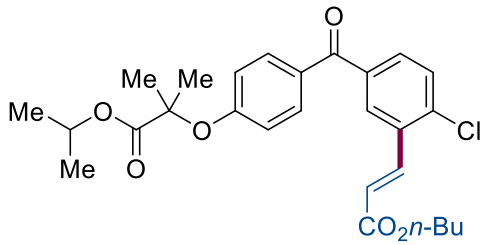
(*E*)-*n*-Butyl-3-(2-(benzyloxy)phenyl)acrylate (50)

The general procedure **A** was followed using (benzyloxy)benzene (**1c'**) (184.2 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 60 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1 to 15:1) yielded **50** (39.3 mg, 60%) as a colorless oil. **50** is a known compound.[31] The ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, *o* : *p* = 20 : 1. ^{1}H-NMR (400 MHz, $CDCl_3$): δ^o = 8.09 (d, *J* = 16.2 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.27 (m, 6H), 7.01 – 6.93 (m, 2H), 6.54 (d, *J* = 16.1 Hz, 1H), 5.17 (s, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 1.76 – 1.62 (m, 2H), 1.51 – 1.38 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ

= 167.6 (C_q), 157.4 (C_q), 139.8 (CH), 136.7 (C_q), 131.4 (CH), 128.7 (CH), 128.7 (CH), 128.0 (CH), 127.2 (CH), 124.0 (C_q), 121.1 (CH), 119.0 (CH), 112.8 (CH), 70.4 (CH_2), 64.3 (CH_2), 30.8 (CH_2), 19.3 (CH_2), 13.8 (CH_3). IR (ATR): 2960, 2873, 2253, 1702, 1632, 1272, 1173, 905, 729, 649 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 311 (10) $[M + H]^+$, 333 (100) $[M + Na]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{20}H_{22}O_3 + Na]^+$ 333.1461 found 333.1467.



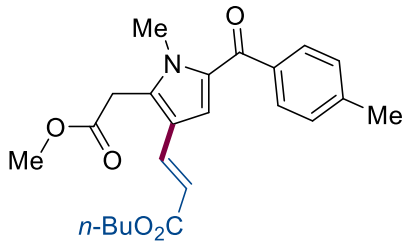
(*E*)-butyl-3-(5-(4-chlorobenzoyl)-2-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)acrylate (53a)



(*E*)-butyl-3-(2-chloro-5-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)phenyl)acrylate (53b)

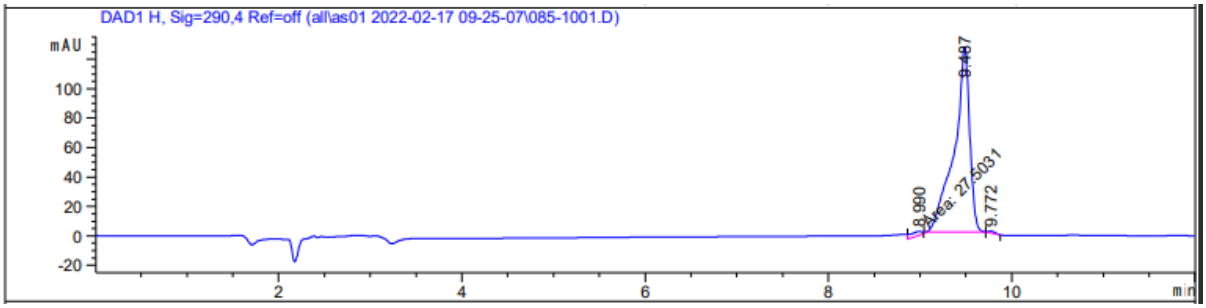
The general procedure **B** was followed using fenofibrate (**51a**) (720.2 mg, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 20:1) yielded 5**3** (54.1 mg, 56%) as a mixture. The site selectivity was determined by ^{1}H-NMR and NOESY NMR, the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, **53a** : **53b** = 8 : 1. For **53a**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 16.0 Hz, 1H), 8.00 (d, *J* = 2.3 Hz, 1H), 7.71 – 7.69 (m, 3H), 7.49 – 7.45 (m, 2H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.49 (d, *J* = 16.2 Hz, 1H), 5.08 (p, *J* = 6.3 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.71 (s, 6H), 1.71 – 1.63 (m, 2H), 1.48 – 1.40 (m, 2H), 1.20 (s, 3H), 1.19 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 193.8 (C_q), 172.7 (C_q), 167.1 (C_q), 157.9 (C_q), 138.9 (CH), 138.7 (C_q), 136.0 (C_q), 132.5 (CH), 131.1 (CH), 130.8 (CH), 130.2 (C_q), 128.7 (CH), 125.2 (C_q), 120.1 (CH), 115.3 (CH), 80.4

(C_q), 69.5 (CH), 64.5 (CH_2), 30.7 (CH_2), 25.4 (CH_3), 21.5 (CH_3), 19.2 (CH_2), 13.7 (CH_3). For **53b**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.09 (d, J = 16.0 Hz, 1H), 7.99 (d, J = 2.1 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.67 (dd, J = 8.2, 2.0 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 6.90 – 6.86 (m, 2H), 6.45 (d, J = 16.0 Hz, 1H), 5.13 – 5.04 (m, 1H), 4.21 (t, J = 6.7 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.67 (s, 6H), 1.48 – 1.40 (m, 2H), 1.21 (s, 3H), 1.20 (s, 3H), 0.96 (t, J = 7.4 Hz, 3H). IR (ATR): 2960, 2935, 2254, 1710, 1655, 1488, 1386, 1266, 1177, 909 cm^{-1}. MS (ESI) m/z (relative intensity): 509 (100) $[M + Na]^+$, 487 (20) $[M + H]^+$. HR-MS (ESI): m/z calcd. for $[C_{27}H_{31}ClO_6 + Na]^+$ 509.1701 found 509.1691. After the reaction, 676.9 mg **51a** was recycled.



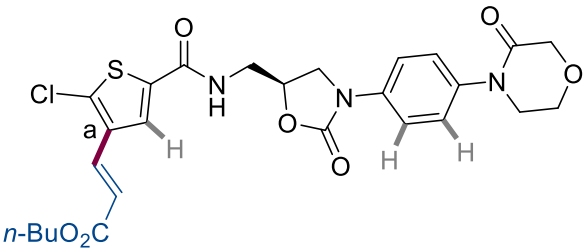
(*E*)-butyl-3-(5-(2-methoxy-2-oxoethyl)-1-methyl-2-(4-methylbenzoyl)-1*H*-pyrrol-3-yl)acrylate (54)

The general procedure **B** was followed using protected tolmetin (**51b**) (271.3 mg, 1.0 mmol, 5 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **54** (70.8 mg, 90%). The site selectivity was determined by 1H-NMR and NOESY NMR. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 15.6 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H), 6.90 (s, 1H), 6.12 (d, J = 15.6 Hz, 1H), 4.16 (t, J = 6.7 Hz, 2H), 3.95 (s, 3H), 3.85 (s, 2H), 3.75 (s, 3H), 2.44 (s, 3H), 1.69 – 1.59 (m, 2H), 1.44 – 1.32 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 186.3 (C_q), 168.9 (C_q), 167.7 (C_q), 142.7 (C_q), 136.7 (C_q), 135.7 (CH), 135.2 (C_q), 132.0 (C_q), 129.5 (CH), 129.0 (CH), 118.9 (CH), 118.7 (C_q), 115.4 (CH), 64.2 (CH_2), 52.7 (CH_3), 33.5 (CH_3), 30.8 (CH_2), 30.3 (CH_2), 21.6 (CH_3), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2355, 2134, 2037, 1734, 1670, 1623, 1465, 1249, 1163, 906 cm^{-1}. MS (ESI) m/z (relative intensity): 420 (100) $[M + Na]^+$, 398 (30) $[M + H]^+$. HR-MS (ESI): m/z calcd. for $[C_{23}H_{27}NO_5 + Na]^+$ 420.1781 found 420.1776. After the reaction, 208.5 mg **51b** was recycled. Purity of **54** by LC/MS is 96.3%.



Signal 3: DAD1 H, Sig=290,4 Ref=off

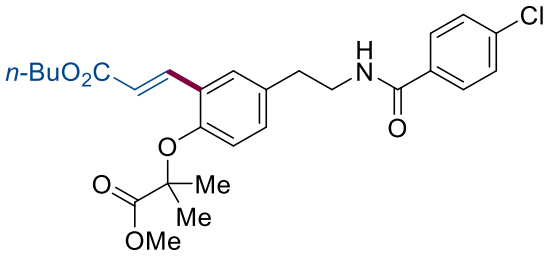
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.990	MM	0.1331	27.50310	2.86478	1.8118
2	9.487	BB	0.1617	1484.20679	125.77014	97.7738
3	9.772	BB	0.0822	6.29132	1.21966	0.4144



(*S,E*)-butyl-3-(2-chloro-5-(((2-oxo-3-(4-(3-oxomorpholino)phenyl)oxazolidin-5-yl)methyl)carbamoyl)thiophen-3-yl)acrylate (55a)

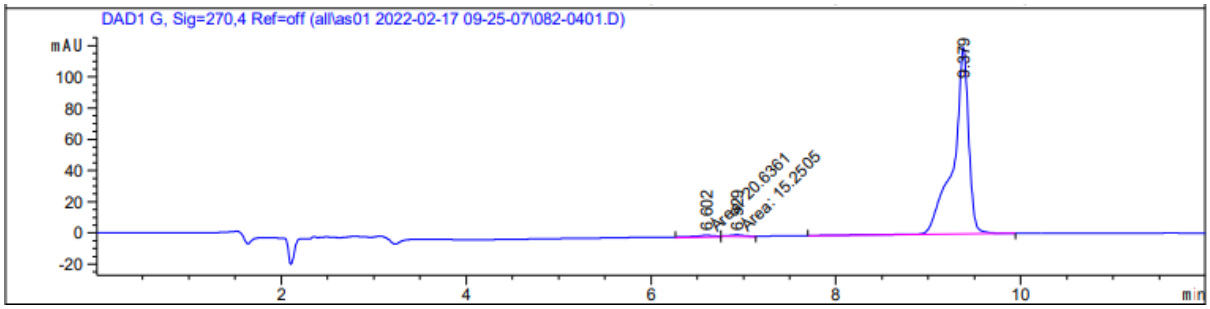
The general procedure **B** was followed using rivaroxaban (**51c**) (180.0 mg, 0.41 mmol, 2.1 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by two column chromatographies (*n*-hexane/Acetone = 1:1 & EtOAc) yielded **55a** (41.4 mg, 37%). Other isomers were also observed, but we failed to isolated and characterized. The site selectivity was determined by NOESY, the ratio of the isomers was determined by the ^{1}H-NMR of the product mixture, **55a** : others = 9 : 1. For **55a**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.75 (s, 1H), 7.60 (d, J = 16.0 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.32 – 7.28 (m, 2H), 6.27 (d, J = 16.0 Hz, 1H), 4.81 – 4.76 (m, 1H), 4.33 (d, J = 1.1 Hz, 2H), 4.20 (t, J = 6.7 Hz, 2H), 4.05 – 4.00 (m, 3H), 3.81 (dd, J = 9.1, 6.7 Hz, 1H), 3.74 – 3.69 (m, 3H), 3.68 – 3.63 (m, 1H), 1.71 – 1.65 (m, 2H), 1.46 – 1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 167.1 (C_q), 166.7 (C_q), 161.5 (C_q), 154.5 (C_q), 137.3 (C_q), 136.9 (C_q), 136.6 (C_q), 136.2 (C_q), 134.2 (C_q), 133.9 (CH), 126.3 (CH), 125.6 (CH), 120.3 (CH), 119.0 (CH),

71.6 (CH), 68.5 (CH_2), 64.8 (CH_2), 64.0 (CH_2), 49.7 (CH_2), 47.6 (CH_2), 42.3 (CH_2), 30.7 (CH_2), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 3323, 3285, 2961, 2928, 2007, 1754, 1713, 1644, 1517, 1278 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 584 (100) $[M + Na]^+$, 562 (10) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{26}H_{28}ClN_3O_7S + Na]^+$ 584.1229 found 584.1229. After the reaction, 148.7 mg **51c** was recycled.



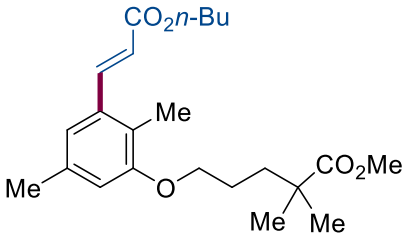
(*E*)-butyl-3-(5-(2-(4-chlorobenzamido)ethyl)-2-((1-methoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)acrylate (56)

The general procedure **B** was followed using protected bezafibrate (**51d**) (375.8 mg, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 2:1) yielded **56** (30.4 mg, 30%). The site selectivity was determined by ^{1}H-NMR and NOESY NMR. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 16.5 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.40 (d, *J* = 2.3 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.10 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.43 (d, *J* = 16.2 Hz, 1H), 6.09 (brs, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 3H), 3.69 – 3.65 (m, 2H), 2.87 (t, *J* = 7.0 Hz, 2H), 1.72 – 1.66 (m, 2H), 1.63 (s, 6H), 1.48 – 1.41 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 174.5 (C_q), 167.3 (C_q), 166.4 (C_q), 153.0 (C_q), 139.6 (CH), 137.7 (C_q), 132.9 (C_q), 132.3 (C_q), 131.0 (CH), 128.9 (CH), 128.5 (CH), 128.2 (CH), 126.5 (C_q), 119.0 (CH), 117.6 (CH), 79.9 (C_q), 64.3 (CH_2), 52.6 (CH_3), 41.1 (CH_2), 34.8 (CH_2), 30.8 (CH_2), 25.3 (CH_3), 19.2 (CH_2), 13.7 (CH_3). IR (ATR): 2959, 2866, 2253, 1731, 1706, 1485, 1248, 1173, 905, 729 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 524 (100) $[M + Na]^+$, 502 (40) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{27}H_{32}ClNO_6 + Na]^+$ 524.1810 found 524.1807. After the reaction, 327.6 mg **51d** was recycled. Purity of **56** by LC/MS is 97.5%.

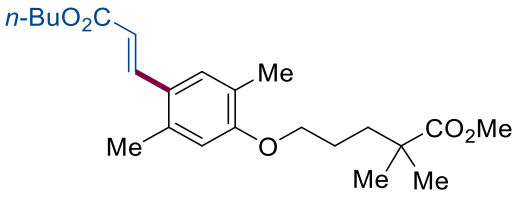


Signal 2: DAD1 G, Sig=270,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.602	MM	0.2889	20.63613	1.19053	1.4495
2	6.929	MM	0.2214	15.25048	1.14785	1.0712
3	9.379	BB	0.1615	1387.83069	119.49273	97.4794



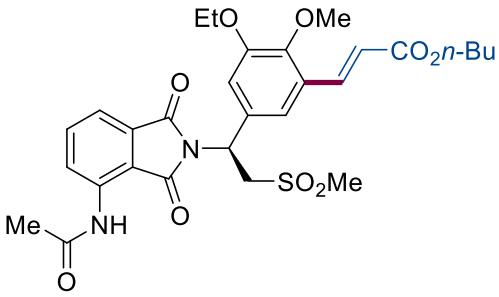
(*E*)-methyl-5-(3-(3-butoxy-3-oxoprop-1-en-1-yl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (57a)



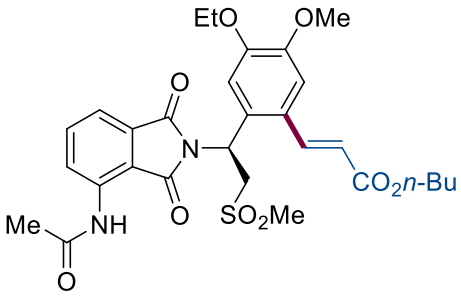
(*E*)-methyl-5-(4-(3-butoxy-3-oxoprop-1-en-1-yl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (57b)

The general procedure **B** was followed using protected gemfibrozil (**51e**) (265.2 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 20:1) yielded **57a** (13.4 mg, 17%) and **57b** (51.4 mg, 66%). The site selectivity was determined by ^{1}H-NMR and HMBC. For **57a**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.99 (d, J = 15.8 Hz, 1H), 6.98 (s, 1H),

6.65 (s, 1H), 6.33 (d, J = 15.8 Hz, 1H), 4.21 (t, J = 6.7 Hz, 2H), 3.91 (t, J = 5.6 Hz, 2H), 3.67 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H), 1.76 – 1.66 (m, 6H), 1.48 – 1.40 (m, 2H), 1.22 (s, 6H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 178.2 (C_q), 167.2 (C_q), 157.1 (C_q), 142.8 (CH), 136.0 (C_q), 134.3 (C_q), 123.8 (C_q), 119.5 (CH), 119.0 (CH), 113.5 (CH), 68.4 (CH_2), 64.3 (CH_2), 51.7 (CH_3), 42.1 (C_q), 37.1 (CH_2), 30.8 (CH_2), 25.2 (CH_3), 25.1 (CH_2), 21.4 (CH_3), 19.2 (CH_2), 13.7 (CH_3), 11.2 (CH_3). For **57b**, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 15.8 Hz, 1H), 7.37 (s, 1H), 6.58 (s, 1H), 6.26 (d, J = 15.8 Hz, 1H), 4.19 (t, J = 6.7 Hz, 2H), 3.94 (t, J = 5.6 Hz, 2H), 3.66 (s, 3H), 2.40 (s, 3H), 2.18 (s, 3H), 1.77 – 1.64 (m, 6H), 1.49 – 1.39 (m, 2H), 1.22 (s, 6H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 178.3 (C_q), 167.7 (C_q), 158.7 (C_q), 141.9 (CH), 137.2 (C_q), 128.7 (CH), 125.1 (C_q), 124.8 (C_q), 116.0 (CH), 112.8 (CH), 68.0 (CH_2), 64.2 (CH_2), 51.8 (CH_3), 42.1 (C_q), 37.0 (CH_2), 30.9 (CH_2), 25.2 (CH_3), 25.1 (CH_2), 19.8 (CH_3), 19.3 (CH_2), 15.8 (CH_3), 13.8 (CH_3). IR (ATR): 2983, 2934, 1738, 1606, 1505, 1373, 1240, 1164, 1094, 1046 cm^{-1}. MS (ESI) m/z (relative intensity): 413 (100) $[M + Na]^+$, 391 (10) $[M + H]^+$. HR-MS (ESI): m/z calcd. for $[C_{23}H_{34}O_5 + Na]^+$ 413.2298 found 413.2296. After the reaction, 206.2 mg **1e** was recycled.

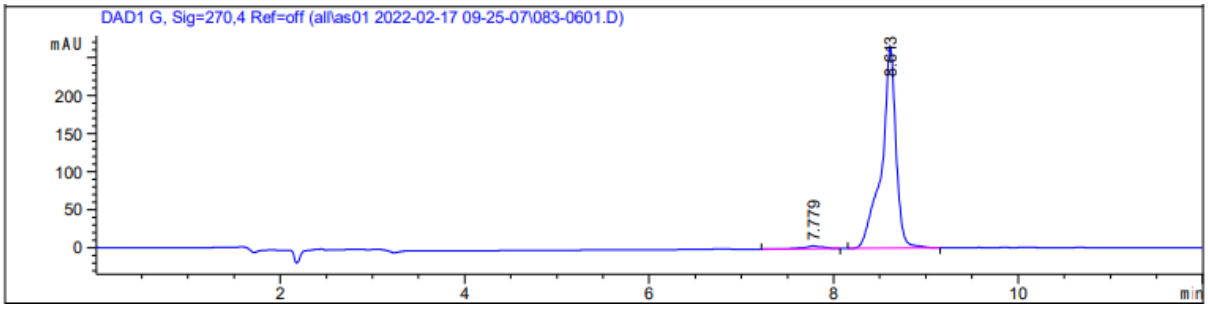


(*S*,*E*)-butyl-3-(5-(1-(4-acetamido-1,3-dioxoisoindolin-2-yl)-2-(methylsulfonyl)ethyl)-3-ethoxy-2-methoxyphenyl)acrylate (58a)



(*S*,*E*)-butyl-3-(2-(1-(4-acetamido-1,3-dioxoisoindolin-2-yl)-2-(methylsulfonyl)ethyl)-4-ethoxy-5-methoxyphenyl)acrylate (58b)

The general procedure **B** was followed using Apremilast (**51f**) (460.5 mg, 1.0 mmol, 5 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 1:1) yielded **58a** (22.4 mg, 19%) and **58b** (15.1 mg, 13%). The site selectivity was determined by ^{1}H-NMR and NOESY NMR. For **58a**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.44 (s, 1H), 8.76 (dd, *J* = 8.6, 0.8 Hz, 1H), 7.92 (d, *J* = 16.6 Hz, 1H), 7.65 (ddd, *J* = 8.5, 7.3, 0.4 Hz, 1H), 7.49 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 6.51 (d, *J* = 16.2 Hz, 1H), 5.88 (dd, *J* = 10.8, 3.9 Hz, 1H), 4.62 (ddd, *J* = 14.4, 10.9, 0.7 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 3.66 (dd, *J* = 14.3, 4.0 Hz, 1H), 2.92 (s, 3H), 2.28 (s, 3H), 1.74 – 1.66 (m, 2H), 1.52 – 1.40 (m, 5H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 169.4 (C_q), 169.2 (C_q), 167.5 (C_q), 167.0 (C_q), 152.8 (C_q), 148.9 (C_q), 138.6 (CH), 137.7 (C_q), 136.2 (CH), 132.7 (C_q), 131.0 (C_q), 129.0 (C_q), 125.1 (CH), 120.5 (CH), 118.6 (CH), 118.3 (CH), 115.0 (C_q), 114.4 (CH), 64.7 (CH_2), 64.5 (CH_2), 61.1 (CH_3), 54.0 (CH_2), 48.4 (CH), 41.8 (CH_3), 30.8 (CH_2), 25.0 (CH_3), 19.2 (CH_2), 14.6 (CH_3), 13.7 (CH_3). For **58b**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.45 (s, 1H), 8.77 (dd, *J* = 8.6, 0.8 Hz, 1H), 8.32 (d, *J* = 15.5 Hz, 1H), 7.66 (dd, *J* = 8.5, 7.3 Hz, 1H), 7.50 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.34 (s, 1H), 7.03 (s, 1H), 6.30 (d, *J* = 15.5 Hz, 1H), 6.28 (dd, *J* = 11.0, 3.7 Hz, 1H), 4.56 (ddd, *J* = 14.7, 10.9, 0.9 Hz, 1H), 4.25 (td, *J* = 6.7, 2.0 Hz, 2H), 4.20 – 4.13 (m, 2H), 3.89 (s, 3H), 3.54 (dd, *J* = 14.6, 3.7 Hz, 1H), 2.95 (s, 3H), 2.27 (s, 3H), 1.77 – 1.71 (m, 2H), 1.50 (t, *J* = 7.0 Hz, 3H), 1.52 – 1.45 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 169.6 (C_q), 169.2 (C_q), 167.8 (C_q), 166.6 (C_q), 150.4 (C_q), 149.6 (C_q), 139.9 (CH), 137.7 (C_q), 136.2 (CH), 131.1 (C_q), 128.8 (C_q), 125.7 (C_q), 125.1 (CH), 120.4 (CH), 118.4 (CH), 115.0 (C_q), 112.2 (CH), 109.4 (CH), 64.7 (CH_2), 64.6 (CH_2), 56.0 (CH_3), 54.5 (CH_2), 44.6 (CH), 41.2 (CH_3), 30.8 (CH_2), 25.0 (CH_3), 19.2 (CH_2), 14.6 (CH_3), 13.8 (CH_3). IR (ATR): 2983, 2925, 2357, 2186, 1699, 1169, 990, 968, 951, 756 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 609 (100) $[M + Na]^+$, 587 (10) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{29}H_{34}N_2O_9S + Na]^+$ 609.1877 found 609.1879. After the reaction, 397.8 mg **51f** was recycled. Purity of **58a** by LC/MS is 98.2%.



Signal 2: DAD1 G, Sig=270,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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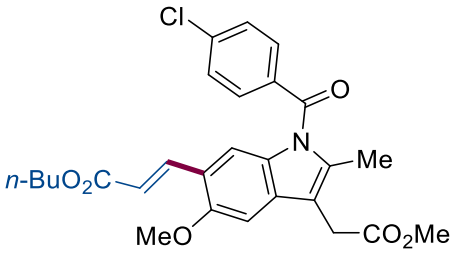
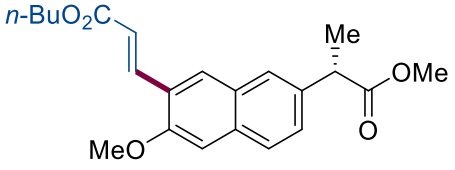
2	8.613	BB	0.1509	2888.75781	265.53745	98.2276

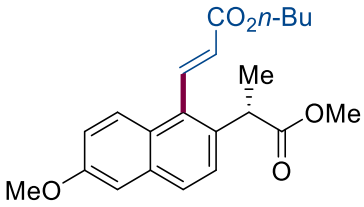


(*E*)-butyl-3-(1-(4-chlorobenzoyl)-5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1H-indol-6-yl)acrylate (59)

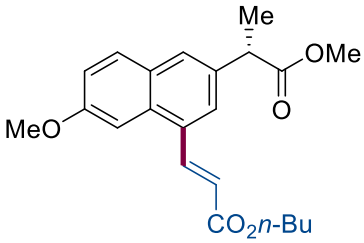
The general procedure **B** was followed using protected indomethacin (**51g**) (742.2 mg, 2.0 mmol, 10 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **59** (65.7 mg, 66%). The site selectivity was determined by ^{1}H-NMR and NOESY NMR. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 16.0 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.52 – 7.48 (m, 2H), 7.23 (s, 1H), 6.93 (s, 1H), 6.23 (d, J = 16.1 Hz, 1H), 4.17 (t, J = 6.7 Hz, 2H), 3.93 (s, 3H), 3.71 (s, 3H), 3.67 (s, 2H), 2.35 (s, 3H), 1.73 – 1.61 (m, 2H), 1.49 – 1.36 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.1 (C_q), 168.2 (C_q), 167.7 (C_q), 155.2 (C_q), 140.7 (CH), 139.7 (C_q), 137.6 (C_q), 133.6 (C_q), 132.2 (C_q), 131.2 (CH), 130.7 (C_q), 129.3 (CH), 120.1 (C_q), 117.7 (CH), 114.4 (CH), 112.7 (C_q), 99.6 (CH), 64.2 (CH_2), 55.9 (CH_3), 52.7 (CH_3), 30.8 (CH_2), 30.2 (CH_2), 19.2 (CH_2), 13.8 (CH_3), 13.7 (CH_3). IR (ATR): 2955, 2933, 2872, 1737, 1693, 1593, 1430, 1329, 1224, 1167 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 520 (100) $[M + Na]^+$, 498 (50) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{27}H_{28}ClNO_6 + Na]^+$ 520.1497 found 520.1491. After the reaction, 665.6 mg **51g** was recycled.



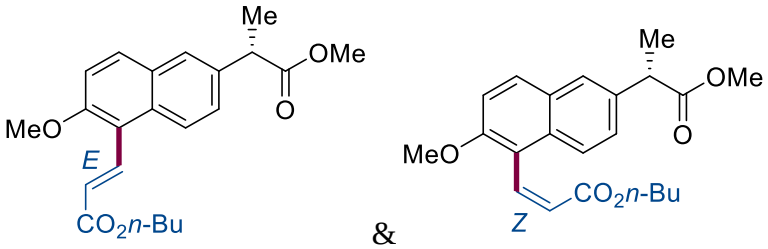
(*S,E*)-butyl-3-(3-methoxy-7-(1-methoxy-1-oxopropan-2-yl)naphthalen-2-yl)acrylate (60a)



(*S,E*)-butyl-3-(3-methoxy-7-(1-methoxy-1-oxopropan-2-yl)naphthalen-1-yl)acrylate (60b)



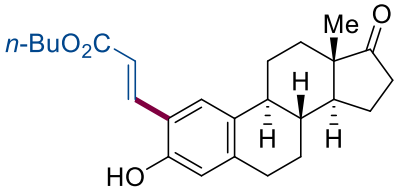
(*S,E*)-butyl-3-(7-methoxy-3-(1-methoxy-1-oxopropan-2-yl)naphthalen-1-yl)acrylate (60c)



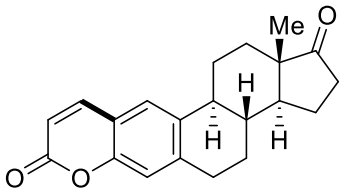
(*S,E*)-butyl-3-(2-methoxy-6-(1-methoxy-1-oxopropan-2-yl)naphthalen-1-yl)acrylate & (*S,Z*)-butyl-3-(2-methoxy-6-(1-methoxy-1-oxopropan-2-yl)naphthalen-1-yl)acrylate (60d)

The general procedure **B** was followed using protected Naproxen (**51h**) (244.3 mg, 1.0 mmol, 5 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **60a** (20.5 mg, 28%), **60b** and **60c** (24.6 mg, 33%, 6% of **60b,** 27% of **60c**) as a mixture, and **60d** (17.3 mg, 23%). The site selectivity was determined by ^{1}H-NMR and NOESY NMR. For **60a**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.06 (dd, *J* = 16.1, 0.6 Hz, 1H), 7.94 (t, *J* = 0.6 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 1.3, 0.7 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.11 (s, 1H), 6.69 (d, *J* = 16.1 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 3.98 (s, 3H), 3.86 (q, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 1.74 – 1.68 (m, 2H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.50 – 1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 175.0 (C_q), 167.5 (C_q), 156.1 (C_q), 140.3 (CH), 136.3

(C_q), 134.3 (C_q), 129.4 (CH), 128.3 (C_q), 127.3 (CH), 126.9 (CH), 126.4 (CH), 125.5 (C_q), 120.2 (CH), 105.5 (CH), 64.4 (CH_2), 55.5 (CH_3), 52.1 (CH_3), 45.3 (CH), 30.8 (CH_2), 19.2 (CH_2), 18.5 (CH_3), 13.8 (CH_3). For **60b**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 16.3 Hz, 1H), 7.87 (d, *J* = 9.1 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.16 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 6.24 (d, *J* = 16.3 Hz, 1H), 4.29 – 4.27 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 1H), 3.92 (s, 3H), 3.65 (s, 3H), 1.77 – 1.69 (m, 2H), 1.51 – 1.44 (m, 5H), 0.99 (t, *J* = 7.4, 3H). For **60c**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 15.7 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 1.8 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.55 (d, *J* = 15.7 Hz, 1H), 4.27 (t, *J* = 6.7 Hz, 2H), 3.95 (s, 3H), 3.86 (q, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 1.76 – 1.71 (m, 2H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.52 – 1.44 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 174.9 (C_q), 167.9 (C_q), 156.6 (C_q), 137.5 (CH), 135.9 (C_q), 131.9 (C_q), 131.3 (CH), 129.0 (C_q), 127.3 (CH), 126.7 (CH), 123.8 (CH), 123.4 (CH), 116.7 (C_q), 113.0 (CH), 64.4 (CH_2), 56.2 (CH_3), 52.1 (CH_3), 45.1 (CH), 30.8 (CH_2), 19.2 (CH_2), 18.4 (CH_3), 13.8 (CH_3). For **60d**, both *trans*- and *cis*-form were observed as a mixture, *E*:*Z*=5:1. For *trans*-form, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 16.2 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.29 (d, *J* = 9.1 Hz, 1H), 6.75 (d, *J* = 16.2 Hz, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 4.00 (s, 3H), 3.87 (q, *J* = 7.1 Hz, 1H), 3.67 (s, 3H), 1.76 – 1.70 (m, 2H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.51 – 1.43 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 174.9 (C_q), 167.9 (C_q), 156.6 (C_q), 137.5 (CH), 135.9 (C_q), 131.9 (C_q), 131.3 (CH), 129.0 (C_q), 127.3 (CH), 126.7 (CH), 123.8 (CH), 123.4 (CH), 116.7 (C_q), 113.0 (CH), 64.4 (CH_2), 56.2 (CH_3), 52.1 (CH_3), 45.1 (CH), 30.8 (CH_2), 19.2 (CH_2), 18.4 (CH_3), 13.8 (CH_3). For *cis*-form, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 9.1 Hz, 1H), 7.73 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.38 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.26 (d, *J* = 9.1 Hz, 1H), 7.24 (d, *J* = 11.9 Hz, 1H), 6.32 (d, *J* = 12.0 Hz, 1H), 3.91 (s, 3H), 3.85 (t, *J* = 6.6 Hz, 2H), 3.85 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 1.57 (d, *J* = 7.1 Hz, 3H), 1.20 – 1.14 (m, 2H), 0.95 – 0.90 (m, 2H), 0.69 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 175.0 (C_q), 166.1 (C_q), 153.5 (C_q), 137.4 (CH), 135.6 (C_q), 131.0 (C_q), 129.5 (CH), 128.7 (C_q), 126.5 (CH), 126.3 (CH), 124.5 (CH), 124.5 (CH), 119.2 (C_q), 113.1 (CH), 63.9 (CH_2), 56.4 (CH_3), 52.0 (CH_3), 45.2 (CH), 30.2 (CH_2), 18.8 (CH_2), 18.5 (CH_3), 13.5 (CH_3). IR (ATR): 2961, 2936, 2254, 1731, 1706, 1627, 1462, 1260, 1172, 905 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 393 (100) $[M + Na]^+$, 371 (0) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{22}H_{26}O_5 + Na]^+$ 393.1672 found 393.1673. After the reaction, 189.5 mg **51h** was recycled.

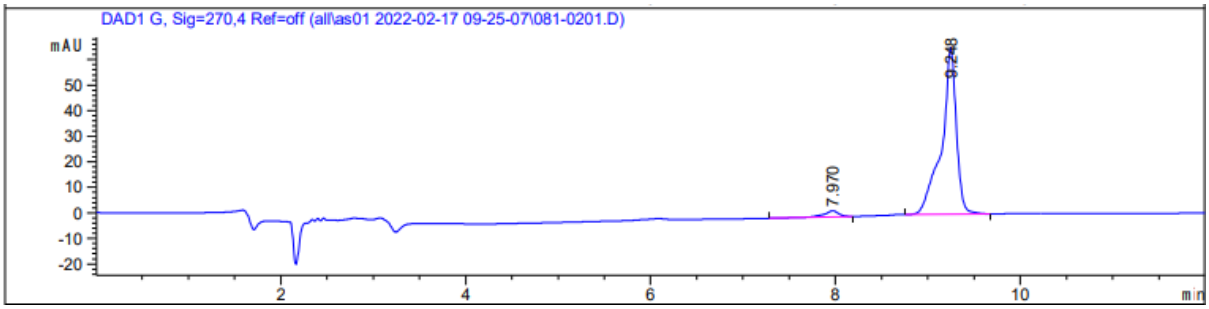


(*E*)-butyl-3-((8R,9S,13S,14S)-3-hydroxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-2-yl)acrylate (61)



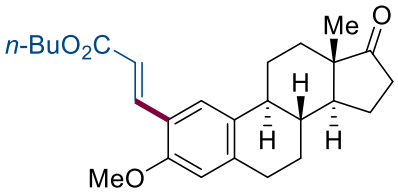
(*3aS,3bR,11bS,13aS*)-13a-methyl-2,3,3a,3b,4,5,11b,12,13,13a-decahydrocyclopenta[5,6]naphtho[1,2-*g*]chromene-1,8-dione (61')

The general procedure **B** was followed using Estrone (**51i**) (270.4 mg, 1.0 mmol, 5 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by recrystallization in EtOAc to remove **51i** and then column chromatography (*n*-hexane/EtOAc = 2:1) yielded **61** (17.1 mg, 22%). **61** and **61'** are known compounds,[32,33] we failed to obtain pure NMR spectra of **61'**. For **61**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.92 (d, J = 16.1 Hz, 1H), 7.38 (s, 1H), 6.56 (s, 1H), 6.56 (d, J = 16.1 Hz, 1H), 5.70 (s, 1H), 4.21 (t, J = 6.7 Hz, 2H), 2.86 (dd, J = 9.0, 4.3 Hz, 2H), 2.54 – 2.48 (m, 1H), 2.46 – 2.40 (m, 1H), 2.27 – 2.20 (m, 1H), 2.19 – 2.11 (m, 1H), 2.09 – 1.94 (m, 3H), 1.72 – 1.65 (m, 2H), 1.65 – 1.60 (m, 1H), 1.59 – 1.48 (m, 4H), 1.48 – 1.40 (m, 3H), 0.96 (t, J = 7.4 Hz, 3H), 0.92 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 220.9 (C_q), 168.1 (C_q), 153.0 (C_q), 140.7 (C_q), 140.3 (CH), 132.5 (C_q), 126.3 (CH), 119.4 (C_q), 117.9 (CH), 116.3 (CH), 64.4 (CH_2), 50.4 (CH), 48.0 (C_q), 43.7 (CH), 38.2 (CH), 35.8 (CH_2), 31.5 (CH_2), 30.8 (CH_2), 29.4 (CH_2), 26.3 (CH_2), 25.9 (CH_2), 21.6 (CH_2), 19.2 (CH_2), 13.8 (CH_3), 13.8 (CH_3). IR (ATR): 3375, 2960, 2251, 1731, 1707, 1627, 1465, 1239, 1171, 907 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 419 (100) $[M + Na]^+$, 397 (10) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{25}H_{32}O_4 + Na]^+$ 419.2193 found 419.2187. After the reaction, 207.0 mg **51i** was recycled. Purity of **61** by LC/MS is 97.8%.

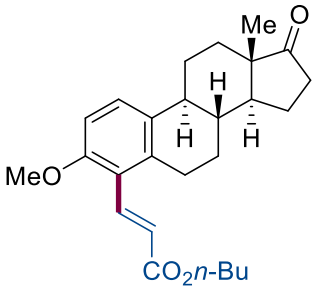


Signal 2: DAD1 G, Sig=270,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.970	BB	0.1580	26.71984	2.39721	3.5331
2	9.248	BB	0.1565	729.55542	65.23555	96.4669



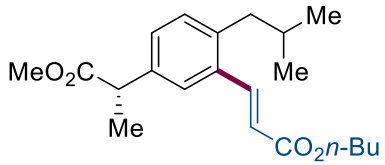
(*E*)-butyl-3-((*8R,9S,13S,14S*)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)acrylate (62a)



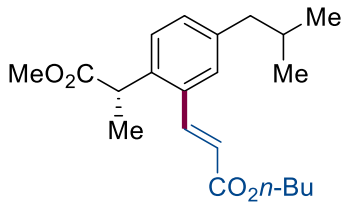
(*E*)-butyl-3-((*8R,9S,13S,14S*)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-4-yl)acrylate (62b)

The general procedure **B** was followed using Estrone-OMe (**51j**) (284.4 mg, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 5:1) yielded **62** (70.3

mg, 86%) as a mixture. we failed to obtain pure NMR spectra of **62b**. For **62a**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 16.1 Hz, 1H), 7.42 (d, *J* = 1.1 Hz, 1H), 6.63 (d, *J* = 1.3 Hz, 1H), 6.50 (d, *J* = 16.1 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.85 (s, 3H), 2.92 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.55 – 2.47 (m, 1H), 2.46 – 2.40 (m, 1H), 2.28 – 2.22 (m, 1H), 2.18 – 2.11 (m, 1H), 2.08 – 2.00 (m, 2H), 1.99 – 1.94 (m, 1H), 1.71 – 1.65 (m, 2H), 1.65 – 1.60 (m, 1H), 1.60 – 1.48 (m, 4H), 1.47 – 1.41 (m, 3H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.91 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 220.7 (C_q), 167.8 (C_q), 156.4 (C_q), 140.5 (C_q), 140.3 (CH), 132.0 (C_q), 126.2 (CH), 121.0 (C_q), 117.8 (CH), 111.4 (CH), 64.2 (CH_2), 55.5 (CH_3), 50.3 (CH), 47.9 (C_q), 43.7 (CH), 38.2 (CH), 35.8 (CH_2), 31.5 (CH_2), 30.8 (CH_2), 29.9 (CH_2), 26.4 (CH_2), 25.9 (CH_2), 21.6 (CH_2), 19.2 (CH_2), 13.8 (CH_3), 13.8 (CH_3). IR (ATR): 2933, 2867, 1710, 1610, 1500, 1408, 1377, 1285, 1256, 1179 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 433 (100) $[M + Na]^+$, 411 (50) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{26}H_{34}O_4 + Na]^+$ 433.2349 found 433.2342. After the reaction, 225.7 mg **51j** was recycled.



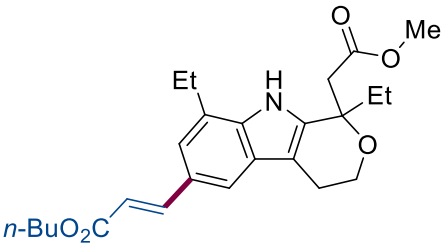
(*S*,*E*)-butyl-3-(2-isobutyl-5-(1-methoxy-1-oxopropan-2-yl)phenyl)acrylate (63a)



(*S*,*E*)-butyl-3-(5-isobutyl-2-(1-methoxy-1-oxopropan-2-yl)phenyl)acrylate (63b)

The general procedure **B** was followed using protected *S*-form ibuprofen (**51k**) (225.7 µL, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 30:1) yielded **63a** (14.4 mg, 21%) and **63b** (9.0 mg, 13%). **63b** was known compound.[34] The site selectivity was determined by ^{1}H-NMR and NOESY NMR. For **63a**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 15.8 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.23 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.71 (q, *J* = 7.2 Hz,

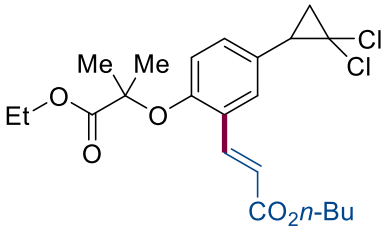
1H), 3.67 (s, 3H), 2.59 (d, *J* = 7.2 Hz, 2H), 1.80 (hept, *J* = 7.0 Hz, 1H), 1.73 – 1.67 (m, 2H), 1.50 (d, *J* = 7.2 Hz, 3H), 1.48 – 1.42 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.91 (s, 3H), 0.90 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 174.8 (C_q), 167.1 (C_q), 142.2 (CH), 140.3 (C_q), 138.51 (C_q), 133.4 (C_q), 131.3 (CH), 128.7 (CH), 125.5 (CH), 119.3 (CH), 64.4 (CH_2), 52.1 (CH_3), 45.0 (CH), 42.1 (CH_2), 30.8 (CH_2), 30.4 (CH), 22.4 (CH_3), 19.2 (CH_2), 18.5 (CH_3), 13.7 (CH_3). For **63b**, ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 15.7 Hz, 1H), 7.32 (d, *J* = 1.9 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.35 (d, *J* = 15.7 Hz, 1H), 4.22 (t, *J* = 6.5 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.66 (s, 3H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.86 (hept, *J* = 6.7 Hz, 1H), 1.73 – 1.67 (m, 2H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.46 – 1.43 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.91 (s, 3H), 0.90 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 174.8 (C_q), 166.9 (C_q), 142.0 (CH), 140.8 (C_q), 137.3 (C_q), 132.8 (C_q), 131.2 (CH), 127.7 (CH), 127.0 (CH), 120.7 (CH), 64.5 (CH_2), 52.1 (CH_3), 44.9 (CH_2), 40.7 (CH), 30.8 (CH_2), 30.1 (CH), 22.4 (CH_3), 22.4 (CH_3), 19.2 (CH_2), 18.6 (CH_3), 13.7 (CH_3). IR (ATR): 2960, 2936, 2169, 1738, 1717, 1449, 1372, 1234, 1169, 1045 cm^{-1}. MS (ESI) *m*/*z* (relative intensity): 369 (100) $[M + Na]^+$, 347 (0) $[M + H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{21}H_{30}O_4 + Na]^+$ 369.2036 found 369.2040. After the reaction, 176.9 mg **51k** was recycled.



(*E*)−butyl-3-(1,8-diethyl-1-(2-methoxy-2-oxoethyl)-1,3,4,9-tetrahydropyrano[3,4-b]indol-6-yl)acrylate (64b)

The general procedure **B** was followed using protected etodolac (**51l**) (301.4 mg, 1.0 mmol, 5.0 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 10:1) yielded **64** (70.9 mg, 83%). **64b** was separated while others couldn't be separated. The site selectivity was determined by ^{1}H-NMR. **64b** : others = 3:1. For **64b**, ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.31 (s, 1H), 7.82 (d, *J* = 15.9 Hz, 1H), 7.54 (d, *J* = 1.6 Hz, 1H), 7.25 (d, *J* = 1.5 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 4.09 – 4.02 (m, 1H), 3.97 – 3.90 (m, 1H), 3.73 (s, 3H), 3.07 – 2.71 (m, 6H), 2.15 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.99 (dq, *J* = 14.6, 7.2 Hz, 1H), 1.75 –

1.65 (m, 2H), 1.52 – 1.42 (m, 2H), 1.38 (t, J = 7.6 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.4 (C_q), 167.9 (C_q), 146.8 (CH), 137.2 (C_q), 135.9 (C_q), 127.1 (C_q), 126.5 (C_q), 126.5 (C_q), 120.0 (CH), 117.8 (CH), 114.6 (CH), 109.3 (C_q), 74.5 (C_q), 64.1 (CH_2), 60.5 (CH_2), 52.1 (CH_3), 42.7 (CH_2), 30.9 (CH_2), 30.5 (CH_2), 24.1 (CH_2), 22.3 (CH_2), 19.3 (CH_2), 13.8 (CH_3), 13.6 (CH_3), 7.5 (CH_3). IR (ATR): 3366, 2981, 2875, 1737, 1630, 1465, 1445, 1372, 1163, 1046 cm^{-1}. MS (ESI) m/z (relative intensity): 450 (100) $[M + Na]^+$, 428 (10) $[M + H]^+$. HR-MS (ESI): m/z calcd. for $[C_{25}H_{33}NO_5 + Na]^+$ 450.2251 found 450.2253. After the reaction, 208.6 mg **51l** was recycled.



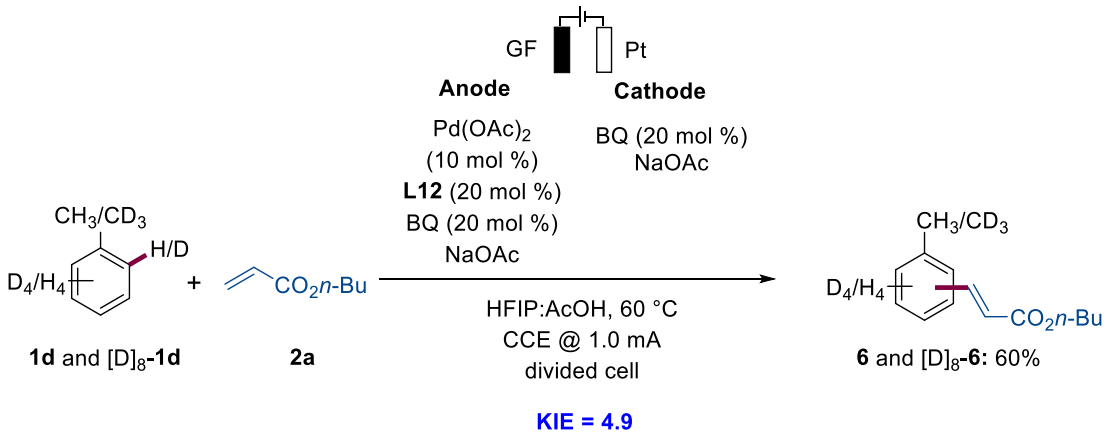
(*E*)-butyl-3-(5-(2,2-dichlorocyclopropyl)-2-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)acrylate (65)

The general procedure **B** was followed using protected ciprofibrate (**51m**) (236.9 µL, 0.93 mmol, 4.7 equiv) and *n*-butyl acrylate (**2a**) (28.8 µL, 0.20 mmol, 1.0 equiv) at 80 °C for 20 h. **L12** was used as ligand. Isolation by column chromatography (*n*-hexane/EtOAc = 15:1) yielded **65** (46.3 mg, 52%) as sole product. The site selectivity was determined by ^{1}H-NMR and NOESY NMR. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 16.2 Hz, 1H), 7.40 (d, J = 2.3 Hz, 1H), 7.11 (dd, J = 8.5, 2.3 Hz, 1H), 6.71 (d, J = 8.6 Hz, 1H), 6.48 (d, J = 16.2 Hz, 1H), 4.27 – 4.17 (m, 4H), 2.83 (dd, J = 10.6, 8.3 Hz, 1H), 1.96 (dd, J = 10.6, 7.5 Hz, 1H), 1.79 (t, J = 7.9 Hz, 1H), 1.74 – 1.60 (m, 8H), 1.52 – 1.38 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.9 (C_q), 167.3 (C_q), 153.8 (C_q), 139.7 (CH), 131.0 (CH), 128.7 (CH), 128.1 (C_q), 125.9 (C_q), 119.1 (CH), 116.83 (CH), 80.0 (C_q), 64.3 (CH_2), 61.6 (CH_2), 60.6 (C_q), 34.7 (CH), 30.8 (CH_2), 25.9 (CH_2), 25.4 (CH_3), 25.4 (CH_3), 19.2 (CH_2), 14.0 (CH_3), 13.8 (CH_3). IR (ATR): 2960, 2934, 1733, 1711, 1633, 1494, 1466, 1384, 1274, 1172 cm^{-1}. MS (ESI) m/z (relative intensity): 465 (100) $[M + Na]^+$, 443 (10) $[M + H]^+$. HR-MS (ESI): m/z calcd. for $[C_{22}H_{28}O_5Cl_2 + Na]^+$ 465.1206 found 465.1200. After the reaction, 255.3 mg **51m** was recycled.

KIE Studies

1) Procedure for **L12** KIE study (Intermolecular competition reaction)

General procedure was followed using **1d** (5.0 equiv), [D]$_8$-**1d** (5.0 equiv), *n*-butyl acrylates **2a** (0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), **L12** (7.9 mg, 20 mol %), 1,4-benzoquinone (4.3 mg, 20 mol %), NaOAc (66.0 mg, 4.0 equiv), AcOH (2.6 mL) and HFIP (1.3 mL) in the anodic chamber, 1,4-Benzoquinone (4.3 mg, 20 mol %) and NaOAc (66.0 mg, 4.0 equiv), AcOH (2.6 mL) and HFIP (1.3 mL) in the cathodic chamber. Electrocatalysis was performed at 60 °C with a constant current of 1.0 mA and a stirring rate of 500 rpm maintained for 20 h.



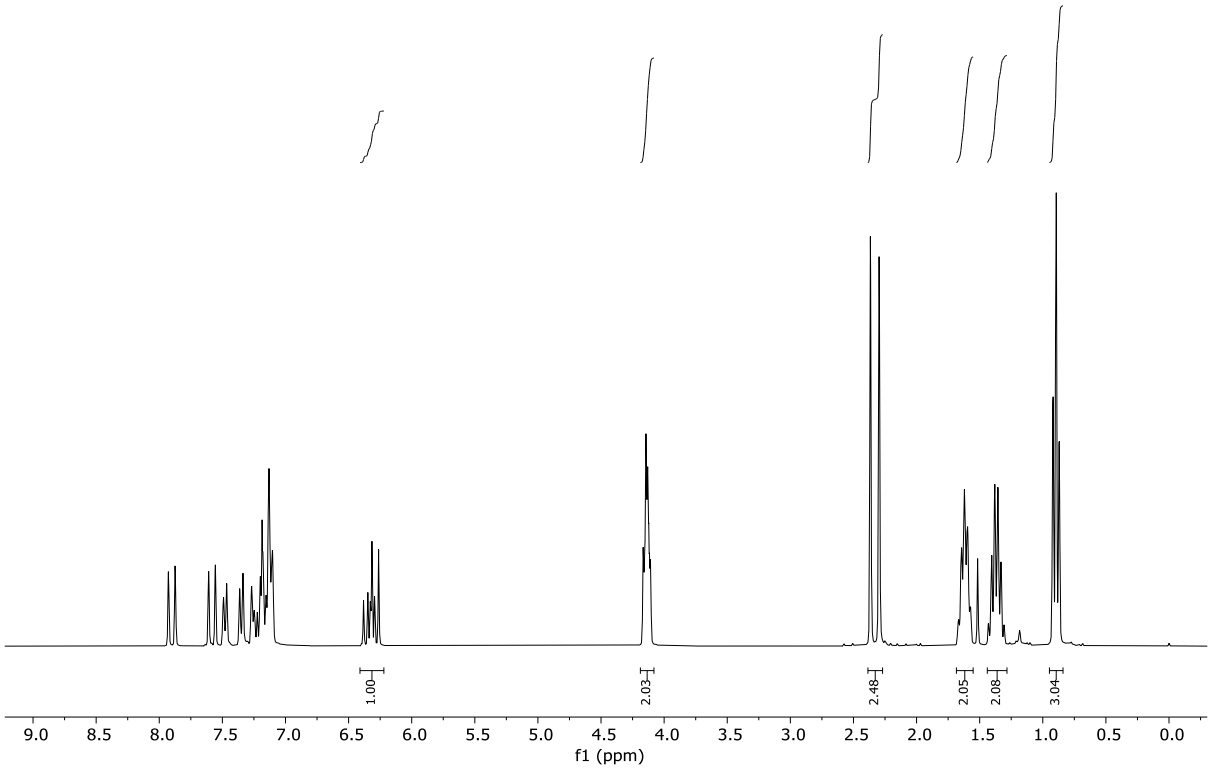


Figure S8. KIE study of **L12** by intermolecular competition reaction. Note: CH_3 of aromatic and CH_3 of butyl group should be compared.

2) Procedure for **L3** KIE study (Intermolecular competition reaction)

General procedure was followed using **1a** (10 equiv), $[D]_{10}$-**1a** (10 equiv), *n*-butyl acrylates **2a** (0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 10 mol %), **L3** (6.5 mg, 20 mol %), 1,4-benzoquinone (4.3 mg, 20 mol %), NaOAc (66.0 mg, 4.0 equiv), AcOH (2.6 mL) and HFIP (1.3 mL) in the anodic chamber, 1,4-Benzoquinone (4.3 mg, 20 mol %) and NaOAc (66.0 mg, 4.0 equiv), AcOH (2.6 mL) and HFIP (1.3 mL) in the cathodic chamber. Electrocatalysis was performed at 60 °C with a constant current of 1.0 mA and a stirring rate of 500 rpm maintained for 20 h.

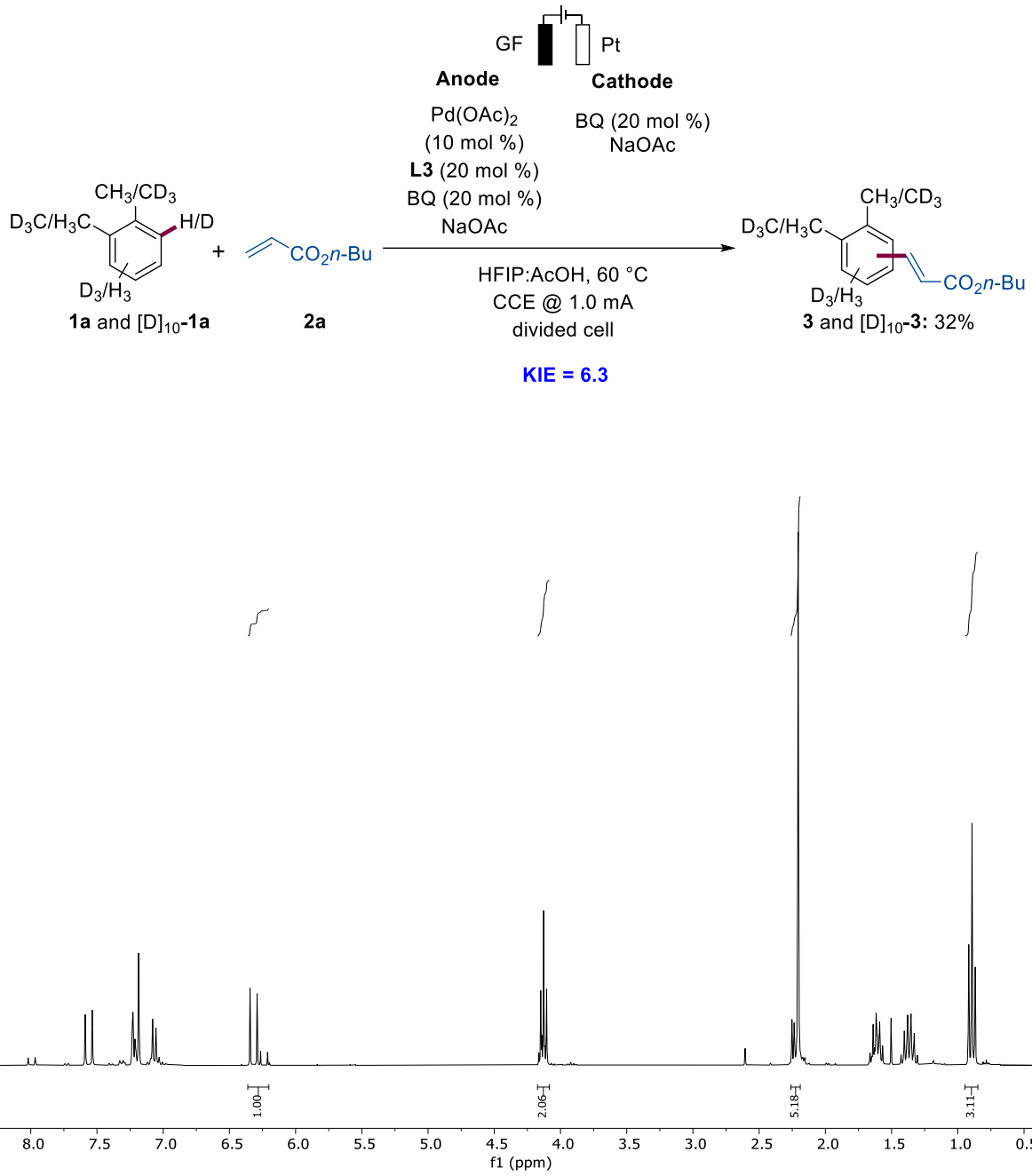


Figure S9. KIE study of **L3** by intermolecular competition reaction.

Synthesis of the palladium complex

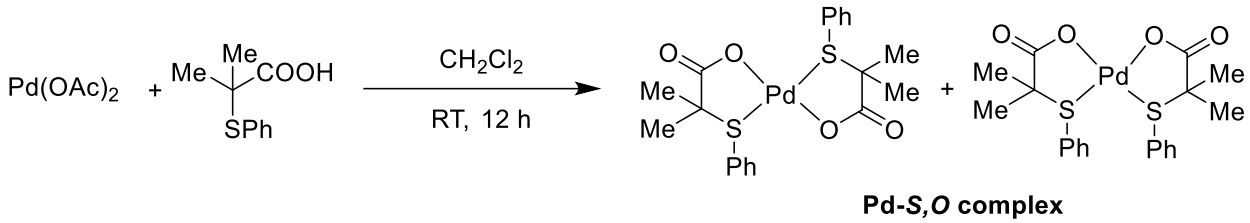


Figure S10 Synthesis of palladium complex

A solution of 2-methyl-2-(phenylthio)propanoic acid (**L12**) (49.0 mg, 0.25 mmol, 2.0 equiv) and $Pd(OAc)_2$ (28.0 mg, 0.125 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight. The reaction mixture was filtrated through a pad of Celite and concentrated. Excess amount of Et_2O was added in the reaction mixture and filtrated. The filtrate was evaporated under air to crystalize and afford **Pd-*S,O* complex**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.04 – 7.13 (m, 10H), 1.83 (m, 6H), 1.22 (t, J = 8.8 Hz, 6H). MS (ESI) *m*/*z* (relative intensity): 518 (100) $[M + Na]^+$, 497 (50) $[M + 2H]^+$. HR-MS (ESI): *m*/*z* calcd. for $[C_{20}H_{22}O_4PdS_2 + Na]^+$ 518.9893 found 518.9890. The analytical data correspond with those reported in the literature.[4]

Computational Methods

All DFT calculations were performed with Gaussian 16, Revision A.03 package.[35] Geometry optimizations were performed at the PBE0[36,37] level of theory including D3 dispersion corrections with a Becke-Johnson damping scheme (D3BJ)[38,39] in the gas phase. Analytical frequency calculations were carried out at the same level of theory to identify all stationary points as either minima (zero imaginary frequencies) or as transition states (one imaginary frequency). All atoms were described with a def2-SVP basis set,[39-42] while palladium was also described with a SSD pseudopotential.[43,44] The electronic energy was then further refined through single point calculations at the PBE0, PW6B95[45] or ωB97XD[46] level of theory including Grimme's D4 dispersion corrections[47,48] for PBE0 and PW6B95 functionals with a def2-TZVP basis set combined with SSD pseudopotential for palladium.[43,44] Solvent effects were taken into account through the use of steered molecular dynamics (SMD) solvent model[49] with a dielectric constant of $\varepsilon = 6.2528$, which corresponds to acetic acid as implemented in Gaussian 16. All reported energies are based on single electronic energies with addition of the gas-phase thermal and non-thermal corrections at 333.15 K and 1 atm.

Wiberg bond order analysis was performed using natural population analysis which is native to Gaussian 16 at the PBE0-D3(BJ)/def2-TZVP level of theory.

To better understand the *o*-xylene C–H activation elementary step, three possible pathways were probed by means of DFT calculations at the PBE0-D4/def2-TZVP+SMD(AcOH)//PBE0-D3BJ/def2-SVP level of theory (**Figure S11**). The difference between each path rely on the nature of the *S,O*-ligand coordination to the metal center. In the neutral pathway, the *S,O*-ligand underwent deprotonation prior to the coordination to the palladium (**Figure S11a**). C–H activation was proven to be facile with a barrier of 11.7 kcal mol^{-1}. Alternatively the C–H cleavage in the absence of acetate was also considered (**Figure S11b**). Such featured a considerably prohibitive barrier of 50.7 kcal mol^{-1}, providing support for an acetate assisted C–H cleavage mechanism. Additionally, the direct ligation of the *S,O*-ligand to the palladium center was also taken into consideration (**Figure S11c**). Here both C_{α}–H and C_{β}–H activation paths were probed, which presented associated barriers of 10.7 (TS(1-2)'$^{\alpha}$) and 10.3 kcal mol^{-1} (TS(1-2)'$^{\beta}$) respectively. Therefore the pathway leading to the formation of the β product was shown to be slightly kinetically preferred. This catalyst mode of action was proven to be the most energetically favored pathway. Other DFT functionals (PW6B95, **Figure S12** and wB97XD, **Figure S13**) were also accounted for, which further confirmed that the non-directed pallada-electrocatalyzed C–H activations follow a cationic pathway.

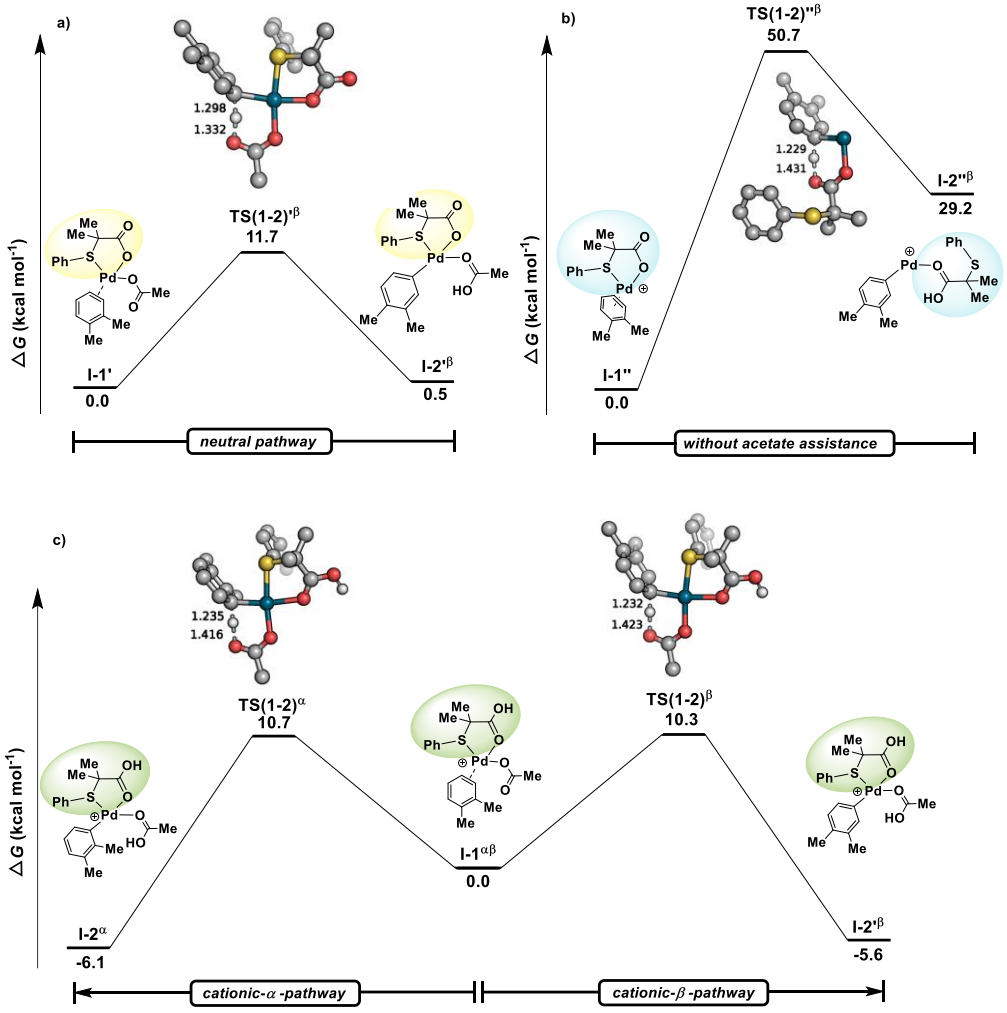


Figure S11. Computed relative Gibbs free energy profile ($\Delta G_{333.15}$) in kcal mol^{-1} for *o*-xylene with three possible C–H activation pathways: a) neutral pathway; b) without the assistance of acetate; c) cationic α and β pathways at the PBE0-D4/def2-TZVP+SMD(AcOH)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms in the transition state structures were omitted for clarity, with bond lengths given in Å.

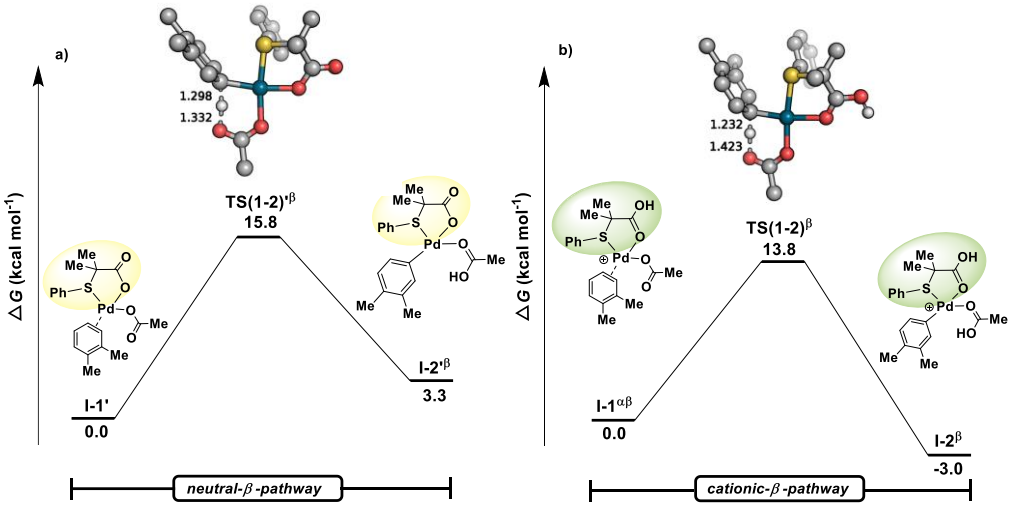


Figure S12. Computed relative Gibbs free energy profile ($\Delta G_{333.15}$) in kcal mol^{-1} for *o*-xylene with a) neutral-α-pathway and b) cationic-β-pathways at the PW6B95-D4/def2-TZVP+SMD(AcOH)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms in the transition state structures were omitted for clarity, with bond lengths given in Å.

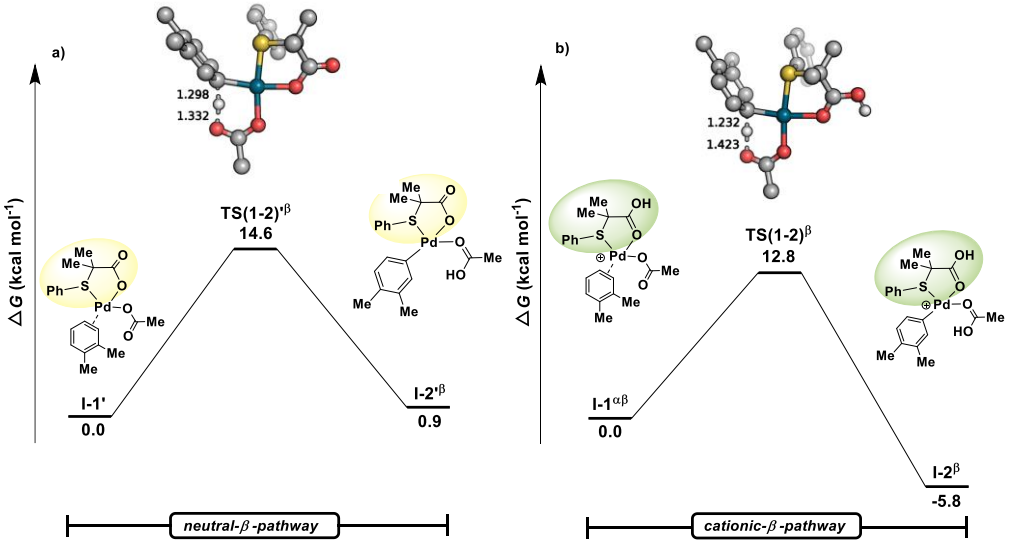


Figure S13. Computed relative Gibbs free energy profile ($\Delta G_{333.15}$) in kcal mol^{-1} for *o*-xylene with a) neutral-α-pathway and b) cationic-β-pathways at the ωB97XD/def2-TZVP+SMD(AcOH)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms in the transition state structures were omitted for clarity, with bond lengths given in Å.

A More O'Ferrall-Jencks analysis on the nature of the C–H cleavage was further carried out for the *o*-xylene Cα–H and Cβ–H pathways. Such provided strong support for C–H activation to occur through a based-assisted internal electrophilic substitution (BIES) mechanism.

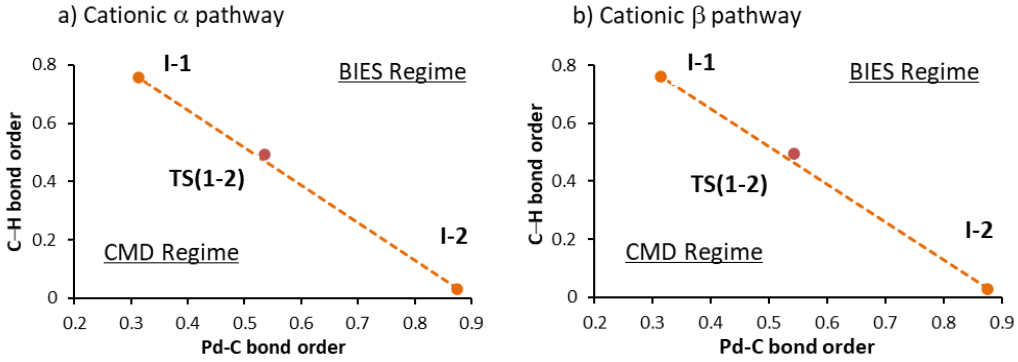


Figure S14. Wiberg bond order analysis of the C–H activation step for both cationic a) α and b) β pathways.

In order to gain better insights into the regioselectivity of anisole, density functional theory (DFT) calculations were carried out for the C–H activation, insertion and β-H elimination elementary steps for *ortho*- and *para*-functionalized products. Both profiles show that the C–H activation was the rate-determining step, with energy barrier of 9.7 kcal mol^{-1} for *ortho*-product and 10.7 kcal mol^{-1} for *para*-product, which is consistent with the KIE results (**Fig.S8**). Later NCIPLOT analysis revealed the presence of attraction interaction between the anisole methoxy group and *S,O*-ligand phenyl group contributes to the preference for ortho product.

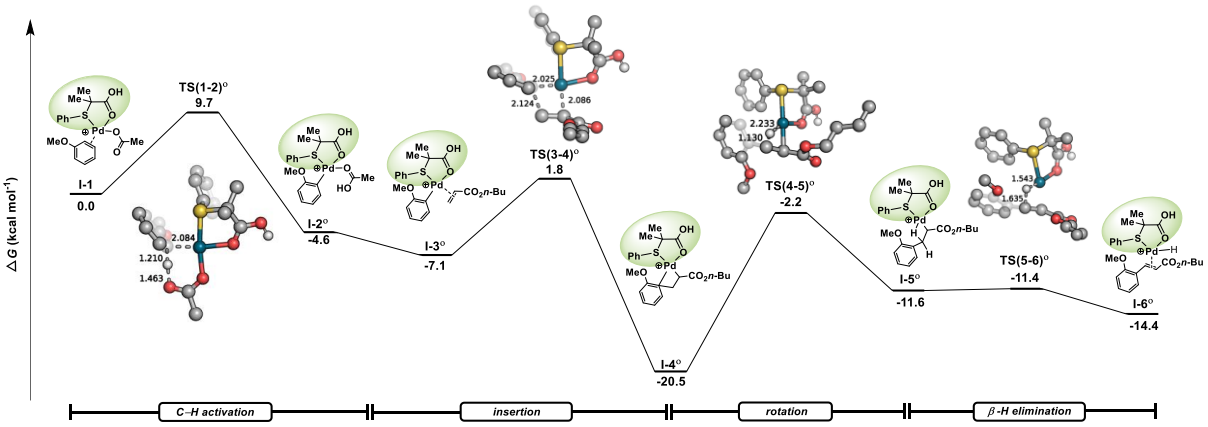


Figure S15. Computed relative Gibbs free energy profile ($\Delta G_{333.15}$) in kcal mol^{-1} for anisole cationic pathways to get ortho product at the

PBE0-D4/def2-TZVP+SMD(AcOH)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms in the transition state structures were omitted for clarity, with bond lengths given in Å.

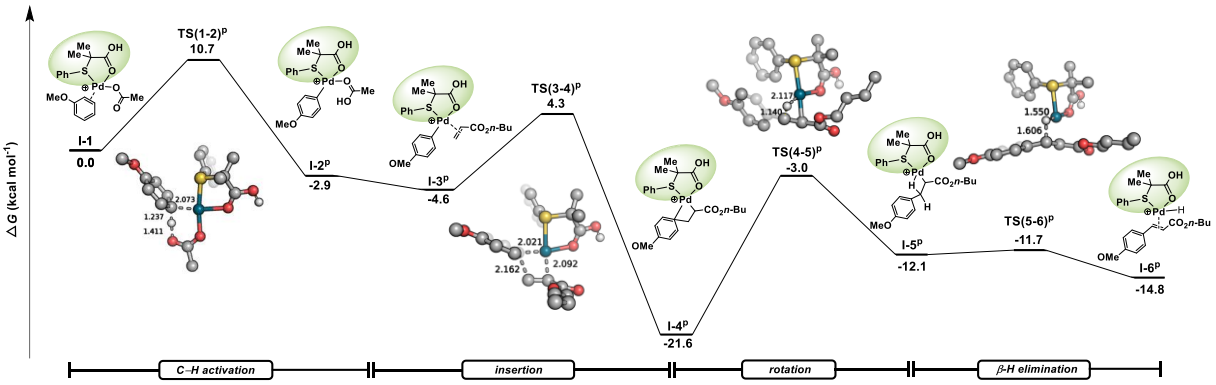


Figure S16. Computed relative Gibbs free energy profile ($\Delta G_{333.15}$) in kcal mol^{-1} for anisole cationic pathways to get para product at the PBE0-D4/def2-TZVP+SMD(AcOH)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms in the transition state structures were omitted for clarity, with bond lengths given in Å.

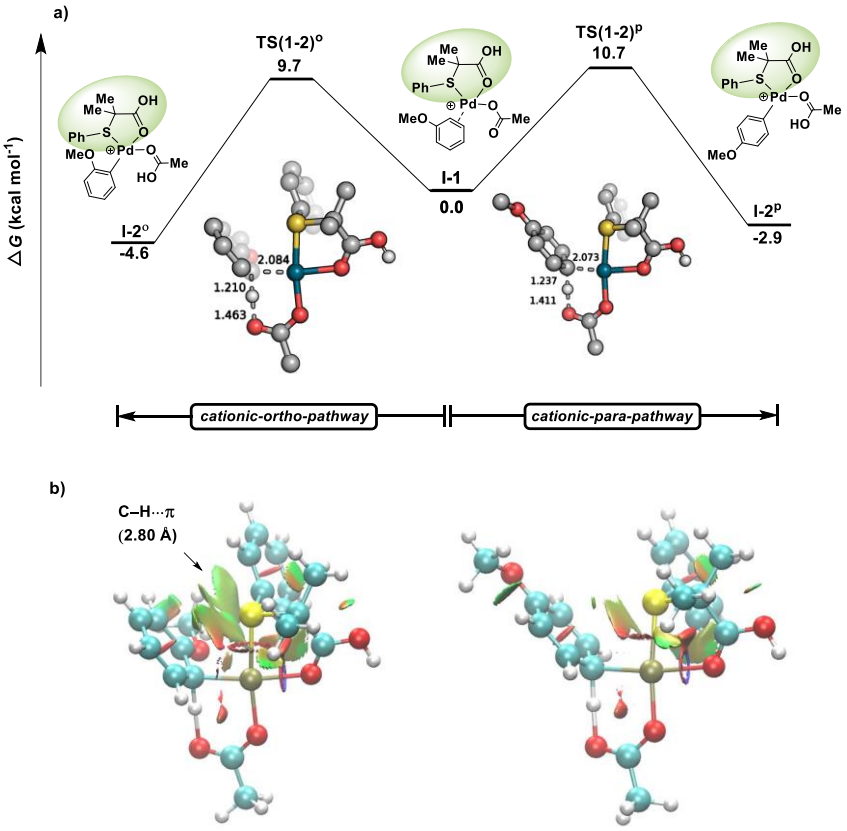


Figure S17. **a**, Computed relative Gibbs free energy profile ($\Delta G_{333.15}$) in kcal mol^{-1} for cationic C–H activation pathways at the PBE0-D4/def2-TZVP+SMD(AcOH)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms in the transition state structures were omitted, with bond lengths given in Å. **b**, Non-covalent interaction plots for the TS(1-2)^{ortho} and TS(1-2)^{para}.

Table S13. Calculated electronic energies for anisole cationic pathways at the **PBE0-D4**/def2-TZVP+SMD(AcOH) level of theory and Gibbs free energies with dispersion corrections for all structures (all in Hartree).

Structure	Electronic Energy	Total Gibbs Free Energy
I-1	-1639.093971	-1638.772166
TS(1-2)^{o}	-1639.075726	-1638.756720
I-2^{o}	-1639.099272	-1638.779469
I-3^{o}	-1834.263116	-1833.833091
TS(3-4)^{o}	-1834.247767	-1833.818921
I-4^{o}	-1834.287186	-1833.854442
TS(4-5)^{o}	-1834.256167	-1833.825201
I-5^{o}	-1834.269301	-1833.840217
TS(5-6)^{o}	-1834.266473	-1833.839987
I-6^{o}	-1834.272705	-1833.844763
TS(1-2)^{p}	-1639.071488	-1638.755138
I-2^{p}	-1639.094692	-1638.776853
I-3^{p}	-1834.259236	-1833.829151
TS(3-4)^{p}	-1834.242206	-1833.814927
I-4^{p}	-1834.286959	-1833.856271
TS(4-5)^{p}	-1834.256632	-1833.826536
I-5^{p}	-1834.266798	-1833.841058
TS(5-6)^{p}	-1834.264526	-1833.840489
I-6^{p}	-1834.273677	-1833.845311
Acetic Acid	-228.937746	-228.906343

Anisole	-424.094301	-423.955947

Table S14. Calculated electronic energies for *o*-xylene at the **PBE0-D4**/def2-TZVP+SMD(AcOH) level of theory and Gibbs free energies with dispersion corrections for all structures (all in Hartree).

Structure	Electronic Energy	Total Gibbs Free Energy
I-1’	-1602.780710	-1602.450299
TS(1-2)’$^{\beta}$	-1602.755194	-1602.431606
I-2’$^{\beta}$	-1602.776783	-1602.449541
I-1$^{\alpha\beta}$	-1603.213915	-1602.870474
TS(1-2)$^{\alpha}$	-1603.193363	-1602.853494
TS(1-2)$^{\beta}$	-1603.192459	-1602.854105
I-2$^{\alpha}$	-1603.219708	-1602.880148
I-2$^{\beta}$	-1603.219399	-1602.879477
I-1’’	-1374.252790	-1373.968194
TS(1-2)’’$^{\beta}$	-1374.165923	-1373.887452
I-2’’$^{\beta}$	-1374.203983	-1373.921725

Table S15. Calculated electronic energies for *o*-xylene at the **PW6B95**-D4/def2-TZVP+SMD(AcOH) level of theory and Gibbs free energies with dispersion corrections for all structures (all in Hartree).

Structure	Electronic Energy	Total Gibbs Free Energy
I-1’	-1605.913081	-1605.581456
TS(1-2)’$^{\beta}$	-1605.879848	-1605.556260
I-2’$^{\beta}$	-1605.903407	-1605.576165
I-1$^{\alpha\beta}$	-1606.344439	-1606.000998

TS(1-2)$^{\beta}$	-1606.317404	-1605.979050
I-2$^{\beta}$	-1606.345668	-1606.005746

Table S16. Calculated electronic energies for *o*-xylene at the **ωB97XD**-D4/def2-TZVP+SMD(AcOH) level of theory and Gibbs free energies with dispersion corrections for all structures (all in Hartree).

Structure	Electronic Energy	Total Gibbs Free Energy
I-1’	-1603.801981	-1603.471570
TS(1-2)’$^{\beta}$	-1603.771547	-1603.447959
I-2’$^{\beta}$	-1603.797176	-1603.469934
I-1$^{\alpha\beta}$	-1604.236726	-1603.893285
TS(1-2)$^{\beta}$	-1604.211188	-1603.872834
I-2$^{\beta}$	-1604.242379	-1603.902457

Table S17. Bond orders for the *o*-xylene cationic I-1, TS(1-2) and I-2.

Structure	Pd-C bond order	C–H bond order
I-1$^{\alpha\beta}$	0.3131	0.8755
TS(1-2)$^{\alpha}$	0.4915	0.5354
I-2$^{\alpha}$	0.7569	0.0316
TS(1-2)$^{\beta}$	0.4956	0.5435
I-2$^{\beta}$	0.7631	0.0284

Cartesian coordinates of the optimized structure

I-1

Lowest frequency = 27.7103 cm^{-1}

Charge = 1, Multiplicity = 1

49

O	0.238846000	-2.310929000	0.424217000
C	-0.914926000	-2.627782000	0.151679000
C	-1.739784000	-1.941978000	-0.915626000
C	-1.326540000	-2.546474000	-2.263901000
H	-1.572390000	-3.618561000	-2.280251000
H	-1.880826000	-2.052086000	-3.074079000
H	-0.248186000	-2.430917000	-2.450407000
C	-3.235519000	-2.028399000	-0.677540000
H	-3.772270000	-1.489973000	-1.471486000
H	-3.549914000	-3.081488000	-0.701353000
H	-3.521903000	-1.603153000	0.293820000
S	-1.190277000	-0.158062000	-1.002063000
Pd	1.002498000	-0.470659000	-0.312658000
O	2.817373000	-0.864067000	0.392912000
C	2.782914000	-0.816655000	1.698048000
O	1.792451000	-0.444927000	2.317642000
C	4.050905000	-1.268934000	2.362908000
H	4.139029000	-2.360947000	2.259041000
H	4.927743000	-0.824556000	1.872903000
H	4.026675000	-1.006614000	3.426925000
C	-1.953180000	0.586708000	0.425001000

C	-1.425939000	0.427681000	1.711120000
C	-3.085856000	1.372742000	0.196270000
C	-2.065688000	1.053401000	2.778693000
H	-0.508067000	-0.142446000	1.889330000
C	-3.711610000	1.993229000	1.274658000
H	-3.471491000	1.498782000	-0.818005000
C	-3.204278000	1.830571000	2.563346000
H	-1.659738000	0.937705000	3.785966000
H	-4.597327000	2.609061000	1.105439000
H	-3.696105000	2.320490000	3.406575000
C	1.809342000	1.453977000	-0.837302000
H	2.618883000	1.472651000	-0.105110000
C	0.745030000	2.413943000	-0.728718000
O	-1.494746000	-3.645015000	0.724029000
H	-0.879476000	-4.056814000	1.357267000
C	2.054025000	0.835362000	-2.104623000
H	2.936164000	0.197548000	-2.204683000
C	1.249133000	1.119891000	-3.203847000
H	1.444018000	0.646609000	-4.167059000
C	0.219958000	2.056031000	-3.064698000
H	-0.398587000	2.305562000	-3.930395000
O	0.462701000	3.058996000	0.385779000
C	1.236366000	2.845072000	1.555500000
H	2.262682000	3.220939000	1.416850000
H	0.747658000	3.422031000	2.347914000
H	1.261263000	1.778528000	1.831721000
C	-0.045567000	2.685266000	-1.850887000
H	-0.844015000	3.422553000	-1.752789000

TS(1-2)^{o}

Lowest frequency = -106.7194 cm^{-1}

Charge = 1, Multiplicity = 1

49

O	-0.000644000	-2.472877000	-0.653446000
C	1.060004000	-2.773144000	-0.119108000
C	1.654162000	-2.032344000	1.064324000
C	0.995866000	-2.600531000	2.328787000
H	1.254241000	-3.664793000	2.431731000
H	1.371136000	-2.065377000	3.212395000
H	-0.100097000	-2.507599000	2.296635000
C	3.168785000	-2.105369000	1.125206000
H	3.535457000	-1.532917000	1.989001000
H	3.480156000	-3.152432000	1.247263000
H	3.637536000	-1.709703000	0.214057000
S	1.080587000	-0.257286000	0.978600000
Pd	-0.960913000	-0.659289000	-0.021416000
O	-2.646634000	-1.238917000	-0.921625000
C	-3.656874000	-0.496154000	-1.196283000
O	-3.775146000	0.690951000	-0.869502000
C	-4.737774000	-1.175662000	-1.993125000
H	-5.643361000	-0.559489000	-2.003606000
H	-4.377404000	-1.314674000	-3.023409000
H	-4.944370000	-2.170942000	-1.578526000
C	-0.788823000	2.242217000	0.309898000
C	2.117209000	0.462034000	-0.278284000
C	1.898737000	0.243184000	-1.642211000
C	3.151685000	1.293955000	0.159361000

C	2.742467000	0.848643000	-2.569409000
H	1.066381000	-0.378788000	-1.978513000
C	3.987360000	1.897302000	-0.779017000
H	3.298518000	1.466766000	1.227923000
C	3.785087000	1.671784000	-2.140107000
H	2.578871000	0.682111000	-3.636276000
H	4.800207000	2.544750000	-0.443309000
H	4.441574000	2.144913000	-2.873685000
C	-1.454066000	1.860701000	3.026687000
H	-1.714757000	1.744121000	4.079743000
C	-1.985573000	1.023520000	2.063688000
H	-2.691876000	0.238000000	2.346875000
C	-1.661225000	1.170855000	0.686900000
H	-2.600890000	1.015513000	-0.059319000
O	1.741468000	-3.822554000	-0.492616000
H	1.263899000	-4.279906000	-1.207650000
C	-0.253851000	3.092444000	1.286244000
H	0.415048000	3.909728000	1.017379000
C	-0.585236000	2.884808000	2.622623000
H	-0.159115000	3.552905000	3.375894000
O	-0.532029000	2.345574000	-0.987046000
C	0.273485000	3.401892000	-1.468319000
H	1.299556000	3.328390000	-1.073220000
H	0.297820000	3.294871000	-2.558265000
H	-0.160615000	4.380214000	-1.208822000

I-2º

Lowest frequency = 7.6703 cm^{-1}

Charge = 1, Multiplicity = 1

49

O	-0.905513000	-2.348630000	0.651243000
C	-1.941123000	-2.365675000	0.001740000
C	-2.177761000	-1.530061000	-1.245812000
C	-1.536379000	-2.275373000	-2.423141000
H	-2.044070000	-3.240416000	-2.567949000
H	-1.649965000	-1.683220000	-3.342189000
H	-0.465675000	-2.463502000	-2.253338000
C	-3.643260000	-1.224195000	-1.499399000
H	-3.743562000	-0.597626000	-2.396971000
H	-4.188808000	-2.162858000	-1.670186000
H	-4.108766000	-0.704614000	-0.651170000
S	-1.200921000	0.050676000	-1.070361000
Pd	0.600258000	-0.837392000	0.018702000
O	2.134448000	-1.795078000	1.052283000
C	3.200994000	-1.398320000	1.532679000
O	3.694514000	-0.215891000	1.313026000
C	4.029686000	-2.270588000	2.407383000
H	3.479727000	-3.178964000	2.672472000
H	4.951973000	-2.536115000	1.867985000
H	4.330770000	-1.715799000	3.306885000
C	1.563053000	1.908475000	-0.353193000
C	-2.153783000	0.971470000	0.122698000
C	-2.122898000	0.691286000	1.491536000
C	-2.928043000	2.019917000	-0.378338000
C	-2.895429000	1.459247000	2.357870000
H	-1.484394000	-0.104574000	1.879226000
C	-3.694489000	2.784992000	0.499827000
H	-2.927947000	2.237219000	-1.448851000

C	-3.681379000	2.502879000	1.864365000
H	-2.876278000	1.247308000	3.429085000
H	-4.302637000	3.605366000	0.112943000
H	-4.282103000	3.103304000	2.551021000
C	3.506392000	1.248356000	-2.268161000
H	4.258945000	0.989684000	-3.015337000
C	1.747470000	0.565645000	-0.741298000
H	3.135185000	0.258905000	0.651556000
O	-2.929536000	-3.171695000	0.295304000
H	-2.680931000	-3.713961000	1.064173000
C	2.370599000	2.905523000	-0.912798000
H	2.251275000	3.947278000	-0.612875000
C	3.332969000	2.568776000	-1.864716000
H	3.954714000	3.357572000	-2.293685000
O	0.596500000	2.136195000	0.558854000
C	0.291077000	3.457423000	0.931993000
H	0.002643000	4.066815000	0.059147000
H	-0.560771000	3.392446000	1.620340000
H	1.137683000	3.939759000	1.448346000
C	2.707098000	0.249513000	-1.705425000
H	2.843761000	-0.789733000	-2.017677000

I-3^{o}

Lowest frequency = 14.3898 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	2.189473000	-2.002786000	-1.072927000

C	3.202435000	-1.918367000	-0.390371000
C	3.248842000	-1.345938000	1.017362000
C	2.808610000	-2.474128000	1.962189000
H	3.513131000	-3.315630000	1.887199000
H	2.813392000	-2.109806000	2.999039000
H	1.798855000	-2.840407000	1.721407000
C	4.606987000	-0.781185000	1.395332000
H	4.568687000	-0.375094000	2.415943000
H	5.360338000	-1.580823000	1.368369000
H	4.924417000	0.017165000	0.710804000
S	1.931460000	-0.041734000	1.197754000
Pd	0.382418000	-0.905598000	-0.358394000
C	-1.128423000	1.546140000	-0.146875000
C	2.615880000	1.391365000	0.392204000
C	2.757952000	1.473383000	-0.996693000
C	2.985749000	2.457004000	1.215538000
C	3.299564000	2.625879000	-1.556680000
H	2.431109000	0.651793000	-1.637011000
C	3.514858000	3.611995000	0.641572000
H	2.856484000	2.382682000	2.297438000
C	3.676180000	3.694080000	-0.739987000
H	3.419527000	2.695613000	-2.640037000
H	3.803761000	4.449178000	1.280334000
H	4.095109000	4.598508000	-1.186540000
C	-2.495089000	0.872428000	2.209231000
H	-3.023269000	0.607271000	3.127305000
C	-0.965557000	0.281377000	0.440407000
O	4.347892000	-2.400973000	-0.797111000
H	4.232036000	-2.815781000	-1.669741000
C	-1.986245000	2.469177000	0.459775000
H	-2.131857000	3.458415000	0.024251000

C	-2.663154000	2.126049000	1.631764000
H	-3.330461000	2.856793000	2.093855000
O	-0.425374000	1.783270000	-1.279655000
C	-0.446022000	3.075686000	-1.833319000
H	-0.075130000	3.826256000	-1.115199000
H	0.222108000	3.053553000	-2.702858000
H	-1.457772000	3.359643000	-2.167874000
C	-1.632842000	-0.053301000	1.610198000
H	-1.497367000	-1.039502000	2.061692000
C	-2.302898000	-2.339265000	-0.470015000
O	-3.231683000	-1.498606000	-0.887005000
C	-4.411044000	-1.347215000	-0.085611000
H	-4.130755000	-1.452635000	0.972941000
H	-5.104253000	-2.168199000	-0.330268000
O	-2.391201000	-3.082029000	0.473867000
C	-5.000823000	0.009962000	-0.378755000
H	-4.207780000	0.763907000	-0.243949000
H	-5.307809000	0.056673000	-1.437369000
C	-6.179112000	0.340706000	0.526131000
H	-6.967977000	-0.421828000	0.403855000
H	-5.854029000	0.271629000	1.579370000
C	-6.754685000	1.721907000	0.260312000
H	-7.599212000	1.942918000	0.929170000
H	-5.993920000	2.504603000	0.411982000
H	-7.118559000	1.811901000	-0.775355000
C	-1.065930000	-2.261527000	-1.312381000
H	-0.480177000	-3.187122000	-1.325154000
C	-0.795970000	-1.232526000	-2.185289000
H	-1.500032000	-0.404677000	-2.293138000
H	-0.001620000	-1.324860000	-2.931975000

TS(3-4)^{o}

Lowest frequency = -239.2277 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	-0.341088000	2.211525000	-0.937634000
C	-0.898283000	2.867500000	-0.065591000
C	-1.199476000	2.356068000	1.332450000
C	0.076532000	2.571958000	2.159480000
H	0.303320000	3.646734000	2.217319000
H	-0.076833000	2.192754000	3.179485000
H	0.940451000	2.054215000	1.715246000
C	-2.410560000	3.018230000	1.965729000
H	-2.576386000	2.603201000	2.969716000
H	-2.235808000	4.099152000	2.060187000
H	-3.319603000	2.865470000	1.368032000
S	-1.411960000	0.510148000	1.258240000
Pd	0.076221000	0.127285000	-0.579901000
C	-0.818315000	-2.631425000	-0.176734000
C	-3.049118000	0.292232000	0.591688000
C	-3.350548000	0.544050000	-0.750909000
C	-4.029257000	-0.184064000	1.465829000
C	-4.649089000	0.339607000	-1.207369000
H	-2.572443000	0.880078000	-1.439129000
C	-5.323979000	-0.398421000	0.994324000
H	-3.776753000	-0.386275000	2.509051000
C	-5.634632000	-0.131793000	-0.337638000
H	-4.891687000	0.540075000	-2.253294000

H	-6.092630000	-0.770966000	1.674769000
H	-6.650610000	-0.295239000	-0.703727000
C	1.139261000	-3.212406000	1.753107000
H	1.903658000	-3.445699000	2.496532000
C	0.316793000	-1.807879000	-0.035541000
O	-1.216984000	4.119856000	-0.256757000
H	-0.923265000	4.393727000	-1.143896000
C	-0.968010000	-3.735403000	0.667562000
H	-1.843439000	-4.380295000	0.585516000
C	0.007420000	-4.015471000	1.625170000
H	-0.121684000	-4.883719000	2.275062000
O	-1.698878000	-2.273244000	-1.131935000
C	-2.905552000	-2.988350000	-1.256669000
H	-3.501830000	-2.925574000	-0.330962000
H	-3.463599000	-2.514415000	-2.072485000
H	-2.726625000	-4.046415000	-1.509158000
C	1.294460000	-2.110416000	0.914048000
H	2.186855000	-1.482799000	0.983011000
C	1.195230000	-1.450487000	-1.936224000
H	0.447446000	-2.039470000	-2.472361000
H	2.069268000	-1.985256000	-1.566308000
C	1.326517000	-0.082681000	-2.236984000
H	0.719059000	0.369051000	-3.028746000
C	2.558544000	0.689723000	-1.903837000
O	3.349829000	0.027118000	-1.056478000
C	4.559855000	0.679749000	-0.657389000
H	4.317662000	1.696568000	-0.308687000
H	5.209460000	0.790019000	-1.540829000
O	2.785593000	1.791387000	-2.330188000
C	5.214530000	-0.149743000	0.419646000
H	4.521651000	-0.241940000	1.274975000

H	5.376191000	-1.172010000	0.037257000
C	6.535772000	0.444698000	0.889656000
H	7.219254000	0.536948000	0.027869000
H	6.365921000	1.474907000	1.248871000
C	7.199853000	-0.375957000	1.983008000
H	8.151271000	0.074675000	2.300522000
H	6.555790000	-0.454118000	2.873428000
H	7.415668000	-1.399901000	1.639415000

I-4º

Lowest frequency = 11.0626 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	-0.422836000	1.987317000	-1.189215000
C	-1.146287000	2.773531000	-0.588822000
C	-1.613718000	2.599281000	0.845946000
C	-0.506001000	3.182218000	1.736021000
H	-0.385813000	4.254933000	1.524778000
H	-0.783018000	3.064103000	2.792969000
H	0.458997000	2.681594000	1.563643000
C	-2.961396000	3.247778000	1.114403000
H	-3.243909000	3.088989000	2.164424000
H	-2.899315000	4.329257000	0.929454000
H	-3.750123000	2.831633000	0.472574000
S	-1.649983000	0.789946000	1.262853000
Pd	0.110255000	0.108369000	-0.319090000
C	-0.648775000	-2.599559000	0.039221000

C	-3.130324000	0.195518000	0.468362000
C	-3.226023000	0.056459000	-0.921126000
C	-4.193072000	-0.182027000	1.293438000
C	-4.399712000	-0.442867000	-1.479994000
H	-2.386005000	0.325593000	-1.565240000
C	-5.357421000	-0.696576000	0.725222000
H	-4.104578000	-0.071966000	2.376458000
C	-5.463064000	-0.822691000	-0.659209000
H	-4.480136000	-0.544940000	-2.564467000
H	-6.188619000	-0.992392000	1.368946000
H	-6.379481000	-1.218305000	-1.102657000
C	0.656254000	-1.639444000	2.360451000
H	1.162056000	-1.282474000	3.258394000
C	0.638527000	-1.971421000	-0.079096000
O	-1.520844000	3.898465000	-1.138293000
H	-1.116153000	3.972735000	-2.021026000
C	-1.238606000	-2.733742000	1.296391000
H	-2.211108000	-3.213865000	1.399369000
C	-0.578857000	-2.266486000	2.440151000
H	-1.058054000	-2.401110000	3.412737000
O	-1.190787000	-3.030996000	-1.097543000
C	-2.446357000	-3.676115000	-1.068647000
H	-3.228936000	-3.003914000	-0.680901000
H	-2.678494000	-3.941848000	-2.106161000
H	-2.406678000	-4.593665000	-0.459888000
C	1.257599000	-1.483016000	1.105355000
H	2.270159000	-1.079931000	1.018401000
C	1.411788000	-1.955404000	-1.397125000
H	0.893898000	-2.574007000	-2.138276000
H	2.430577000	-2.338740000	-1.252386000
C	1.382786000	-0.489804000	-1.772430000

H	0.849394000	-0.223251000	-2.694661000
C	2.594029000	0.362301000	-1.608793000
O	3.518029000	-0.202851000	-0.821106000
C	4.709710000	0.553549000	-0.586229000
H	4.434689000	1.522061000	-0.136795000
H	5.184577000	0.776014000	-1.555059000
O	2.715902000	1.457156000	-2.099927000
C	5.615624000	-0.251122000	0.312882000
H	5.089471000	-0.467895000	1.259477000
H	5.815823000	-1.226886000	-0.161595000
C	6.928210000	0.463998000	0.605406000
H	7.442576000	0.682283000	-0.346604000
H	6.715425000	1.446239000	1.062909000
C	7.849883000	-0.334293000	1.512707000
H	8.789024000	0.204568000	1.704708000
H	7.377307000	-0.536298000	2.487144000
H	8.109934000	-1.305757000	1.063589000

TS(4-5)^{o}

Lowest frequency = -118.0199 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	-0.761960000	0.768068000	1.583332000
C	-0.854371000	1.991943000	1.584349000
C	-0.822536000	2.866760000	0.343476000
C	-2.249001000	2.865519000	-0.225236000
H	-2.940132000	3.315316000	0.502925000

H	-2.277544000	3.463865000	-1.146666000
H	-2.598476000	1.847306000	-0.452365000
C	-0.321687000	4.273327000	0.623556000
H	-0.323368000	4.856866000	-0.307543000
H	-0.984951000	4.768774000	1.346191000
H	0.697243000	4.270364000	1.034380000
S	0.216739000	2.045370000	-0.962124000
Pd	-0.254364000	-0.245277000	-0.223484000
C	1.891655000	2.315871000	-0.417539000
C	2.476111000	1.540746000	0.589807000
C	2.630647000	3.304129000	-1.074502000
C	3.800111000	1.773849000	0.950194000
H	1.909315000	0.744754000	1.078550000
C	3.957180000	3.524847000	-0.710051000
H	2.167368000	3.892775000	-1.869342000
C	4.539563000	2.763707000	0.302614000
H	4.259898000	1.167112000	1.732946000
H	4.537613000	4.295350000	-1.221877000
H	5.579882000	2.939006000	0.585378000
C	3.539362000	-1.052581000	-1.578314000
H	3.996285000	-0.296743000	-2.218923000
C	1.562975000	-2.284395000	-0.863179000
O	-1.072701000	2.645193000	2.693864000
H	-1.150525000	2.012337000	3.429891000
C	3.725977000	-2.741276000	0.149721000
H	4.349086000	-3.296043000	0.851263000
C	2.175242000	-1.325406000	-1.677171000
H	1.571708000	-0.795150000	-2.420996000
C	0.072210000	-2.526271000	-0.914654000
H	-0.213590000	-3.543366000	-1.247226000
H	-0.370629000	-1.885981000	-1.733730000

C	-0.599905000	-2.129695000	0.361043000
H	-0.076692000	-2.354003000	1.296396000
C	-2.080108000	-2.192552000	0.500841000
O	-2.681518000	-2.161444000	-0.696936000
C	-4.104802000	-2.007236000	-0.704240000
H	-4.533468000	-2.593870000	0.121448000
H	-4.437241000	-2.432705000	-1.660789000
O	-2.655991000	-2.188517000	1.557841000
C	-4.477456000	-0.543327000	-0.584981000
H	-4.074339000	-0.158463000	0.367802000
H	-3.979737000	0.012006000	-1.400279000
C	-5.978801000	-0.298627000	-0.635830000
H	-6.385448000	-0.705424000	-1.577807000
H	-6.467052000	-0.866186000	0.174720000
C	-6.336775000	1.173936000	-0.517381000
H	-7.424835000	1.328505000	-0.551656000
H	-5.972917000	1.597891000	0.432718000
H	-5.893530000	1.761424000	-1.337781000
C	2.359329000	-3.013190000	0.046574000
C	4.304382000	-1.760767000	-0.658702000
H	5.374786000	-1.562339000	-0.568960000
O	1.706943000	-3.939777000	0.769850000
C	2.426756000	-4.740694000	1.677459000
H	2.892512000	-4.132829000	2.471207000
H	1.700994000	-5.426551000	2.129960000
H	3.206168000	-5.327033000	1.163677000

I-5^{o}

Lowest frequency = 10.0009 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	0.106913000	-1.972732000	-1.707257000
C	0.821109000	-2.909478000	-1.366994000
C	1.250571000	-3.206011000	0.059565000
C	0.155499000	-4.100283000	0.660831000
H	0.078701000	-5.033521000	0.083609000
H	0.415592000	-4.351168000	1.698463000
H	-0.826513000	-3.603344000	0.653956000
C	2.621672000	-3.855445000	0.136903000
H	2.881798000	-4.051293000	1.186417000
H	2.606226000	-4.813811000	-0.400623000
H	3.402257000	-3.221342000	-0.305104000
S	1.184443000	-1.641373000	1.069114000
Pd	-0.308029000	-0.389262000	-0.351865000
C	1.091601000	2.868161000	0.546408000
C	2.751354000	-0.836728000	0.798313000
C	2.965989000	0.021138000	-0.285372000
C	3.745807000	-1.025632000	1.763316000
C	4.185136000	0.682833000	-0.405015000
H	2.176951000	0.188787000	-1.023148000
C	4.965190000	-0.364705000	1.630867000
H	3.560011000	-1.680405000	2.617587000
C	5.184308000	0.488369000	0.549299000
H	4.347798000	1.362276000	-1.244076000
H	5.744861000	-0.512654000	2.381121000
H	6.138983000	1.010017000	0.452081000
C	1.288409000	4.368115000	-1.806218000
H	1.355096000	4.962563000	-2.718932000
C	0.127536000	2.708579000	-0.469803000

O	1.213404000	-3.804886000	-2.233036000
H	0.843562000	-3.591313000	-3.108194000
C	2.149925000	3.761799000	0.374450000
H	2.903591000	3.884794000	1.151933000
C	2.239070000	4.508929000	-0.799858000
H	3.063806000	5.214864000	-0.920584000
O	0.921630000	2.091906000	1.637888000
C	1.870394000	2.143474000	2.677197000
H	1.916004000	3.148074000	3.128088000
H	1.538176000	1.425649000	3.436768000
H	2.871998000	1.853634000	2.318387000
C	0.240228000	3.465470000	-1.636205000
H	-0.514414000	3.358878000	-2.419046000
C	-0.988682000	1.730148000	-0.275594000
H	-1.800289000	2.060743000	0.394676000
H	-0.556272000	0.935003000	0.622421000
C	-1.443355000	0.941739000	-1.407872000
H	-0.978946000	1.093749000	-2.387696000
C	-2.836194000	0.416249000	-1.499485000
O	-3.488816000	0.525179000	-0.341628000
C	-4.831206000	0.024320000	-0.309204000
H	-4.815917000	-1.043874000	-0.580511000
H	-5.419785000	0.543316000	-1.082585000
O	-3.289039000	-0.076929000	-2.498760000
C	-5.390505000	0.250038000	1.073357000
H	-4.744793000	-0.257808000	1.810679000
H	-5.343710000	1.327327000	1.307440000
C	-6.823624000	-0.248516000	1.207195000
H	-7.456612000	0.257317000	0.457468000
H	-6.861760000	-1.322984000	0.955554000
C	-7.400969000	-0.027554000	2.595655000

H	-8.434942000	-0.395716000	2.663065000
H	-6.810363000	-0.551948000	3.363593000
H	-7.411174000	1.041853000	2.859069000

TS(5-6)^{o}

Lowest frequency = -348.7796 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	-0.323858000	2.134567000	-1.559065000
C	-1.087026000	2.980312000	-1.111459000
C	-1.459508000	3.128173000	0.355043000
C	-0.408750000	4.058956000	0.978228000
H	-0.442178000	5.039801000	0.481474000
H	-0.628583000	4.200779000	2.045469000
H	0.608693000	3.651477000	0.878049000
C	-2.872866000	3.647204000	0.558130000
H	-3.088094000	3.729688000	1.632710000
H	-2.966416000	4.645244000	0.107776000
H	-3.622409000	2.987513000	0.100115000
S	-1.221396000	1.498193000	1.224746000
Pd	0.295082000	0.484137000	-0.291063000
C	-0.849087000	-2.891125000	0.362845000
C	-2.716537000	0.578666000	0.904682000
C	-2.952630000	-0.063007000	-0.315883000
C	-3.631463000	0.470822000	1.955860000
C	-4.118156000	-0.804568000	-0.483341000
H	-2.222352000	-0.002537000	-1.126240000

C	-4.793227000	-0.278824000	1.778559000
H	-3.430853000	0.968082000	2.907531000
C	-5.036607000	-0.913400000	0.561348000
H	-4.298435000	-1.313546000	-1.432076000
H	-5.510831000	-0.365409000	2.597264000
H	-5.947144000	-1.501336000	0.426556000
C	-1.784594000	-3.611458000	-2.173034000
H	-2.138167000	-3.909424000	-3.161588000
C	-0.166958000	-2.445345000	-0.790747000
O	-1.599334000	3.908726000	-1.876467000
H	-1.262072000	3.799744000	-2.783187000
C	-1.990197000	-3.685229000	0.241310000
H	-2.525791000	-4.028300000	1.126080000
C	-2.446326000	-4.044429000	-1.025937000
H	-3.331546000	-4.678644000	-1.112341000
O	-0.343164000	-2.457272000	1.532822000
C	-1.012464000	-2.765201000	2.734022000
H	-1.044078000	-3.852824000	2.907487000
H	-0.438340000	-2.291597000	3.539114000
H	-2.039277000	-2.362375000	2.730674000
C	-0.651697000	-2.811670000	-2.049204000
H	-0.117082000	-2.488550000	-2.945001000
C	1.024390000	-1.587339000	-0.612267000
H	1.768358000	-1.930850000	0.117166000
H	0.597432000	-0.678048000	0.677574000
C	1.470960000	-0.673310000	-1.595170000
H	0.967267000	-0.606908000	-2.564240000
C	2.855546000	-0.119427000	-1.612320000
O	3.534569000	-0.420662000	-0.506917000
C	4.874012000	0.080473000	-0.418701000
H	4.846970000	1.178683000	-0.508219000

H	5.449718000	-0.297702000	-1.278621000
O	3.282031000	0.541713000	-2.522319000
C	5.463993000	-0.366116000	0.895809000
H	4.831996000	0.007812000	1.719955000
H	5.427233000	-1.467614000	0.949229000
C	6.897222000	0.115349000	1.080365000
H	7.516113000	-0.254599000	0.244442000
H	6.924691000	1.216868000	1.008787000
C	7.506128000	-0.326536000	2.400981000
H	8.539535000	0.034203000	2.506684000
H	6.929949000	0.059175000	3.257028000
H	7.527349000	-1.424639000	2.484165000

I-6º

Lowest frequency = 11.4032 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	1.396597000	-1.177818000	-1.718318000
C	2.271749000	-1.938919000	-1.330777000
C	2.209491000	-2.726758000	-0.031292000
C	1.334453000	-3.959450000	-0.296270000
H	1.812137000	-4.593260000	-1.057998000
H	1.232583000	-4.546733000	0.627215000
H	0.330028000	-3.683364000	-0.652360000
C	3.576464000	-3.103596000	0.511824000
H	3.462531000	-3.657955000	1.453957000
H	4.094048000	-3.750387000	-0.210345000

H	4.203937000	-2.220559000	0.694092000
S	1.267735000	-1.727276000	1.229835000
Pd	-0.240311000	-0.709584000	-0.259845000
C	0.373502000	2.931462000	-0.424056000
C	2.417163000	-0.435420000	1.672687000
C	2.686314000	0.653015000	0.836903000
C	3.041657000	-0.554159000	2.917545000
C	3.607341000	1.612679000	1.247959000
H	2.177892000	0.763763000	-0.123144000
C	3.954254000	0.418418000	3.321438000
H	2.811692000	-1.402575000	3.565825000
C	4.240557000	1.497098000	2.486363000
H	3.821983000	2.459932000	0.593395000
H	4.442978000	0.329962000	4.293936000
H	4.959889000	2.255220000	2.803891000
C	1.580335000	2.809274000	-2.957175000
H	2.042506000	2.776392000	-3.945113000
C	-0.098816000	2.006426000	-1.391831000
O	3.329169000	-2.201487000	-2.055333000
H	3.269316000	-1.714172000	-2.895344000
C	1.428792000	3.793055000	-0.742527000
H	1.789325000	4.518872000	-0.014080000
C	2.021969000	3.725970000	-2.001022000
H	2.839783000	4.410094000	-2.239755000
O	-0.224206000	2.887072000	0.771786000
C	0.181860000	3.773685000	1.789198000
H	0.042175000	4.824226000	1.486922000
H	-0.455320000	3.561390000	2.655353000
H	1.235690000	3.604456000	2.065892000
C	0.526408000	1.961080000	-2.647763000
H	0.157123000	1.261592000	-3.400050000

C	-1.217142000	1.145253000	-1.029720000
H	-1.846371000	1.499550000	-0.209479000
H	-1.259520000	-0.552070000	0.828053000
C	-1.647890000	0.018845000	-1.724489000
H	-1.187151000	-0.283405000	-2.670091000
C	-2.966557000	-0.640674000	-1.487606000
O	-3.647992000	-0.083522000	-0.492829000
C	-4.910688000	-0.676108000	-0.165615000
H	-4.748791000	-1.738133000	0.081379000
H	-5.556730000	-0.647624000	-1.057512000
O	-3.340627000	-1.581210000	-2.138512000
C	-5.507619000	0.088272000	0.989742000
H	-4.804379000	0.060417000	1.840090000
H	-5.609047000	1.148902000	0.703082000
C	-6.860384000	-0.467472000	1.415019000
H	-7.550113000	-0.446056000	0.553330000
H	-6.749674000	-1.532667000	1.683858000
C	-7.474265000	0.292434000	2.579385000
H	-8.448921000	-0.129517000	2.864480000
H	-6.823968000	0.257560000	3.467913000
H	-7.632310000	1.352711000	2.326247000

TS(1-2)^{p}

Lowest frequency = -205.3275 cm^{-1}

Charge = 1, Multiplicity = 1

49

O	2.132145000	1.647293000	-0.585103000

C	2.745701000	0.781604000	-1.196276000
C	2.106434000	-0.471456000	-1.766277000
C	1.518686000	-0.095121000	-3.132859000
H	2.328764000	0.212491000	-3.810490000
H	1.013817000	-0.967955000	-3.570218000
H	0.796002000	0.730918000	-3.053722000
C	3.060214000	-1.648552000	-1.858638000
H	2.531643000	-2.526610000	-2.256060000
H	3.883256000	-1.400621000	-2.543674000
H	3.489713000	-1.907977000	-0.881586000
S	0.631369000	-0.897555000	-0.704646000
Pd	0.068439000	1.252019000	-0.084807000
O	-0.207706000	3.183871000	0.368245000
C	-1.209389000	3.673583000	0.994050000
O	-2.197831000	3.020765000	1.366832000
C	-1.157703000	5.155008000	1.244558000
H	-1.750974000	5.405244000	2.131813000
H	-0.121600000	5.497882000	1.347785000
H	-1.604523000	5.663893000	0.376366000
C	-1.844874000	-0.484538000	1.281680000
C	-3.261609000	-1.790856000	-0.172461000
H	-1.294061000	-0.379894000	2.220688000
C	1.356194000	-1.650577000	0.737683000
C	1.983717000	-0.899431000	1.737049000
C	1.243704000	-3.038943000	0.846166000
C	2.518321000	-1.554961000	2.842774000
H	2.042119000	0.188744000	1.660850000
C	1.779921000	-3.682609000	1.959618000
H	0.735518000	-3.608900000	0.065237000
C	2.418091000	-2.942739000	2.953734000
H	3.008438000	-0.975828000	3.628241000

H	1.695073000	-4.767510000	2.050458000
H	2.835140000	-3.449532000	3.826659000
C	-3.302190000	-0.734296000	-1.106382000
H	-3.885689000	-0.821608000	-2.022762000
C	-2.602861000	0.427747000	-0.839050000
H	-2.652142000	1.251601000	-1.557031000
C	-1.850573000	0.600834000	0.354212000
H	-2.027415000	1.710196000	0.873005000
O	4.016353000	0.907637000	-1.472647000
H	4.336586000	1.761920000	-1.132136000
C	-2.527040000	-1.650361000	1.028989000
H	-2.538926000	-2.480835000	1.737033000
O	-3.886403000	-2.944368000	-0.330238000
C	-4.681856000	-3.179367000	-1.475019000
H	-4.077833000	-3.137846000	-2.395431000
H	-5.094833000	-4.187422000	-1.358116000
H	-5.507999000	-2.453757000	-1.539480000

I-2^{p}

Lowest frequency = 13.7656 cm^{-1}

Charge = 1, Multiplicity = 1

49

O	-2.144446000	-1.970260000	0.042053000
C	-3.034091000	-1.373675000	-0.545254000
C	-2.803548000	-0.210638000	-1.496764000
C	-2.469421000	-0.816304000	-2.866795000
H	-3.325366000	-1.405811000	-3.227268000

H	-2.273130000	-0.012102000	-3.589751000
H	-1.587808000	-1.472905000	-2.818031000
C	-3.974312000	0.753373000	-1.570777000
H	-3.734947000	1.579745000	-2.255040000
H	-4.857732000	0.227309000	-1.958910000
H	-4.225752000	1.172266000	-0.587083000
S	-1.252112000	0.688728000	-0.980454000
Pd	-0.114085000	-1.056549000	-0.063093000
O	0.809841000	-2.736246000	0.758043000
C	1.900428000	-2.945457000	1.297665000
O	2.836690000	-2.049832000	1.404129000
C	2.239307000	-4.275321000	1.872486000
H	1.365086000	-4.933498000	1.853572000
H	3.056228000	-4.718694000	1.282866000
H	2.613893000	-4.150490000	2.898224000
C	1.778275000	1.035795000	0.737972000
H	1.075922000	1.232669000	1.553009000
C	-1.776746000	1.690420000	0.396559000
C	-2.052718000	1.147412000	1.656242000
C	-1.880768000	3.064373000	0.168686000
C	-2.454983000	1.992731000	2.685999000
H	-1.941988000	0.075069000	1.833180000
C	-2.278389000	3.901165000	1.210087000
H	-1.646597000	3.474755000	-0.816006000
C	-2.567977000	3.366576000	2.463812000
H	-2.672738000	1.577130000	3.672153000
H	-2.358769000	4.976578000	1.038623000
H	-2.877946000	4.024928000	3.278219000
C	3.592143000	0.583830000	-1.339914000
H	4.285916000	0.392862000	-2.158909000
C	1.520940000	0.021812000	-0.200466000

H	2.557237000	-1.217605000	0.951561000
O	-4.288041000	-1.742331000	-0.462266000
H	-4.351136000	-2.529721000	0.106081000
C	2.934059000	1.800689000	0.646894000
H	3.152138000	2.584471000	1.374769000
C	3.852549000	1.584699000	-0.393248000
C	2.429642000	-0.184376000	-1.242140000
H	2.249097000	-0.958735000	-1.992593000
O	4.933533000	2.371903000	-0.398927000
C	5.896556000	2.214845000	-1.410801000
H	5.469412000	2.402867000	-2.410596000
H	6.679635000	2.956203000	-1.212870000
H	6.344739000	1.206746000	-1.391385000

I-3^{p}

Lowest frequency = 9.6396 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	2.715410000	-1.990440000	-0.550651000
C	3.647938000	-1.586110000	0.131174000
C	3.505807000	-0.642113000	1.315047000
C	3.107060000	-1.508144000	2.519118000
H	3.902022000	-2.239031000	2.728755000
H	2.979669000	-0.871526000	3.405877000
H	2.168607000	-2.054501000	2.338490000
C	4.756045000	0.175714000	1.588214000
H	4.583772000	0.842047000	2.445155000

H	5.590805000	-0.495635000	1.833445000
H	5.045218000	0.785135000	0.721186000
S	2.045205000	0.480004000	1.039936000
Pd	0.732171000	-0.976177000	-0.283021000
C	2.635564000	1.693877000	-0.121195000
C	2.850914000	1.395260000	-1.471295000
C	2.854415000	2.982400000	0.370967000
C	3.307647000	2.394966000	-2.324760000
H	2.654169000	0.391572000	-1.855468000
C	3.304638000	3.977083000	-0.495369000
H	2.668556000	3.204370000	1.423952000
C	3.534069000	3.683654000	-1.837992000
H	3.478893000	2.169348000	-3.379469000
H	3.474677000	4.986889000	-0.116264000
H	3.886311000	4.465702000	-2.514024000
C	-2.553932000	1.005199000	1.513104000
H	-3.117749000	0.896832000	2.440007000
C	-0.799422000	0.208401000	0.057480000
O	4.872078000	-2.006993000	-0.056927000
H	4.881711000	-2.660034000	-0.778289000
C	-2.092727000	2.141115000	-0.573318000
H	-2.331210000	2.949415000	-1.267175000
C	-2.845753000	2.030825000	0.605839000
C	-1.526864000	0.096904000	1.236288000
H	-1.322740000	-0.701765000	1.953749000
C	-1.768179000	-2.714860000	-0.178496000
O	-2.737379000	-2.158829000	-0.881333000
C	-4.001762000	-1.945965000	-0.238457000
H	-3.822628000	-1.770892000	0.832734000
H	-4.595981000	-2.869271000	-0.331552000
O	-1.866890000	-3.172093000	0.931362000

C	-4.666411000	-0.762452000	-0.897452000
H	-3.944507000	0.070006000	-0.907235000
H	-4.887975000	-0.999521000	-1.951577000
C	-5.935070000	-0.328525000	-0.177165000
H	-6.676191000	-1.146179000	-0.199499000
H	-5.702441000	-0.167221000	0.891170000
C	-6.539569000	0.937075000	-0.763754000
H	-7.458201000	1.228231000	-0.233282000
H	-5.831474000	1.778758000	-0.700937000
H	-6.800171000	0.800545000	-1.824976000
C	-0.467916000	-2.706590000	-0.923862000
H	0.209525000	-3.519808000	-0.641203000
C	-0.218269000	-1.919824000	-2.025092000
H	-0.999887000	-1.255398000	-2.403255000
H	0.647108000	-2.113108000	-2.666392000
O	-3.820776000	2.938441000	0.771197000
C	-4.592195000	2.909333000	1.945150000
H	-3.967474000	3.048435000	2.843931000
H	-5.302946000	3.740985000	1.872054000
H	-5.156197000	1.965450000	2.038313000
C	-1.072657000	1.237898000	-0.847215000
H	-0.496175000	1.352833000	-1.769165000

TS(3-4)^{p}

Lowest frequency = -236.4805 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	0.882890000	-2.527352000	-0.405639000
C	1.510461000	-2.783147000	0.614868000
C	1.690005000	-1.819673000	1.775070000
C	0.433933000	-1.949125000	2.649024000
H	0.361888000	-2.972421000	3.046058000
H	0.500406000	-1.251101000	3.495262000
H	-0.481642000	-1.728815000	2.078954000
C	2.963583000	-2.064145000	2.565146000
H	3.037577000	-1.334419000	3.383552000
H	2.943133000	-3.073512000	2.999481000
H	3.859115000	-1.976951000	1.934819000
S	1.636077000	-0.080184000	1.118044000
Pd	0.145883000	-0.519579000	-0.712780000
C	3.237694000	0.145033000	0.374309000
C	3.570792000	-0.419183000	-0.862357000
C	4.153671000	0.944699000	1.062860000
C	4.836886000	-0.194996000	-1.395766000
H	2.842204000	-1.023022000	-1.408269000
C	5.415910000	1.167895000	0.516017000
H	3.875517000	1.391241000	2.019923000
C	5.758178000	0.596601000	-0.708198000
H	5.103106000	-0.634372000	-2.359511000
H	6.133816000	1.793377000	1.050679000
H	6.748004000	0.773618000	-1.134452000
C	-0.370844000	1.431462000	-0.815476000
O	2.024316000	-3.966918000	0.818281000
H	1.802117000	-4.546080000	0.067699000
C	0.551759000	3.663712000	-0.829354000
H	1.302402000	4.388981000	-1.148715000
C	-1.409432000	1.868285000	0.010354000
H	-2.194862000	1.172703000	0.317023000

C	-1.194935000	0.322189000	-2.478221000
H	-0.557508000	0.793738000	-3.228957000
H	-2.127762000	0.837002000	-2.252794000
C	-1.122150000	-1.065818000	-2.285010000
H	-0.459606000	-1.678349000	-2.906005000
C	-2.219063000	-1.836781000	-1.629682000
O	-3.098435000	-1.037001000	-1.020812000
C	-4.193496000	-1.671774000	-0.352017000
H	-3.797914000	-2.451386000	0.318761000
H	-4.818132000	-2.181923000	-1.103074000
O	-2.277353000	-3.038165000	-1.631872000
C	-4.968418000	-0.616314000	0.397814000
H	-4.299383000	-0.129030000	1.129417000
H	-5.282044000	0.169436000	-0.310468000
C	-6.185481000	-1.186297000	1.114639000
H	-6.845852000	-1.673911000	0.376822000
H	-5.862753000	-1.986934000	1.803100000
C	-6.967482000	-0.134070000	1.883504000
H	-7.840745000	-0.572484000	2.387738000
H	-6.344110000	0.344807000	2.655495000
H	-7.334543000	0.659889000	1.214146000
O	-0.446043000	5.392840000	0.365326000
C	-1.454077000	5.915010000	1.195332000
H	-1.468479000	5.415215000	2.178791000
H	-1.220337000	6.976545000	1.337970000
H	-2.449322000	5.826549000	0.727836000
C	0.603735000	2.344175000	-1.247693000
H	1.417443000	2.023678000	-1.904207000
C	-1.465422000	3.194264000	0.434416000
H	-2.285085000	3.511367000	1.079365000
C	-0.480394000	4.103484000	0.018829000

I-4[p]

Lowest frequency = 9.5025 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	0.399826000	-2.484509000	-0.348202000
C	1.142861000	-2.842680000	0.557578000
C	1.615594000	-1.952256000	1.693908000
C	0.518121000	-2.011146000	2.767294000
H	0.410475000	-3.043211000	3.132191000
H	0.797239000	-1.369144000	3.614378000
H	-0.454078000	-1.678231000	2.372665000
C	2.973497000	-2.355288000	2.243452000
H	3.257210000	-1.675879000	3.059174000
H	2.926840000	-3.378705000	2.641029000
H	3.753980000	-2.318164000	1.471159000
S	1.623393000	-0.185108000	1.124998000
Pd	-0.133609000	-0.421933000	-0.590111000
C	3.124094000	-0.016743000	0.185307000
C	3.306063000	-0.654978000	-1.046637000
C	4.099221000	0.845260000	0.691512000
C	4.482325000	-0.441437000	-1.758850000
H	2.527603000	-1.302665000	-1.456094000
C	5.266441000	1.065618000	-0.038371000
H	3.937438000	1.348670000	1.646798000
C	5.460390000	0.420034000	-1.257757000
H	4.632352000	-0.941879000	-2.717957000

H	6.028905000	1.742743000	0.352413000
H	6.377826000	0.590383000	-1.825280000
C	-0.335363000	2.568679000	0.643613000
H	-0.731690000	2.806935000	1.629803000
C	-0.643783000	1.462255000	-1.535227000
O	1.535080000	-4.085700000	0.657684000
H	1.125598000	-4.607987000	-0.054897000
C	1.405425000	2.697306000	-1.053279000
H	2.393679000	3.063186000	-1.336464000
C	0.923347000	3.018491000	0.239641000
C	-1.100584000	1.781444000	-0.227538000
H	-2.114865000	1.488618000	0.056554000
C	-1.565682000	0.745723000	-2.520027000
H	-1.160476000	0.825569000	-3.537083000
H	-2.573841000	1.180930000	-2.509421000
C	-1.536569000	-0.682921000	-2.020848000
H	-1.107560000	-1.438794000	-2.691536000
C	-2.696591000	-1.244423000	-1.272673000
O	-3.533379000	-0.293670000	-0.835391000
C	-4.667458000	-0.734813000	-0.083393000
H	-4.315445000	-1.304260000	0.792704000
H	-5.253174000	-1.433438000	-0.701886000
O	-2.848605000	-2.419904000	-1.048835000
C	-5.475071000	0.475747000	0.315403000
H	-4.841820000	1.154111000	0.914531000
H	-5.754960000	1.034551000	-0.593841000
C	-6.724598000	0.107155000	1.104510000
H	-7.347286000	-0.574867000	0.499904000
H	-6.434459000	-0.468199000	2.001286000
C	-7.545479000	1.318058000	1.516527000
H	-8.441134000	1.022079000	2.081676000

H	-6.961214000	2.001164000	2.153527000
H	-7.881285000	1.891199000	0.638012000
C	0.646134000	1.942293000	-1.915105000
H	1.021403000	1.719814000	-2.917000000
O	1.751185000	3.734387000	0.997330000
C	1.350108000	4.115021000	2.293938000
H	2.177192000	4.697449000	2.715722000
H	0.444878000	4.743045000	2.265601000
H	1.164851000	3.232374000	2.928934000

TS(4-5)^{p}

Lowest frequency = -234.6048 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	1.004708000	0.878162000	-1.588498000
C	0.937841000	2.090177000	-1.402736000
C	0.762322000	2.746290000	-0.045300000
C	2.156527000	2.799059000	0.596782000
H	2.820557000	3.433204000	-0.009141000
H	2.081525000	3.236693000	1.602159000
H	2.609281000	1.799230000	0.678077000
C	0.119899000	4.119817000	-0.128364000
H	0.020693000	4.542116000	0.881226000
H	0.752026000	4.791711000	-0.725598000
H	-0.875064000	4.078700000	-0.592287000
S	-0.228363000	1.614327000	1.050739000
Pd	0.556931000	-0.445131000	0.005559000

C	-1.898115000	1.776250000	0.446291000
C	-2.356769000	1.060918000	-0.664986000
C	-2.762048000	2.611656000	1.161006000
C	-3.679925000	1.205323000	-1.073239000
H	-1.694368000	0.374603000	-1.198442000
C	-4.084968000	2.747337000	0.745456000
H	-2.397913000	3.149827000	2.038906000
C	-4.541434000	2.049145000	-0.372293000
H	-4.044351000	0.638447000	-1.931991000
H	-4.761000000	3.402463000	1.299106000
H	-5.578873000	2.157493000	-0.696557000
C	-3.222995000	-1.713689000	1.244053000
H	-3.736875000	-1.280335000	2.101567000
C	-1.143419000	-2.521908000	0.255182000
O	1.095239000	2.928575000	-2.390328000
H	1.268515000	2.433305000	-3.210798000
C	-3.206592000	-2.557778000	-1.022735000
H	-3.760250000	-2.785343000	-1.935480000
C	-3.905373000	-1.984293000	0.052738000
C	-1.858610000	-1.978941000	1.329947000
H	-1.339323000	-1.753453000	2.266384000
C	0.356835000	-2.729979000	0.372392000
H	0.669676000	-3.745858000	0.687642000
H	0.733443000	-2.134764000	1.269127000
C	1.105785000	-2.202487000	-0.802294000
H	0.677307000	-2.323735000	-1.802612000
C	2.593013000	-2.167427000	-0.822867000
O	3.097520000	-2.254432000	0.414967000
C	4.500020000	-2.004503000	0.563227000
H	5.035036000	-2.445425000	-0.290507000
H	4.791607000	-2.529665000	1.482808000

O	3.243086000	-1.997908000	-1.821217000
C	4.762049000	-0.515289000	0.663399000
H	4.404825000	-0.034831000	-0.264072000
H	4.160091000	-0.108366000	1.495887000
C	6.231271000	-0.178865000	0.875725000
H	6.593995000	-0.679984000	1.789800000
H	6.823651000	-0.598912000	0.044984000
C	6.481981000	1.316841000	0.978155000
H	7.548812000	1.537259000	1.127254000
H	6.161853000	1.838897000	0.061855000
H	5.931764000	1.758385000	1.824885000
C	-1.851595000	-2.823646000	-0.920170000
H	-1.337136000	-3.273673000	-1.772800000
O	-5.200313000	-1.718321000	-0.157342000
C	-5.972819000	-1.199507000	0.896831000
H	-6.992352000	-1.086402000	0.509402000
H	-5.991996000	-1.886382000	1.759542000
H	-5.599395000	-0.214017000	1.224269000

I-5^{p}

Lowest frequency = 6.5388 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	-0.984422000	1.709016000	1.588254000
C	-1.313977000	2.815495000	1.173130000
C	-1.408636000	3.181496000	-0.296931000
C	-2.772774000	2.681718000	-0.793369000

H	-3.577334000	3.207148000	-0.257926000
H	-2.873836000	2.894756000	-1.866847000
H	-2.894316000	1.599018000	-0.634633000
C	-1.215891000	4.665033000	-0.556484000
H	-1.287856000	4.864360000	-1.634763000
H	-2.002427000	5.236768000	-0.044215000
H	-0.240956000	5.020809000	-0.196382000
S	-0.152855000	2.172534000	-1.232216000
Pd	-0.328605000	0.231950000	0.188368000
C	1.395590000	2.946331000	-0.808963000
C	2.043284000	2.696490000	0.405912000
C	1.962337000	3.803963000	-1.756058000
C	3.254679000	3.327193000	0.675677000
H	1.607138000	2.009333000	1.134552000
C	3.177144000	4.426448000	-1.476727000
H	1.454685000	3.978334000	-2.707248000
C	3.820274000	4.191182000	-0.262700000
H	3.764488000	3.136011000	1.622357000
H	3.623656000	5.096002000	-2.214811000
H	4.773352000	4.679200000	-0.047660000
C	3.290857000	-3.968024000	-0.741185000
H	3.548802000	-4.844718000	-1.334795000
C	1.592395000	-2.409654000	0.031042000
O	-1.683325000	3.762463000	1.991171000
H	-1.657683000	3.427801000	2.905422000
C	3.891162000	-2.159160000	0.755622000
H	4.666330000	-1.638856000	1.320441000
C	4.263675000	-3.289824000	0.004651000
C	1.972843000	-3.518398000	-0.726407000
H	1.224034000	-4.058189000	-1.312384000
C	0.166213000	-1.986243000	0.045521000

H	-0.494037000	-2.605686000	-0.577879000
H	0.143239000	-0.989042000	-0.804860000
C	-0.471585000	-1.502136000	1.255838000
H	0.114050000	-1.438686000	2.178979000
C	-1.928399000	-1.694880000	1.508287000
O	-2.586396000	-2.065916000	0.406245000
C	-3.999554000	-2.259055000	0.536785000
H	-4.449759000	-1.330217000	0.923824000
H	-4.181291000	-3.040414000	1.292092000
O	-2.444482000	-1.500826000	2.577356000
C	-4.555884000	-2.638808000	-0.813013000
H	-4.315004000	-1.843103000	-1.539551000
H	-4.044275000	-3.549477000	-1.168504000
C	-6.060941000	-2.870204000	-0.775777000
H	-6.289494000	-3.659266000	-0.038448000
H	-6.561842000	-1.959074000	-0.403809000
C	-6.636006000	-3.253895000	-2.129312000
H	-7.722229000	-3.415057000	-2.072160000
H	-6.455324000	-2.467739000	-2.879586000
H	-6.181871000	-4.183098000	-2.507993000
C	2.578414000	-1.729702000	0.764422000
H	2.313828000	-0.841622000	1.346157000
O	5.553200000	-3.630703000	0.058709000
C	6.003647000	-4.750934000	-0.663327000
H	7.078227000	-4.837250000	-0.464271000
H	5.501266000	-5.674759000	-0.330455000
H	5.848110000	-4.622410000	-1.747823000

TS(5-6)^{p}

Lowest frequency = -384.3055 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	-0.593870000	1.863538000	1.627214000
C	-0.699235000	3.013916000	1.220194000
C	-0.772077000	3.394013000	-0.248395000
C	-2.228926000	3.197463000	-0.689840000
H	-2.881188000	3.881725000	-0.127350000
H	-2.324427000	3.428491000	-1.760117000
H	-2.572210000	2.165678000	-0.518056000
C	-0.277141000	4.801845000	-0.527600000
H	-0.345189000	5.012992000	-1.603952000
H	-0.905425000	5.526957000	0.008527000
H	0.763243000	4.943087000	-0.204719000
S	0.203339000	2.140431000	-1.225206000
Pd	-0.318207000	0.282871000	0.170027000
C	1.897099000	2.564056000	-0.867559000
C	2.536784000	2.145559000	0.303981000
C	2.582225000	3.317574000	-1.825122000
C	3.864088000	2.504651000	0.521435000
H	2.003125000	1.536371000	1.036871000
C	3.910850000	3.669314000	-1.597353000
H	2.077100000	3.622072000	-2.744384000
C	4.549360000	3.266417000	-0.425560000
H	4.369150000	2.179720000	1.433525000
H	4.449848000	4.257304000	-2.343130000
H	5.591920000	3.541235000	-0.251418000
C	2.637229000	-4.211139000	-0.813655000
H	2.822929000	-4.989782000	-1.552983000
C	1.098788000	-2.603620000	0.174134000

O	-0.829910000	4.020082000	2.042630000
H	-0.843239000	3.687141000	2.957528000
C	3.356625000	-2.810155000	1.032238000
H	4.149895000	-2.520269000	1.723138000
C	3.635096000	-3.820423000	0.090246000
C	1.390228000	-3.597588000	-0.766129000
H	0.619576000	-3.910740000	-1.475792000
C	-0.248531000	-2.017684000	0.196882000
H	-0.964397000	-2.460922000	-0.505938000
H	-0.126464000	-0.836657000	-0.884840000
C	-0.828881000	-1.373323000	1.322990000
H	-0.279726000	-1.316222000	2.267638000
C	-2.305098000	-1.256050000	1.499731000
O	-2.979421000	-1.621546000	0.407880000
C	-4.406932000	-1.529165000	0.474084000
H	-4.684249000	-0.487270000	0.704647000
H	-4.763346000	-2.147575000	1.313328000
O	-2.813953000	-0.851445000	2.512396000
C	-4.976033000	-1.986653000	-0.845951000
H	-4.559672000	-1.361137000	-1.654716000
H	-4.636887000	-3.017801000	-1.043784000
C	-6.497767000	-1.926630000	-0.873205000
H	-6.901087000	-2.545502000	-0.052895000
H	-6.826835000	-0.894490000	-0.659055000
C	-7.086188000	-2.386708000	-2.196882000
H	-8.184470000	-2.333190000	-2.187589000
H	-6.729724000	-1.763701000	-3.032559000
H	-6.806283000	-3.428688000	-2.418275000
C	2.112668000	-2.215453000	1.070186000
H	1.924831000	-1.430192000	1.806860000
O	4.863020000	-4.336030000	0.132266000

C	5.219455000	-5.358124000	-0.768116000
H	6.258506000	-5.622965000	-0.540632000
H	4.583777000	-6.249643000	-0.637240000
H	5.155958000	-5.014325000	-1.814094000

I-6[p]

Lowest frequency = 12.0804 cm^{-1}

Charge = 1, Multiplicity = 1

62

O	0.819498000	-1.273261000	-1.780341000
C	1.438776000	-2.303852000	-1.553737000
C	1.204427000	-3.193482000	-0.343366000
C	-0.022064000	-4.062836000	-0.651043000
H	0.197937000	-4.720034000	-1.505296000
H	-0.255678000	-4.693723000	0.218250000
H	-0.907443000	-3.456154000	-0.896053000
C	2.414735000	-4.029601000	0.032836000
H	2.185412000	-4.637644000	0.919140000
H	2.666075000	-4.706491000	-0.795702000
H	3.294276000	-3.407433000	0.247071000
S	0.693391000	-2.113622000	1.089855000
Pd	-0.576900000	-0.589910000	-0.167323000
C	2.204861000	-1.253205000	1.498444000
C	2.672566000	-0.158889000	0.763713000
C	2.914460000	-1.727855000	2.605814000
C	3.875804000	0.440441000	1.127866000
H	2.104596000	0.236581000	-0.080416000

C	4.112267000	-1.113703000	2.965121000
H	2.529646000	-2.572334000	3.181821000
C	4.595311000	-0.036215000	2.223954000
H	4.245857000	1.290284000	0.549915000
H	4.669114000	-1.480990000	3.829659000
H	5.537053000	0.439274000	2.506782000
C	1.777790000	3.587592000	0.410525000
H	2.075415000	4.190294000	1.268087000
C	0.094159000	2.205047000	-0.684860000
O	2.327484000	-2.773892000	-2.390343000
H	2.376527000	-2.191020000	-3.167721000
C	2.223643000	2.618883000	-1.772735000
H	2.909881000	2.504609000	-2.613594000
C	2.649895000	3.384769000	-0.669102000
C	0.520957000	2.999380000	0.391337000
H	-0.146932000	3.144084000	1.244264000
C	-1.193376000	1.536204000	-0.584442000
H	-1.837114000	1.854751000	0.241042000
H	-1.508404000	-0.361082000	0.987652000
C	-1.752996000	0.641771000	-1.493961000
H	-1.287709000	0.444475000	-2.464373000
C	-3.171459000	0.184264000	-1.428019000
O	-3.821561000	0.677513000	-0.379250000
C	-5.182661000	0.262401000	-0.211235000
H	-5.209006000	-0.836705000	-0.131422000
H	-5.749382000	0.533440000	-1.116180000
O	-3.646202000	-0.561482000	-2.245005000
C	-5.734079000	0.931958000	1.022889000
H	-5.109763000	0.656979000	1.890653000
H	-5.644385000	2.025596000	0.907128000
C	-7.185911000	0.554817000	1.287180000

H	-7.797513000	0.822653000	0.408028000
H	-7.266393000	-0.542013000	1.385479000
C	-7.755455000	1.222443000	2.528130000
H	-8.803350000	0.933182000	2.693962000
H	-7.186870000	0.944037000	3.429642000
H	-7.723252000	2.320091000	2.442336000
C	0.970045000	2.042869000	-1.780490000
H	0.663728000	1.451394000	-2.645268000
O	3.895090000	3.858567000	-0.732216000
C	4.373927000	4.697797000	0.294737000
H	5.393289000	4.983227000	0.010640000
H	3.757421000	5.606445000	0.389304000
H	4.401890000	4.172482000	1.264256000

I-1’

Lowest frequency = 24.1114 cm^{-1}

Charge = 0, Multiplicity = 1

50

O	-1.116645000	1.828407000	-0.715481000
C	-0.456960000	2.722770000	-0.043423000
C	0.193300000	2.246587000	1.275616000
C	1.347287000	3.130984000	1.691380000
H	0.970574000	4.160275000	1.774200000
H	1.764482000	2.814478000	2.659402000
H	2.145539000	3.137436000	0.936018000
C	-0.893034000	2.150117000	2.347113000
H	-0.485457000	1.761093000	3.292708000

H	-1.288384000	3.160822000	2.527447000
H	-1.731239000	1.513202000	2.022715000
S	0.773636000	0.494394000	1.029720000
Pd	-1.062187000	-0.114126000	-0.214586000
O	-2.682289000	-0.420095000	-1.352494000
C	-3.784275000	-0.175917000	-0.704273000
O	-3.847170000	0.001345000	0.503348000
C	-5.001359000	-0.118666000	-1.596572000
H	-4.991304000	0.841097000	-2.135153000
H	-4.975210000	-0.918527000	-2.348954000
H	-5.913291000	-0.182925000	-0.990955000
C	-1.447622000	-2.177313000	0.730147000
C	0.541482000	-2.635161000	2.018551000
C	-0.691390000	-2.329828000	-0.453738000
H	-2.534173000	-2.078864000	0.693718000
H	1.036479000	-2.762935000	2.984967000
C	0.699864000	-2.617872000	-0.401796000
H	-1.208930000	-2.380999000	-1.415233000
O	-0.368457000	3.885914000	-0.362447000
C	2.775529000	-3.094897000	0.933972000
H	2.999062000	-4.069549000	0.469954000
H	3.384394000	-2.345780000	0.403652000
H	3.113738000	-3.134045000	1.978303000
C	1.480032000	-2.745498000	-1.672813000
H	2.263139000	-1.971104000	-1.730783000
H	1.988328000	-3.720424000	-1.742490000
H	0.831821000	-2.630326000	-2.551618000
C	-0.804264000	-2.336585000	1.977516000
H	-1.382344000	-2.236804000	2.898072000
C	1.314475000	-2.772806000	0.842796000
C	2.112043000	0.659144000	-0.137065000

C	3.404305000	0.442711000	0.348509000
C	1.897562000	0.960061000	-1.485629000
C	4.490263000	0.522700000	-0.521295000
H	3.552407000	0.210877000	1.405654000
C	2.991179000	1.042014000	-2.344162000
H	0.883577000	1.129801000	-1.854405000
C	4.283609000	0.820848000	-1.867373000
H	5.501127000	0.353417000	-0.143506000
H	2.827654000	1.280650000	-3.397312000
H	5.134786000	0.883701000	-2.549174000

TS(1-2)'$^{\beta}$

Lowest frequency = -744.2935 cm^{-1}

Charge = 0, Multiplicity = 1

50

O	-1.832547000	1.955972000	0.074030000
C	-1.153018000	2.890427000	-0.506727000
C	-0.038775000	2.439260000	-1.487033000
C	-0.688377000	2.138114000	-2.837305000
H	-1.161937000	3.060348000	-3.205183000
H	0.057860000	1.805521000	-3.574696000
H	-1.470113000	1.368915000	-2.745127000
C	1.063687000	3.469277000	-1.603654000
H	1.810771000	3.173937000	-2.356137000
H	0.599224000	4.420790000	-1.898772000
H	1.567256000	3.636197000	-0.641430000
S	0.650777000	0.808415000	-0.922515000

Pd	-1.296306000	0.011770000	-0.033728000
O	-3.123444000	-0.461209000	0.735384000
C	-3.424007000	-1.634316000	1.091240000
O	-2.658076000	-2.622928000	0.997942000
C	-4.809436000	-1.848617000	1.635762000
H	-5.251037000	-0.898608000	1.957096000
H	-5.431166000	-2.279976000	0.836329000
H	-4.778689000	-2.571656000	2.460844000
C	-0.416688000	-1.926057000	-0.171244000
C	1.928156000	-2.567011000	0.206220000
H	-1.546561000	-2.178174000	0.416493000
O	-1.363989000	4.077483000	-0.385040000
C	1.634860000	1.231997000	0.503275000
C	1.072723000	1.745186000	1.676210000
C	3.007877000	0.996445000	0.411874000
C	1.904018000	2.029989000	2.756271000
H	-0.004682000	1.914532000	1.739922000
C	3.828372000	1.277307000	1.502745000
H	3.424468000	0.589395000	-0.512157000
C	3.277191000	1.794613000	2.673623000
H	1.470624000	2.435112000	3.673321000
H	4.902778000	1.091813000	1.435221000
H	3.920459000	2.015495000	3.528485000
C	2.007753000	-3.036806000	-1.124589000
C	3.119610000	-2.629502000	1.114629000
H	2.892036000	-2.190515000	2.095349000
H	3.455028000	-3.667415000	1.274075000
H	3.977932000	-2.080093000	0.695064000
C	0.874199000	-2.970830000	-1.944416000
H	0.939455000	-3.351019000	-2.967705000
C	-0.317508000	-2.426451000	-1.482361000

H	-1.186835000	-2.383336000	-2.144610000
C	3.289441000	-3.607831000	-1.648635000
H	3.612399000	-4.478977000	-1.055442000
H	3.190648000	-3.926760000	-2.694874000
H	4.108590000	-2.872202000	-1.592093000
C	0.720264000	-2.036893000	0.654664000
H	0.661517000	-1.673713000	1.685930000

I-2'$^{\beta}$

Lowest frequency = 17.1129 cm^{-1}

Charge = 0, Multiplicity = 1

50

O	1.983530000	1.889774000	0.321737000
C	3.061355000	1.401208000	-0.175654000
C	2.889567000	0.362109000	-1.327349000
C	2.691829000	1.137301000	-2.629107000
H	3.583781000	1.759821000	-2.793985000
H	2.569254000	0.460530000	-3.488579000
H	1.818852000	1.804793000	-2.568792000
C	4.057693000	-0.596868000	-1.411437000
H	3.966734000	-1.269487000	-2.278243000
H	4.971489000	0.006461000	-1.504604000
H	4.157289000	-1.198243000	-0.497144000
S	1.301970000	-0.588934000	-1.109199000
Pd	0.123052000	1.071594000	-0.129209000
O	-0.846780000	2.702372000	0.798233000
C	-1.831776000	2.715944000	1.529599000

O	-2.611037000	1.686380000	1.728854000
C	-2.241259000	3.947267000	2.265482000
H	-1.469317000	4.717057000	2.166088000
H	-3.193087000	4.311125000	1.850063000
H	-2.417458000	3.705953000	3.322937000
C	-1.899373000	-1.076460000	0.086450000
C	-4.030783000	-1.197213000	-1.058117000
H	-1.188312000	-1.529181000	0.786499000
O	4.198343000	1.714366000	0.119130000
C	-3.104732000	-1.750402000	-0.152802000
C	1.642633000	-1.690984000	0.253582000
C	1.989579000	-1.222261000	1.525335000
C	1.518829000	-3.059149000	0.006198000
C	2.225088000	-2.140532000	2.544398000
H	2.067856000	-0.148043000	1.708847000
C	1.743891000	-3.968608000	1.038966000
H	1.243298000	-3.404591000	-0.992611000
C	2.099592000	-3.510387000	2.305647000
H	2.503006000	-1.779605000	3.537169000
H	1.643819000	-5.039614000	0.848702000
H	2.279284000	-4.223382000	3.113622000
C	-3.711084000	0.010216000	-1.687593000
H	-4.426733000	0.443185000	-2.393243000
C	-3.393837000	-3.047404000	0.543284000
H	-4.303167000	-2.982026000	1.163289000
H	-3.565012000	-3.862974000	-0.178346000
H	-2.560224000	-3.343268000	1.195153000
C	-5.330831000	-1.889267000	-1.342885000
H	-5.170571000	-2.898512000	-1.756785000
H	-5.931791000	-2.017890000	-0.427596000
H	-5.935095000	-1.322925000	-2.064875000

C	-2.511112000	0.674038000	-1.438416000
H	-2.305381000	1.618878000	-1.949597000
C	-1.578842000	0.139473000	-0.538302000
H	-2.341443000	0.950321000	1.125511000

I-1$^{\alpha\beta}$

Lowest frequency = 31.2206 cm^{-1}

Charge = 1, Multiplicity = 1

51

O	-1.257092000	2.069089000	-0.101011000
C	-0.314697000	2.737853000	-0.513828000
C	0.759443000	2.188777000	-1.428584000
C	0.188127000	2.178628000	-2.852062000
H	-0.019665000	3.209469000	-3.174878000
H	0.925021000	1.742788000	-3.541459000
H	-0.743875000	1.597039000	-2.915516000
C	2.074676000	2.939229000	-1.340641000
H	2.815881000	2.474808000	-2.006387000
H	1.924935000	3.979071000	-1.664307000
H	2.474066000	2.951264000	-0.317636000
S	0.989611000	0.387680000	-0.987726000
Pd	-1.199367000	-0.049199000	-0.339047000
O	-3.064061000	-0.246192000	0.291285000
C	-3.093601000	0.012462000	1.575383000
O	-2.077580000	0.228035000	2.221593000
C	-4.474739000	0.030744000	2.162465000
H	-4.411498000	0.042545000	3.256760000

H	-4.999101000	0.934658000	1.817570000
H	-5.055328000	-0.834943000	1.816292000
C	-1.033109000	-2.237995000	-0.052924000
C	1.166896000	-2.830871000	-0.895431000
H	-1.746707000	-2.303958000	0.771919000
C	0.318624000	-2.618869000	0.194211000
C	1.864558000	0.456206000	0.564430000
C	1.200195000	0.636458000	1.782256000
C	3.251194000	0.279177000	0.512765000
C	1.950528000	0.657251000	2.956526000
H	0.109115000	0.718034000	1.839173000
C	3.985028000	0.301132000	1.696458000
H	3.750091000	0.124574000	-0.446830000
C	3.335212000	0.493196000	2.915962000
H	1.438843000	0.790585000	3.912002000
H	5.068147000	0.165381000	1.664738000
H	3.912569000	0.506727000	3.843022000
C	0.666074000	-2.656566000	-2.209348000
H	1.341033000	-2.842922000	-3.048808000
C	0.779705000	-2.822993000	1.601262000
H	0.996300000	-3.886674000	1.794589000
H	1.709346000	-2.268483000	1.802099000
H	0.022665000	-2.487726000	2.322066000
C	2.582795000	-3.268011000	-0.682629000
H	3.129173000	-2.555209000	-0.044598000
H	2.622442000	-4.241419000	-0.168046000
H	3.123715000	-3.366307000	-1.632704000
C	-0.633727000	-2.267626000	-2.461257000
H	-0.994908000	-2.161042000	-3.485781000
C	-1.513083000	-2.052232000	-1.377571000
H	-2.584926000	-1.920963000	-1.546703000

O	-0.209783000	4.007952000	-0.242071000
H	-0.962708000	4.286202000	0.310156000

TS(1-2)$^{\alpha}$

Lowest frequency = -209.1494 cm^{-1}

Charge = 1, Multiplicity = 1

51

O	-0.180273000	-2.580779000	-0.409808000
C	0.862808000	-2.884221000	0.158062000
C	1.531872000	-2.033268000	1.221118000
C	0.877201000	-2.391689000	2.562381000
H	1.074130000	-3.447947000	2.797834000
H	1.309332000	-1.771767000	3.360461000
H	-0.211659000	-2.234173000	2.541876000
C	3.041225000	-2.190738000	1.261222000
H	3.463368000	-1.533223000	2.034367000
H	3.295290000	-3.229824000	1.514012000
H	3.506570000	-1.944978000	0.297062000
S	1.063330000	-0.253577000	0.915370000
Pd	-1.013231000	-0.643096000	-0.005227000
O	-2.749670000	-1.198915000	-0.832239000
C	-3.722841000	-0.415938000	-1.105717000
O	-3.744286000	0.799355000	-0.849409000
C	-4.916065000	-1.060193000	-1.754011000
H	-5.620381000	-1.347875000	-0.958058000
H	-5.419820000	-0.337619000	-2.407085000
H	-4.626378000	-1.962145000	-2.304950000

C	-1.550706000	1.299633000	0.553414000
C	-0.038571000	3.211877000	0.767140000
H	-2.568983000	1.078299000	-0.110345000
C	-0.704485000	2.276727000	-0.046486000
C	2.113596000	0.237363000	-0.435529000
C	1.934862000	-0.235104000	-1.740265000
C	3.114868000	1.165249000	-0.138697000
C	2.783013000	0.217148000	-2.747061000
H	1.127656000	-0.932027000	-1.975481000
C	3.951555000	1.617689000	-1.157862000
H	3.232172000	1.532683000	0.883233000
C	3.788144000	1.142066000	-2.457837000
H	2.649695000	-0.146028000	-3.768265000
H	4.735583000	2.343619000	-0.932188000
H	4.445056000	1.497610000	-3.254574000
C	-0.241569000	3.156362000	2.152331000
H	0.279880000	3.881531000	2.783907000
C	-0.558754000	2.329726000	-1.533524000
H	-0.853907000	3.321184000	-1.913317000
H	0.486916000	2.174442000	-1.843857000
H	-1.184826000	1.575036000	-2.027338000
C	0.861158000	4.248046000	0.165585000
H	1.653768000	3.785949000	-0.444488000
H	0.301350000	4.922561000	-0.501951000
H	1.338876000	4.863792000	0.939054000
C	-1.097976000	2.227839000	2.753230000
H	-1.248910000	2.243797000	3.834480000
C	-1.749058000	1.301674000	1.957956000
H	-2.434649000	0.574806000	2.402142000
O	1.455543000	-4.025603000	-0.065956000
H	0.933045000	-4.541998000	-0.705405000

TS(1-2)$^{\beta}$

Lowest frequency = -196.6596 cm^{-1}

Charge = 1, Multiplicity = 1

51

O	-1.072289000	2.489807000	-0.021796000
C	-0.125528000	2.988773000	-0.618936000
C	0.833224000	2.205108000	-1.495434000
C	0.178659000	2.078047000	-2.877690000
H	0.053946000	3.077407000	-3.320111000
H	0.825698000	1.484406000	-3.538704000
H	-0.808301000	1.594794000	-2.820442000
C	2.219714000	2.817410000	-1.572687000
H	2.868718000	2.192697000	-2.202626000
H	2.154593000	3.816019000	-2.027377000
H	2.681235000	2.918395000	-0.581108000
S	0.913825000	0.459571000	-0.837995000
Pd	-1.246193000	0.351001000	-0.021994000
O	-3.122330000	0.497822000	0.650875000
C	-3.835556000	-0.469108000	1.092659000
O	-3.473867000	-1.654850000	1.129558000
C	-5.214779000	-0.092886000	1.558529000
H	-5.566509000	-0.814239000	2.305206000
H	-5.228497000	0.929566000	1.953648000
H	-5.890864000	-0.136133000	0.690571000
C	-0.009127000	-2.162978000	0.690379000
C	0.891308000	-3.394550000	-1.178251000

H	0.056045000	-1.845426000	1.735686000
C	0.994558000	-2.972036000	0.173174000
C	1.975445000	0.591322000	0.585706000
C	1.526324000	1.095693000	1.810401000
C	3.284527000	0.125617000	0.437733000
C	2.406751000	1.143877000	2.887854000
H	0.494069000	1.434011000	1.927021000
C	4.155593000	0.177650000	1.524029000
H	3.615216000	-0.277569000	-0.522155000
C	3.717867000	0.686507000	2.745753000
H	2.063112000	1.534149000	3.848157000
H	5.180234000	-0.183855000	1.414495000
H	4.401368000	0.723039000	3.596784000
C	-0.211286000	-2.998324000	-1.952317000
H	-0.285193000	-3.349907000	-2.984319000
C	2.155267000	-3.392141000	1.021632000
H	2.191420000	-4.486855000	1.139946000
H	3.114463000	-3.090403000	0.572009000
H	2.097272000	-2.945057000	2.022725000
C	1.944903000	-4.271752000	-1.769876000
H	2.938192000	-3.798726000	-1.706388000
H	2.020566000	-5.221197000	-1.215051000
H	1.738986000	-4.505389000	-2.822000000
C	-1.196777000	-2.178466000	-1.427443000
H	-2.053523000	-1.889054000	-2.042094000
C	-1.116319000	-1.733518000	-0.085648000
H	-2.194421000	-1.708457000	0.509055000
O	0.091935000	4.275938000	-0.600768000
H	-0.600364000	4.713429000	-0.073618000

I-2$^{\alpha}$

Lowest frequency = 14.1399 cm^{-1}

Charge = 1, Multiplicity = 1

51

O	1.471661000	-2.200504000	-0.681631000
C	2.531159000	-1.975124000	-0.117167000
C	2.683985000	-1.068458000	1.093822000
C	2.375710000	-1.923815000	2.330556000
H	3.107537000	-2.741759000	2.403791000
H	2.453105000	-1.306771000	3.236760000
H	1.366633000	-2.360089000	2.282850000
C	4.046722000	-0.404471000	1.187926000
H	4.081275000	0.251249000	2.069494000
H	4.822985000	-1.174627000	1.297667000
H	4.276155000	0.193513000	0.295701000
S	1.337022000	0.219153000	1.054774000
Pd	-0.279953000	-0.975139000	-0.018427000
O	-1.654846000	-2.162273000	-1.045278000
C	-2.880216000	-2.158027000	-1.194145000
O	-3.670400000	-1.269988000	-0.667568000
C	-3.566700000	-3.199145000	-2.005970000
H	-4.174690000	-2.715267000	-2.783943000
H	-2.834863000	-3.878091000	-2.454398000
H	-4.258965000	-3.759006000	-1.359418000
C	-1.604732000	0.284778000	0.712068000
C	-2.955543000	2.292382000	0.552058000
H	-3.148740000	-0.620423000	-0.137456000
C	-2.011686000	1.409825000	-0.026110000

C	1.918529000	1.418237000	-0.128440000
C	2.049602000	1.131069000	-1.491232000
C	2.215794000	2.688195000	0.369427000
C	2.500738000	2.125112000	-2.353386000
H	1.784411000	0.145631000	-1.879999000
C	2.653339000	3.680391000	-0.507230000
H	2.100796000	2.898250000	1.435058000
C	2.799577000	3.398487000	-1.863659000
H	2.607824000	1.908651000	-3.418431000
H	2.883067000	4.676867000	-0.124220000
H	3.145201000	4.176485000	-2.547790000
C	-3.454878000	2.021879000	1.828486000
H	-4.184873000	2.706490000	2.267204000
C	-1.483059000	1.686976000	-1.404445000
H	-2.300272000	1.844284000	-2.125366000
H	-0.864456000	2.599300000	-1.419229000
H	-0.858994000	0.861055000	-1.773478000
C	-3.412947000	3.505427000	-0.200983000
H	-2.565473000	4.153416000	-0.475501000
H	-3.918685000	3.231418000	-1.140985000
H	-4.115419000	4.101889000	0.395708000
C	-3.043637000	0.902299000	2.547298000
H	-3.448713000	0.707907000	3.542920000
C	-2.108790000	0.031136000	1.993804000
H	-1.778640000	-0.844558000	2.558435000
O	3.644922000	-2.568019000	-0.469181000
H	3.460790000	-3.182522000	-1.200918000

I-2$^{\beta}$

Lowest frequency = 17.3226 cm^{-1}

Charge = 1, Multiplicity = 1

51

O	-2.021730000	-2.007920000	0.413313000
C	-2.989321000	-1.495757000	-0.128164000
C	-2.903988000	-0.460262000	-1.238150000
C	-2.734007000	-1.232801000	-2.553506000
H	-3.616066000	-1.867638000	-2.723925000
H	-2.648424000	-0.525712000	-3.390520000
H	-1.839487000	-1.873361000	-2.537185000
C	-4.093998000	0.481971000	-1.280831000
H	-3.960068000	1.216282000	-2.087820000
H	-5.008711000	-0.092432000	-1.483652000
H	-4.227008000	1.020774000	-0.332979000
S	-1.318474000	0.503170000	-1.043012000
Pd	-0.036096000	-1.101161000	-0.056888000
O	1.045725000	-2.642286000	0.841387000
C	2.161868000	-2.720559000	1.362522000
O	3.023093000	-1.745775000	1.383656000
C	2.627360000	-3.975761000	2.011901000
H	1.796706000	-4.680344000	2.119722000
H	3.414034000	-4.423322000	1.384764000
H	3.081264000	-3.747674000	2.986020000
C	1.884932000	1.076213000	0.231620000
C	3.870036000	1.427245000	-1.116589000
H	1.243148000	1.397528000	1.058138000
C	3.040100000	1.821381000	-0.046473000
C	-1.682110000	1.676437000	0.247807000
C	-1.793302000	1.302690000	1.591596000

C	-1.826628000	3.010264000	-0.140015000
C	-2.071051000	2.276499000	2.546250000
H	-1.651471000	0.261337000	1.889810000
C	-2.097709000	3.977397000	0.826529000
H	-1.722224000	3.288140000	-1.191099000
C	-2.222909000	3.611165000	2.165080000
H	-2.160596000	1.992880000	3.597065000
H	-2.209603000	5.022154000	0.529227000
H	-2.434819000	4.371179000	2.920244000
C	3.513344000	0.303493000	-1.868946000
H	4.154494000	-0.003038000	-2.699922000
C	3.377216000	3.023283000	0.782308000
H	4.357392000	2.911114000	1.272875000
H	3.440409000	3.931149000	0.161292000
H	2.625069000	3.198373000	1.563206000
C	5.111098000	2.200889000	-1.443350000
H	4.877541000	3.248744000	-1.691486000
H	5.805682000	2.227365000	-0.588456000
H	5.643916000	1.763075000	-2.297608000
C	2.366145000	-0.439379000	-1.589860000
H	2.125206000	-1.314071000	-2.198971000
C	1.550651000	-0.053050000	-0.524561000
H	2.681960000	-0.975130000	0.871375000
O	-4.215544000	-1.859330000	0.154799000
H	-4.191056000	-2.570362000	0.818683000

I-1’’

Lowest frequency = 6.3188 cm^{-1}

Charge = 1, Multiplicity = 1

43

O	-0.405068000	-1.162672000	1.181645000
C	0.656357000	-1.941853000	1.189187000
C	1.415667000	-2.096079000	-0.138432000
C	2.887493000	-2.366619000	0.082957000
H	2.966739000	-3.271785000	0.702793000
H	3.410547000	-2.536605000	-0.869432000
H	3.379428000	-1.549852000	0.628151000
C	0.739058000	-3.191628000	-0.961798000
H	1.247742000	-3.331079000	-1.926647000
H	0.799235000	-4.133723000	-0.397337000
H	-0.324230000	-2.973213000	-1.143752000
S	1.194247000	-0.531874000	-1.134215000
Pd	-0.899641000	-0.057086000	-0.365417000
C	-1.916481000	2.220883000	-0.265973000
C	-3.191210000	0.179429000	0.222982000
H	-1.454775000	3.157861000	0.051511000
O	0.990190000	-2.554710000	2.166285000
C	-2.580097000	1.414957000	0.669577000
C	2.250041000	0.659637000	-0.338458000
C	3.303216000	1.160530000	-1.108056000
C	2.060931000	1.068421000	0.986562000
C	4.183462000	2.079215000	-0.538980000
H	3.437417000	0.828657000	-2.140135000
C	2.952114000	1.980928000	1.541746000
H	1.231236000	0.674809000	1.577335000
C	4.009781000	2.486055000	0.782243000
H	5.010600000	2.473757000	-1.132714000
H	2.819939000	2.300160000	2.577706000

H	4.703497000	3.203170000	1.226384000
C	-3.201162000	-0.142152000	-1.154206000
H	-3.738825000	-1.028788000	-1.495846000
C	-2.640461000	1.794552000	2.111441000
H	-3.684229000	1.897044000	2.446704000
H	-2.176567000	1.015712000	2.736725000
H	-2.121651000	2.743229000	2.296076000
C	-3.845837000	-0.724414000	1.214396000
H	-3.105364000	-1.083946000	1.946885000
H	-4.631704000	-0.193656000	1.773008000
H	-4.294102000	-1.597266000	0.724356000
C	-2.417486000	0.601452000	-2.047320000
H	-2.333272000	0.302343000	-3.093939000
C	-1.735414000	1.757234000	-1.586082000
H	-1.126934000	2.334911000	-2.285360000

TS(1-2)"$^{\beta}$

Lowest frequency = -320.2015 cm^{-1}

Charge = 1, Multiplicity = 1

43

O	0.441855000	-2.053831000	-0.110550000
C	1.139133000	-1.191729000	0.513064000
C	2.653358000	-1.527194000	0.608856000
C	3.195940000	-1.054839000	1.944657000
H	2.727614000	-1.631856000	2.757128000
H	4.280233000	-1.230205000	1.981669000
H	2.989818000	0.008502000	2.115126000

C	2.934067000	-3.000900000	0.352569000
H	4.015430000	-3.182133000	0.422667000
H	2.428482000	-3.618071000	1.109461000
H	2.585682000	-3.317125000	-0.639505000
S	3.338188000	-0.642405000	-0.856469000
Pd	-1.427369000	-1.780678000	-0.670096000
C	-1.748861000	0.066441000	0.106725000
C	-3.953812000	0.704082000	0.975805000
H	-0.620507000	0.059480000	0.592558000
O	0.731767000	-0.140277000	1.016010000
C	3.262573000	1.073521000	-0.432375000
C	4.234539000	1.651380000	0.394136000
C	2.268365000	1.873699000	-1.008509000
C	4.183874000	3.014725000	0.670846000
H	5.035675000	1.033627000	0.803914000
C	2.226981000	3.236733000	-0.732172000
H	1.538225000	1.417209000	-1.680461000
C	3.179841000	3.806099000	0.112839000
H	4.942043000	3.464770000	1.315302000
H	1.452759000	3.861464000	-1.183177000
H	3.148768000	4.876753000	0.326751000
C	-4.091508000	1.605750000	-0.117714000
C	-5.027993000	0.593018000	2.012152000
H	-4.765985000	-0.142678000	2.783241000
H	-5.203049000	1.559291000	2.510706000
H	-5.986808000	0.289034000	1.563219000
C	-3.058591000	1.730478000	-1.067104000
H	-3.176591000	2.446307000	-1.884058000
C	-1.906887000	0.971662000	-0.978940000
H	-1.105860000	1.093620000	-1.712604000
C	-2.795966000	-0.056590000	1.063944000

H	-2.662690000	-0.730100000	1.915906000
C	-5.325425000	2.429123000	-0.252106000
H	-6.223131000	1.791100000	-0.293161000
H	-5.454913000	3.080488000	0.628399000
H	-5.303956000	3.060272000	-1.148870000

I-2''$^{\beta}$

Lowest frequency = 8.2804 cm^{-1}

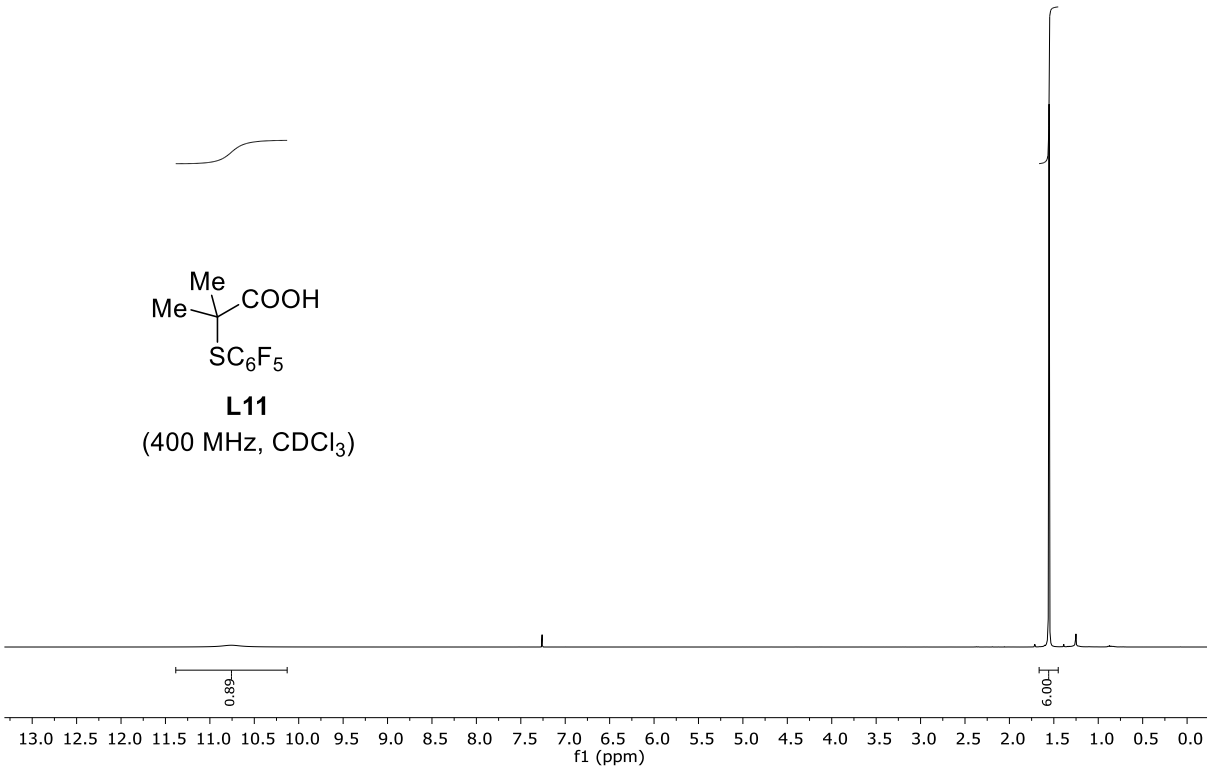
Charge = 1, Multiplicity = 1

43

O	-0.224887000	-2.275122000	0.062721000
C	0.671369000	-1.578156000	0.574015000
C	2.117813000	-1.933861000	0.382429000
C	2.980370000	-1.577274000	1.577148000
H	2.708194000	-2.214113000	2.433443000
H	4.034891000	-1.764985000	1.333514000
H	2.869726000	-0.526691000	1.871862000
C	2.286775000	-3.377269000	-0.063337000
H	3.348161000	-3.569933000	-0.267120000
H	1.951118000	-4.061914000	0.730264000
H	1.710611000	-3.595081000	-0.972613000
S	2.482035000	-0.892762000	-1.138283000
Pd	-2.233538000	-1.994510000	-0.147203000
C	-2.132038000	-0.088412000	-0.246832000
C	-2.901374000	2.024456000	0.616425000
H	-0.492535000	-0.220577000	1.177375000
O	0.438095000	-0.507720000	1.275570000

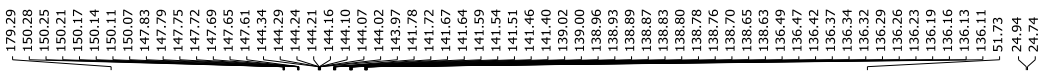
C	2.938350000	0.692525000	-0.488237000
C	4.281081000	0.946817000	-0.182463000
C	1.985747000	1.709028000	-0.354130000
C	4.659838000	2.204124000	0.280838000
H	5.024409000	0.158657000	-0.319234000
C	2.371544000	2.963642000	0.109443000
H	0.944922000	1.513414000	-0.614580000
C	3.706202000	3.210898000	0.430347000
H	5.707453000	2.401068000	0.518357000
H	1.626908000	3.756163000	0.214162000
H	4.007616000	4.197308000	0.789858000
C	-2.314590000	2.657507000	-0.502647000
C	-3.628836000	2.819510000	1.655414000
H	-4.013988000	2.182531000	2.462068000
H	-2.972226000	3.580994000	2.105133000
H	-4.480915000	3.359135000	1.212500000
C	-1.637643000	1.888032000	-1.455366000
H	-1.181278000	2.383556000	-2.316443000
C	-1.511583000	0.501962000	-1.338101000
H	-0.945559000	-0.072941000	-2.075564000
C	-2.792413000	0.630402000	0.746550000
H	-3.243789000	0.138432000	1.614799000
C	-2.407720000	4.143636000	-0.662357000
H	-3.457775000	4.471347000	-0.722747000
H	-1.963870000	4.668386000	0.198563000
H	-1.894887000	4.484239000	-1.570889000

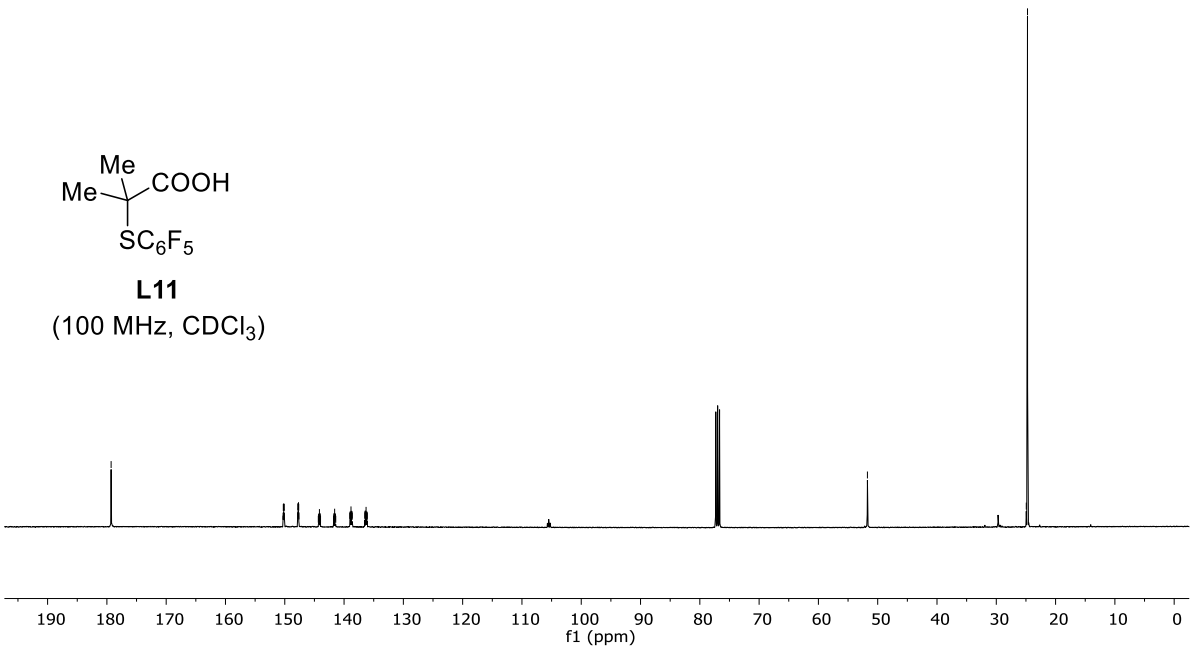
NMR spectrum



L11

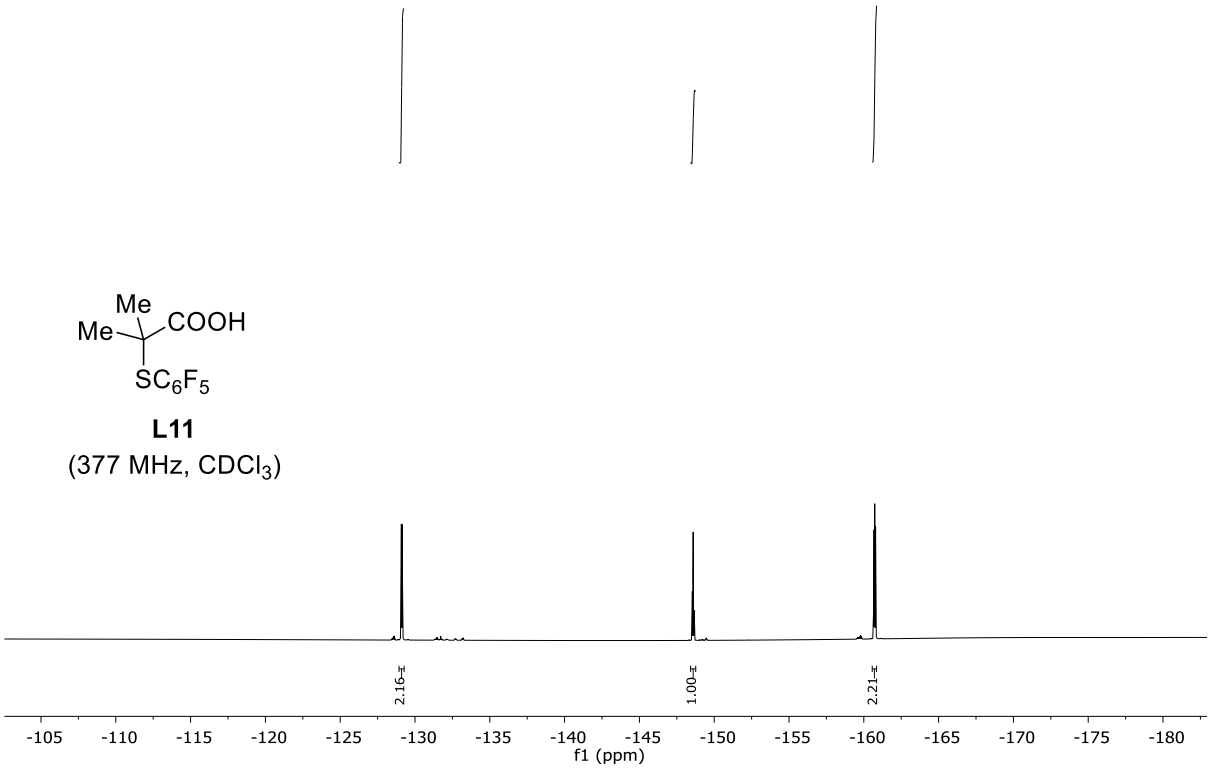
(400 MHz, $CDCl_3$)

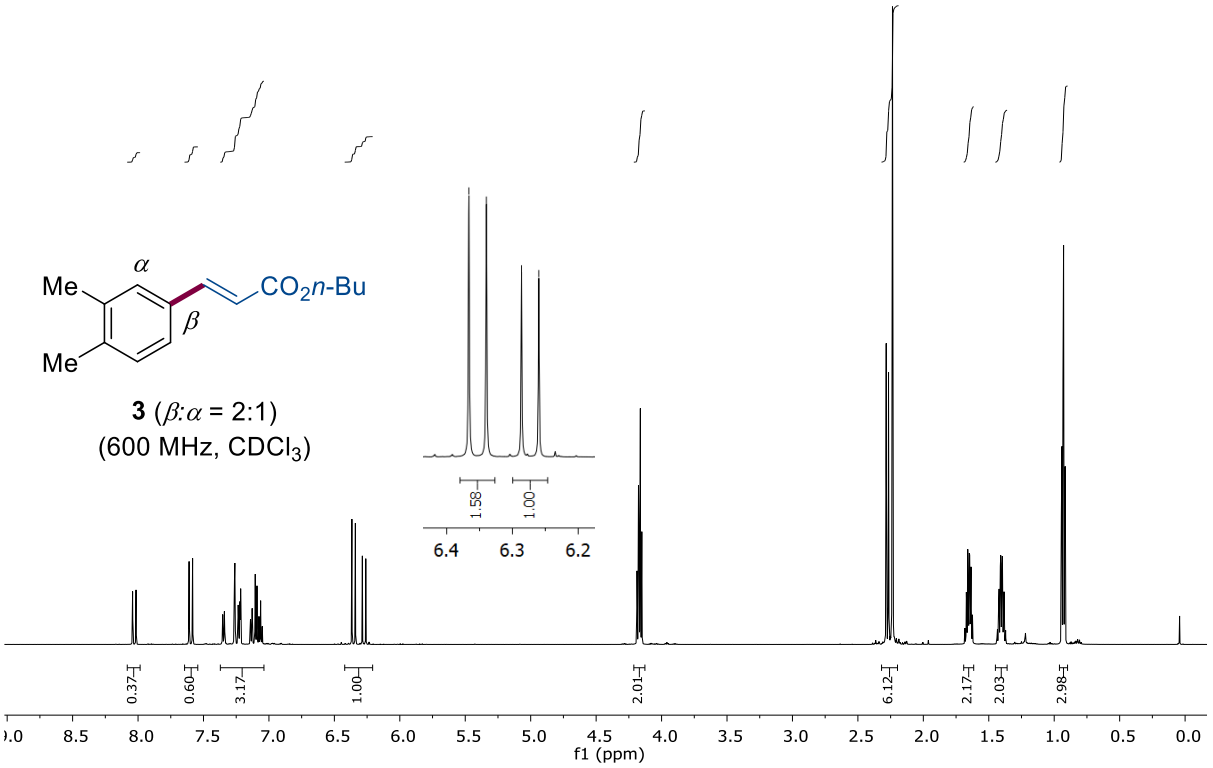


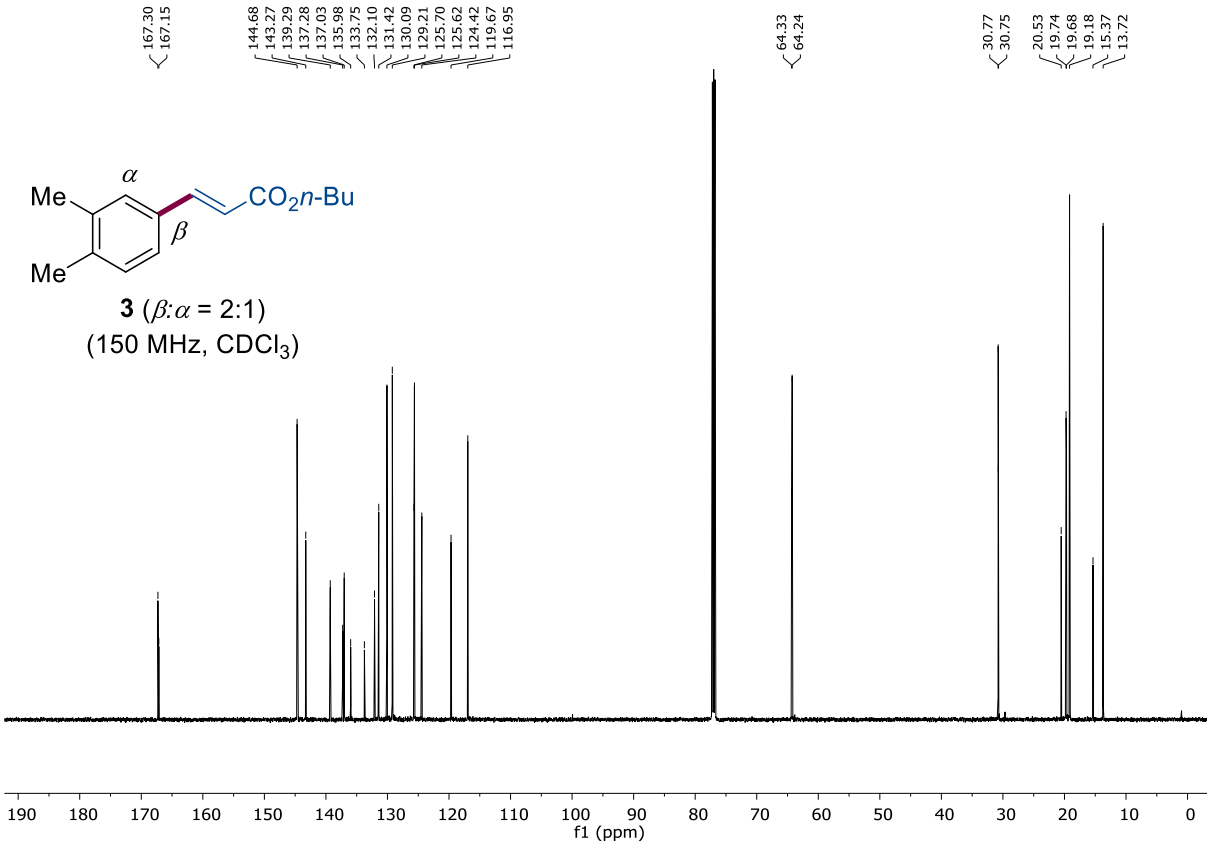


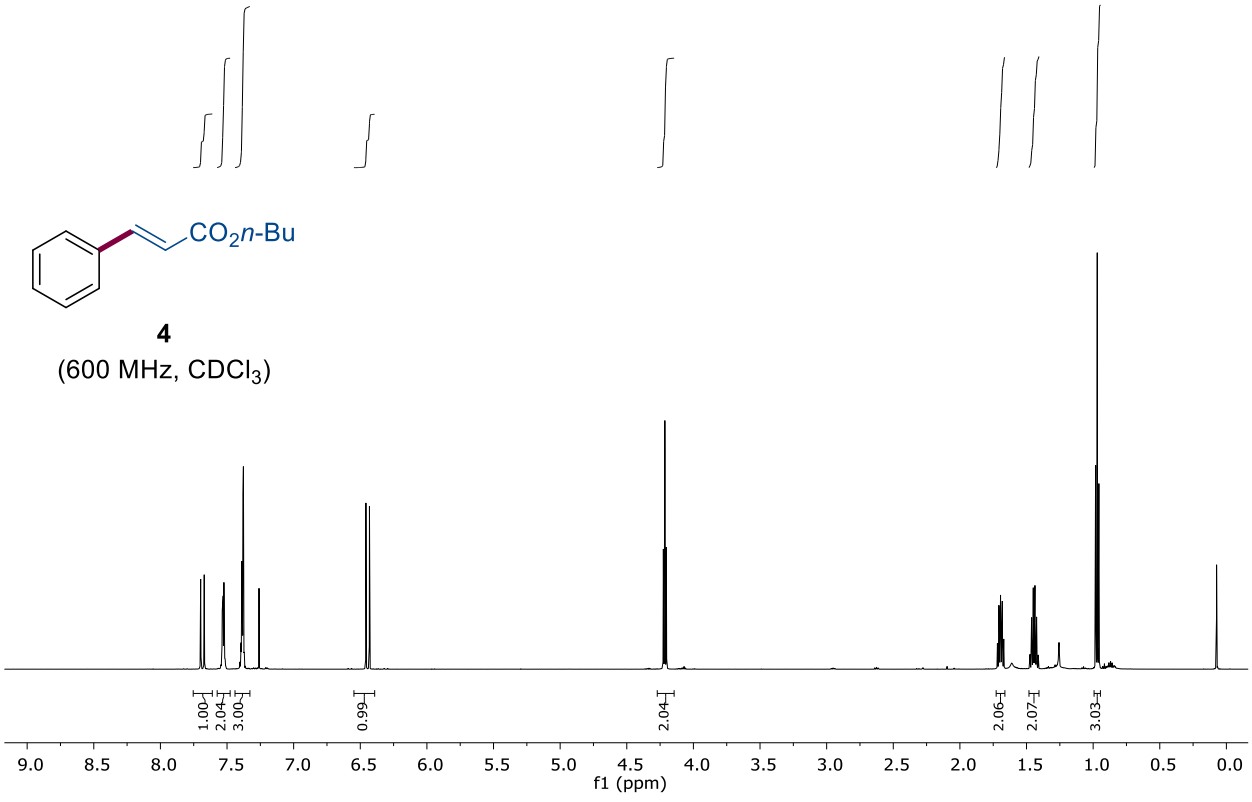
L11

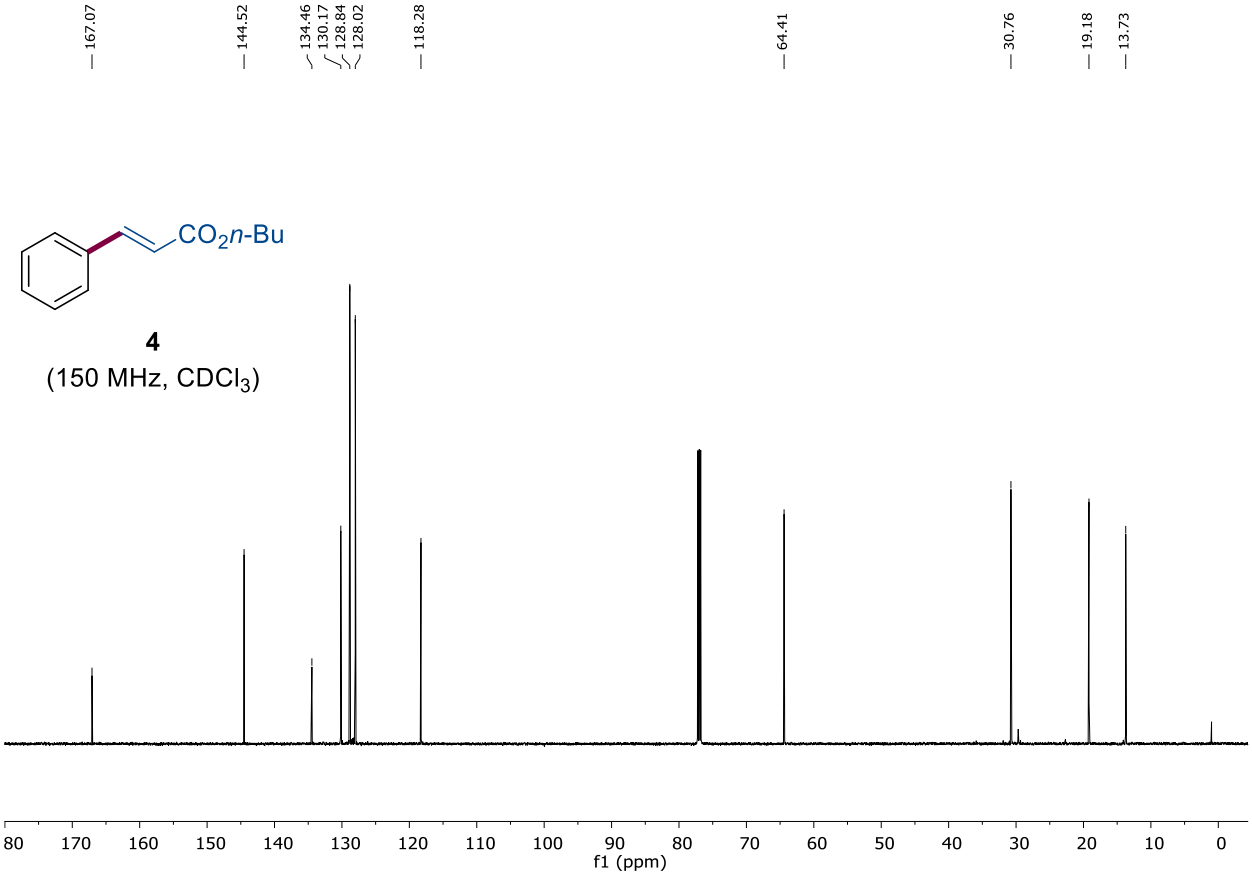
(100 MHz, $CDCl_3$)

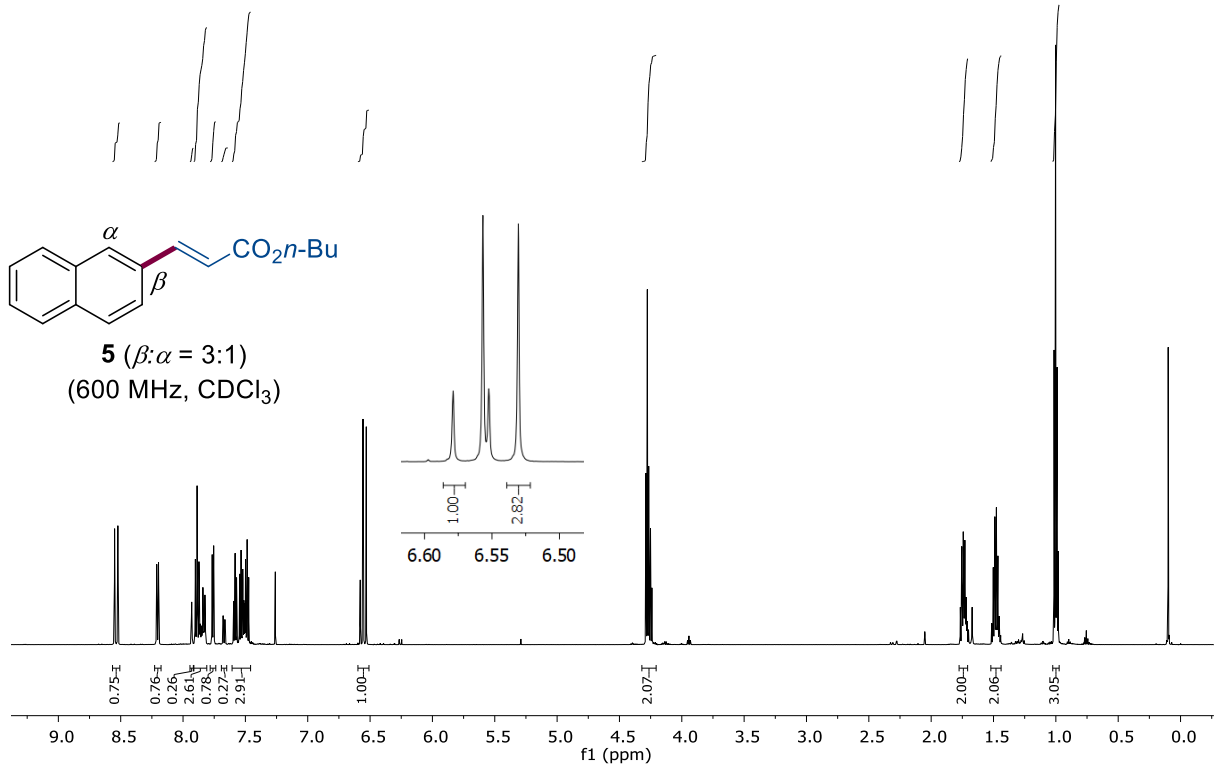

Me
Me
COOH
SC6F5
L11
(377 MHz, CDCl3)
2.16
1.00
2.21
-105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180
f1 (ppm)

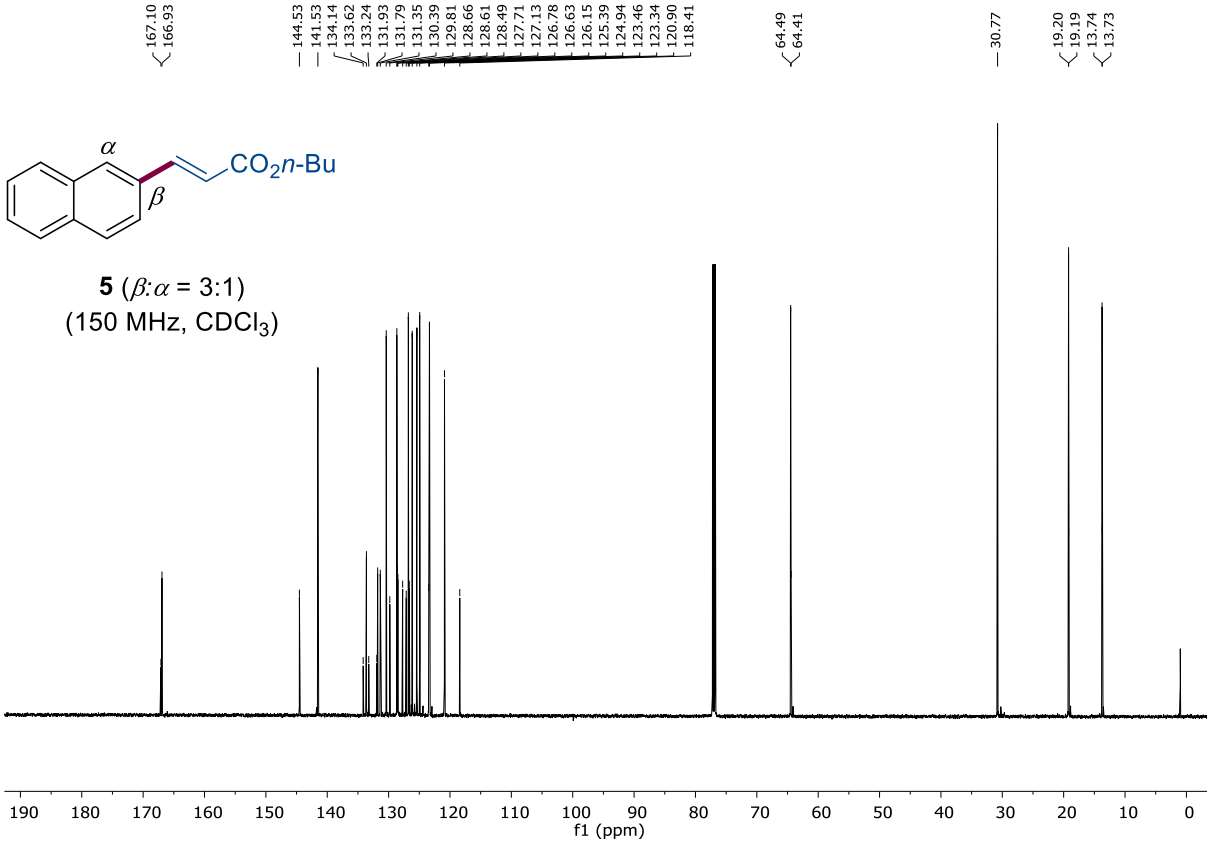

α
Me
CO2n-Bu
β
Me
3 (β:α = 2:1)
(600 MHz, CDCl3)
1.58
1.00
6.4 6.3 6.2
0.37
0.60
3.17
1.00
2.01
6.12
2.17
2.03
2.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

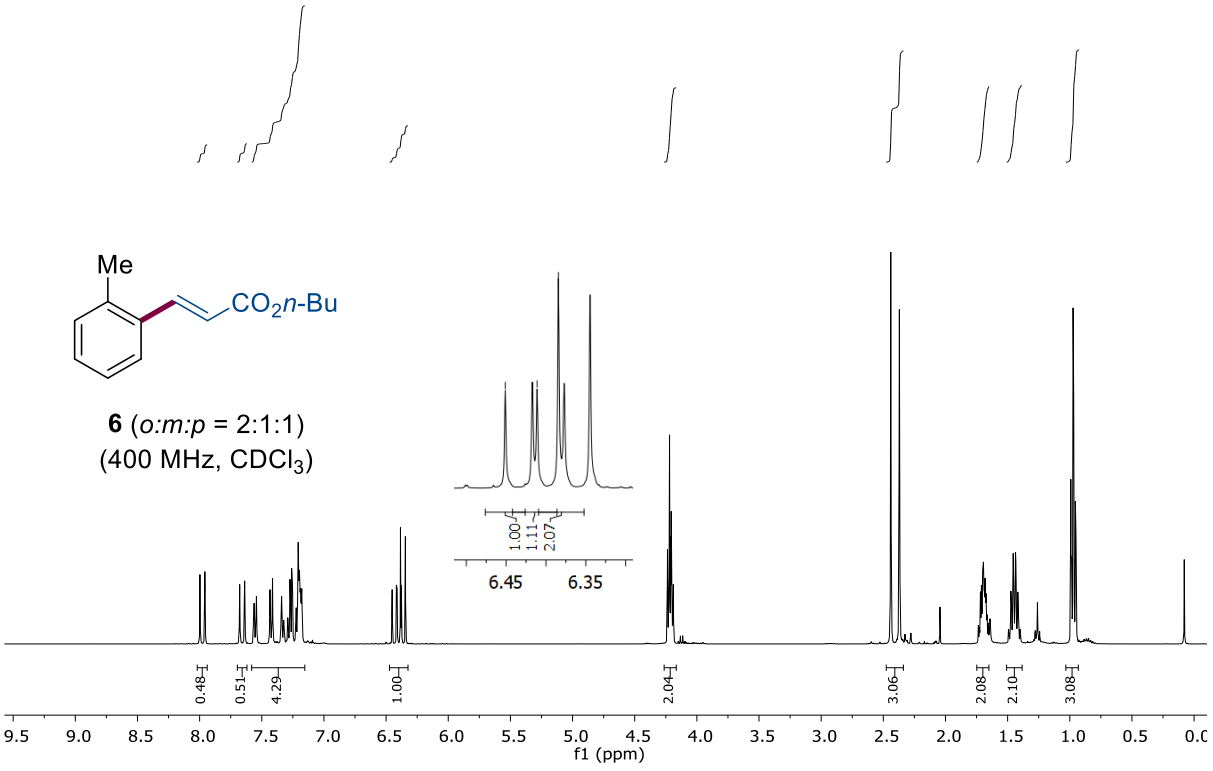

167.30
167.15
144.68
143.27
139.29
137.28
137.03
135.98
133.75
132.10
131.42
130.09
129.21
125.70
125.62
124.42
119.67
116.95
64.33
64.24
30.77
30.75
20.53
19.74
19.68
19.18
15.37
13.72
α
β
Me
Me
CO2n-Bu
3 (β:α = 2:1)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

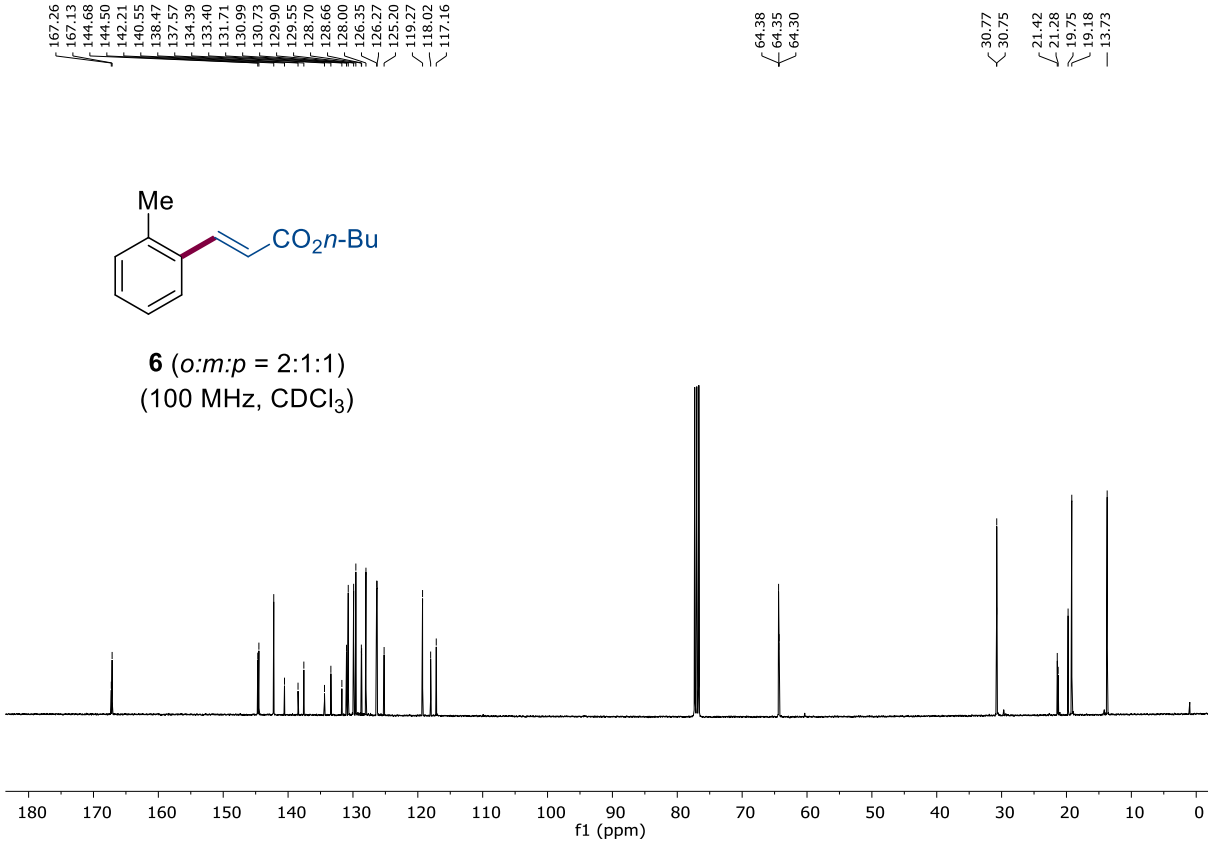

CO2n-Bu
4
(600 MHz, CDCl3)
1.00
2.04
3.00
0.99
2.04
2.06
2.07
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

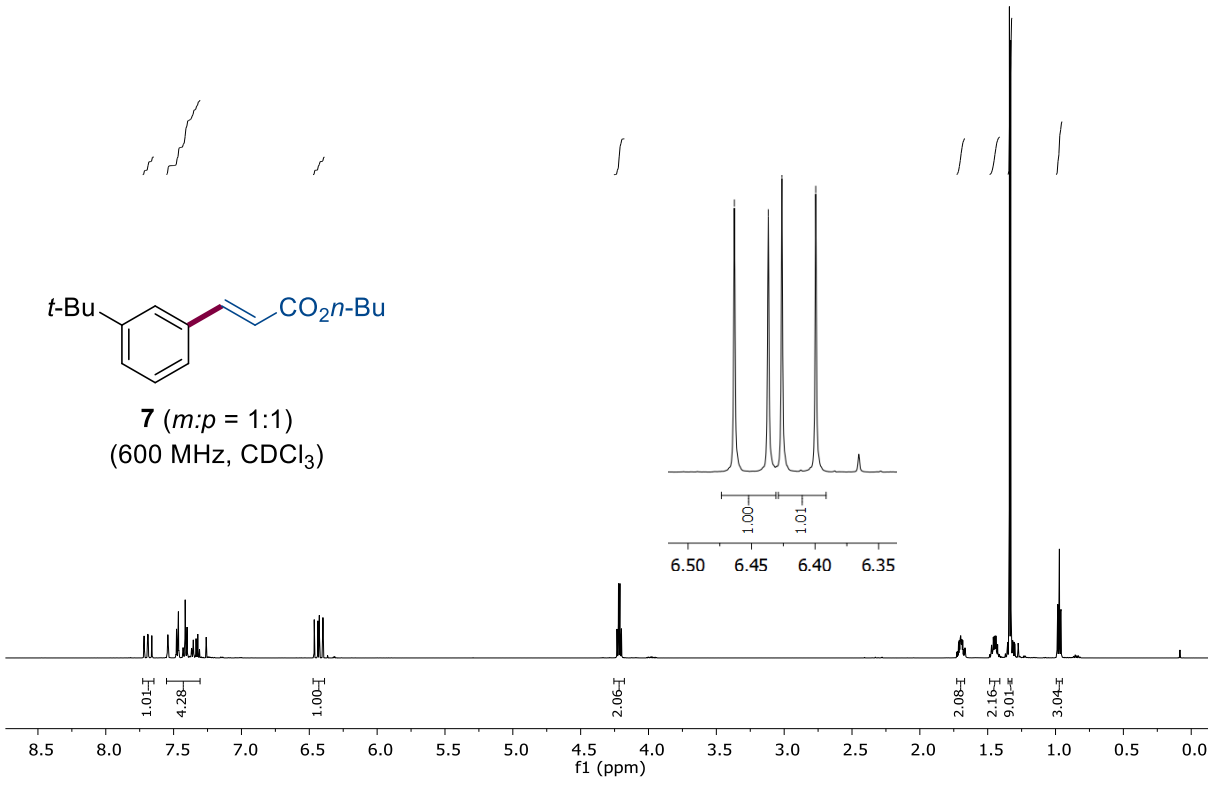

167.07
144.52
134.46
130.17
128.84
128.02
118.28
64.41
30.76
19.18
13.73
CO2n-Bu
4
(150 MHz, CDCl3)
f1 (ppm)

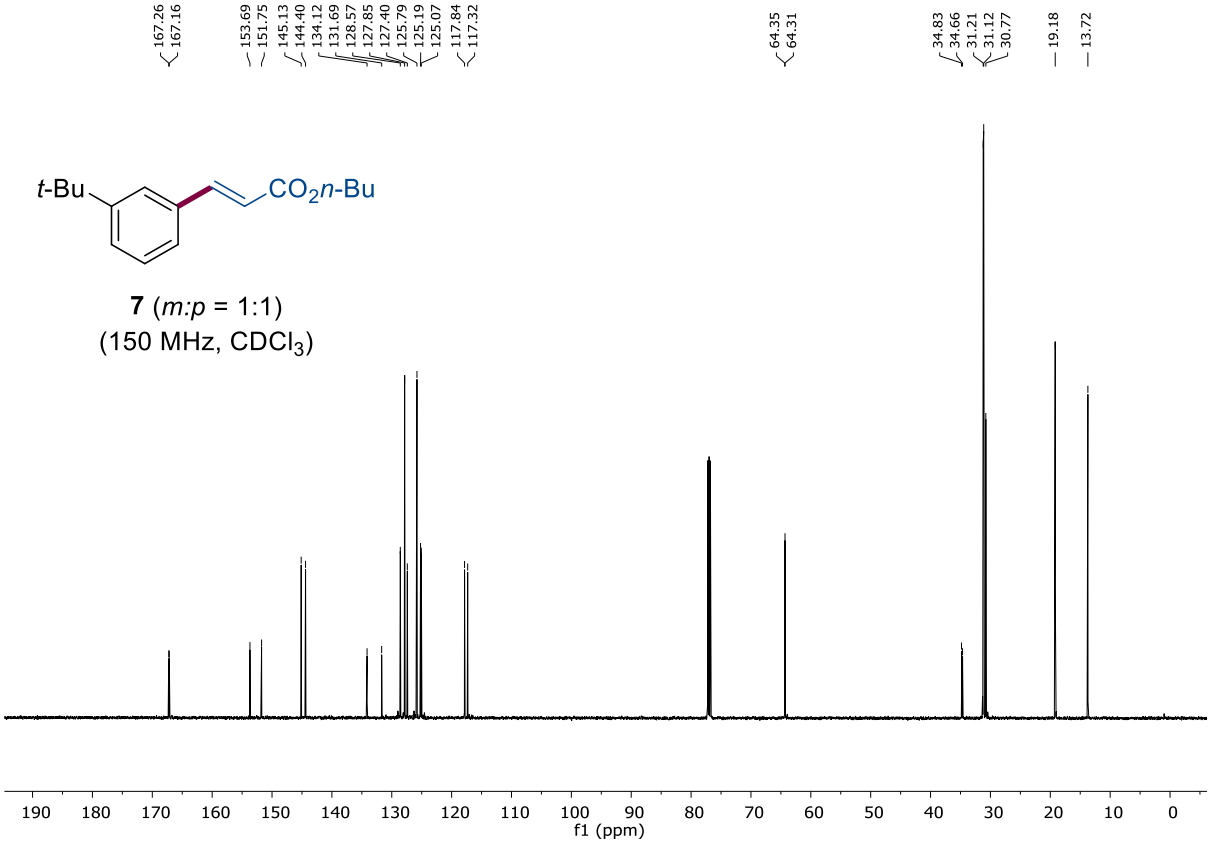

α
β
CO2n-Bu
5 (β:α = 3:1)
(600 MHz, CDCl3)
1.00
2.82
6.60
6.55
6.50
0.75
0.76
0.26
2.61
0.78
0.27
2.91
1.00
2.07
2.00
2.06
3.05
f1 (ppm)

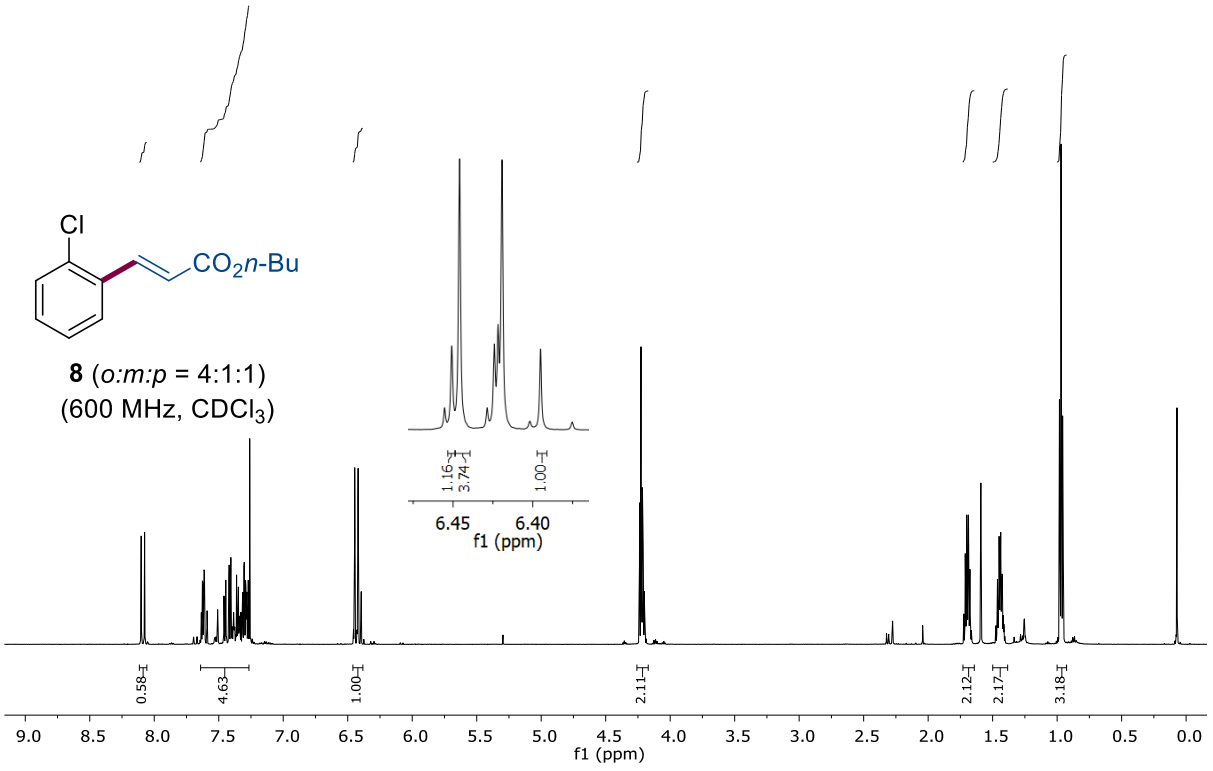

167.10
166.93
144.53
141.53
134.14
133.62
133.24
131.93
131.79
131.35
130.39
129.81
128.66
128.61
128.49
127.71
127.13
126.78
126.63
126.15
125.39
124.94
123.46
123.34
120.90
118.41
64.49
64.41
30.77
19.20
19.19
13.74
13.73
α
β
CO2n-Bu
5 (β:α = 3:1)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

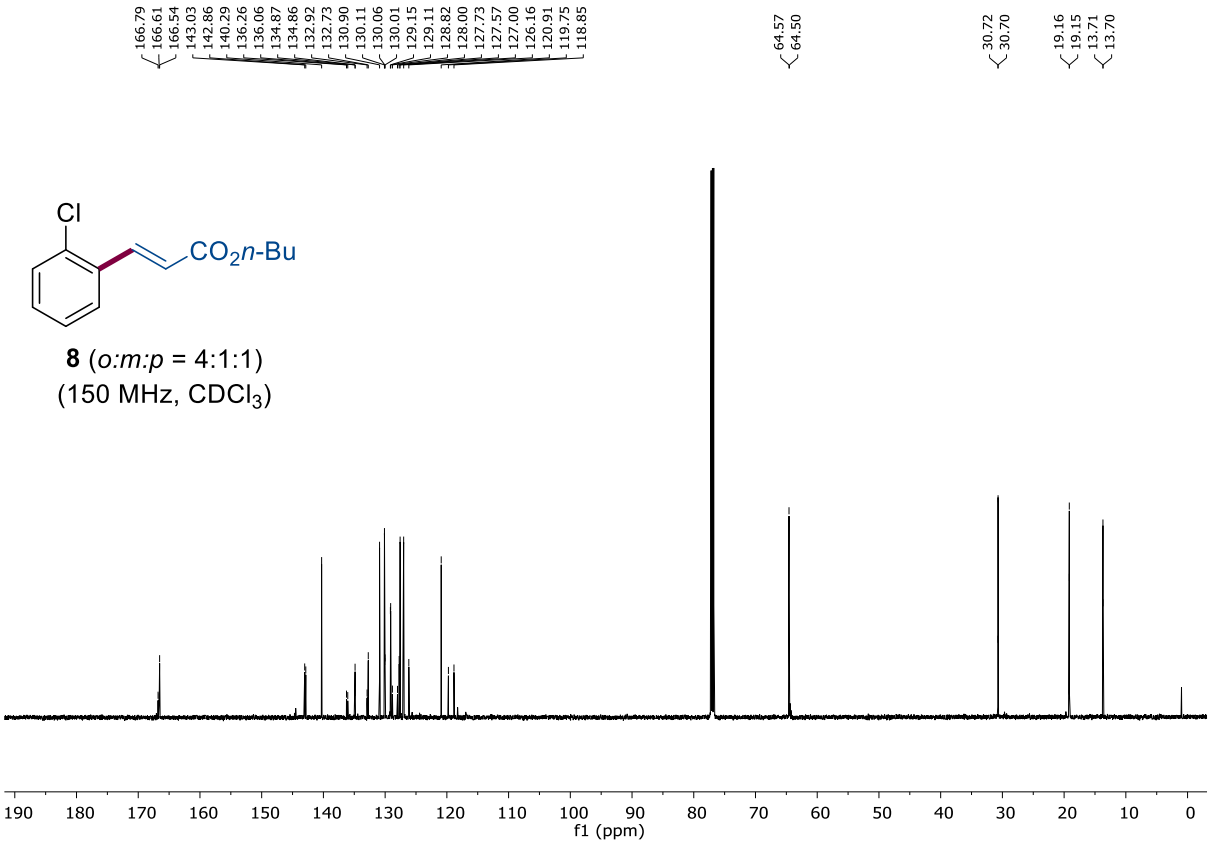

Me
CO2n-Bu
6 (o:m:p = 2:1:1)
(400 MHz, CDCl3)
1.00
1.11
2.07
6.45
6.35
0.48
0.51
4.29
1.00
2.04
3.06
2.08
2.10
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

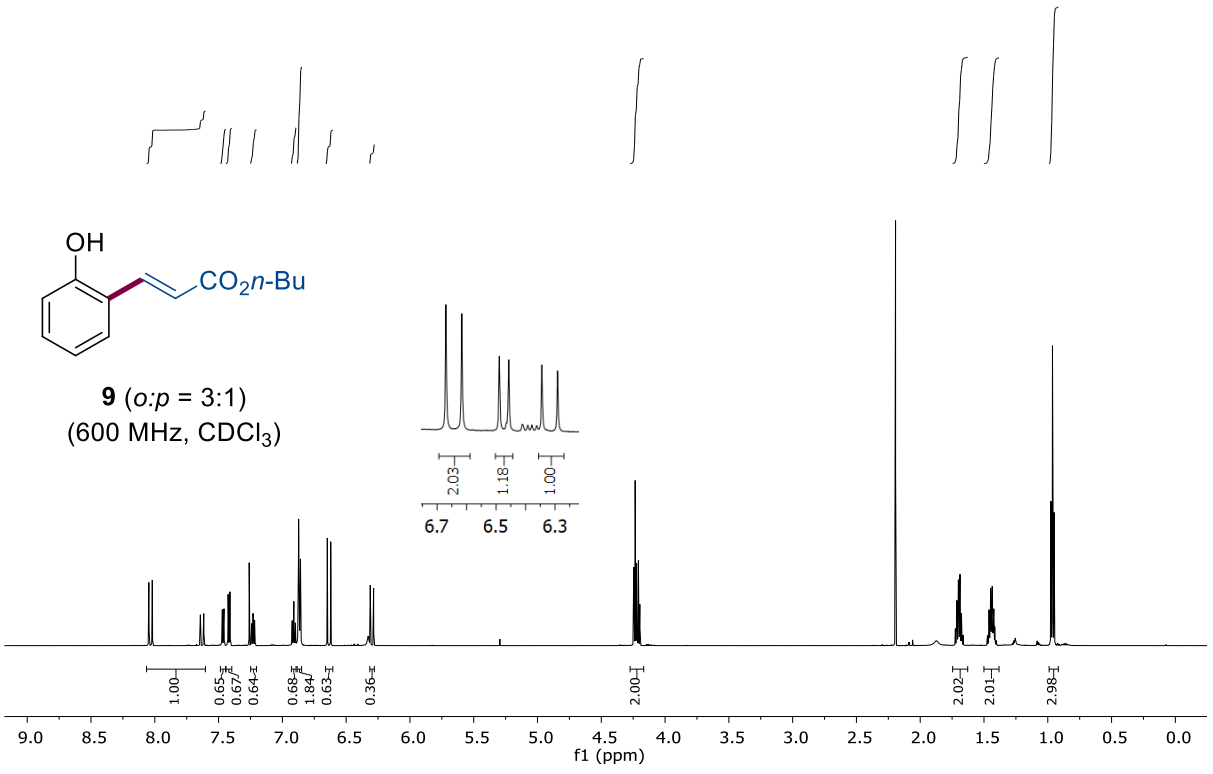

167.26
167.13
144.68
144.50
142.21
140.55
138.47
137.57
134.39
133.40
131.71
130.99
130.73
129.90
129.55
128.70
128.66
128.00
126.35
126.27
125.20
119.27
118.02
117.16
64.38
64.35
64.30
30.77
30.75
21.42
21.28
19.75
19.18
13.73
Me
CO2n-Bu
6 (o:m:p = 2:1:1)
(100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

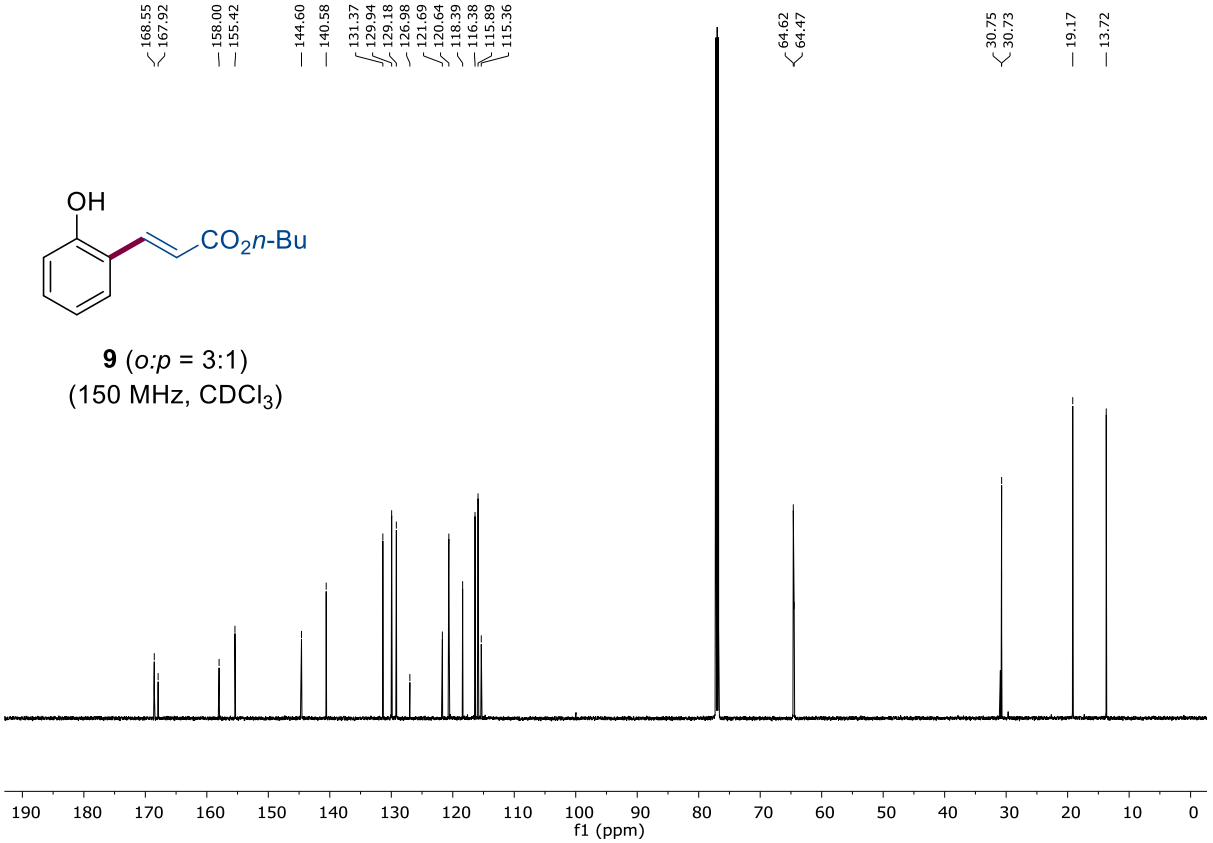

t-Bu
CO2n-Bu
7 (m:p = 1:1)
(600 MHz, CDCl3)
1.00
1.01
6.50 6.45 6.40 6.35
1.01
4.28
1.00
2.06
2.08
2.16
9.01
3.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.26
167.16
153.69
151.75
145.13
144.40
134.12
131.69
128.57
127.85
127.40
125.79
125.19
125.07
117.84
117.32
64.35
64.31
34.83
34.66
31.21
31.12
30.77
19.18
13.72
t-Bu
CO2n-Bu
7 (m:p = 1:1)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

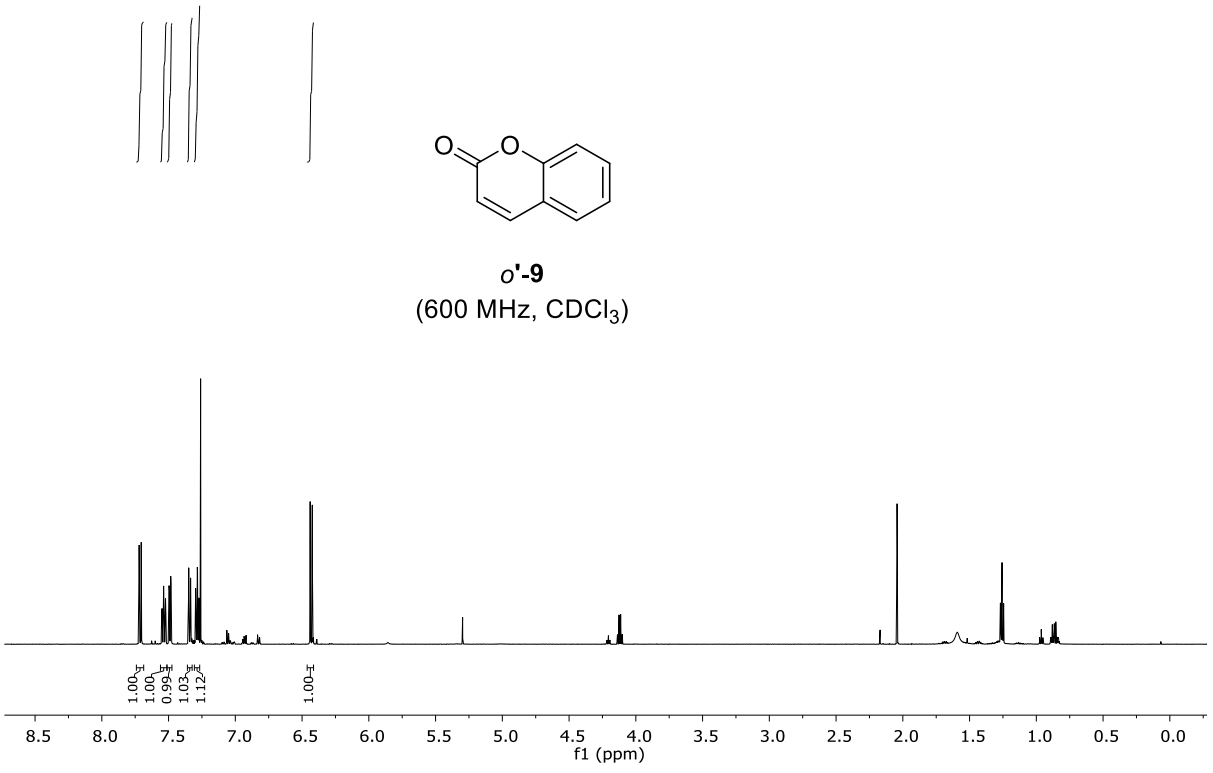

Cl
CO2n-Bu
8 (o:m:p = 4:1:1)
(600 MHz, CDCl3)
1.16
3.74
1.00
6.45
6.40
f1 (ppm)
0.58
4.63
1.00
2.11
2.12
2.17
3.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.79
166.61
166.54
143.03
142.86
140.29
136.26
136.06
134.87
134.86
132.92
132.73
130.90
130.11
130.06
130.01
129.15
129.11
128.82
128.00
127.73
127.57
127.00
126.16
120.91
119.75
118.85
64.57
64.50
30.72
30.70
19.16
19.15
13.71
13.70
Cl
CO2n-Bu
8 (o:m:p = 4:1:1)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

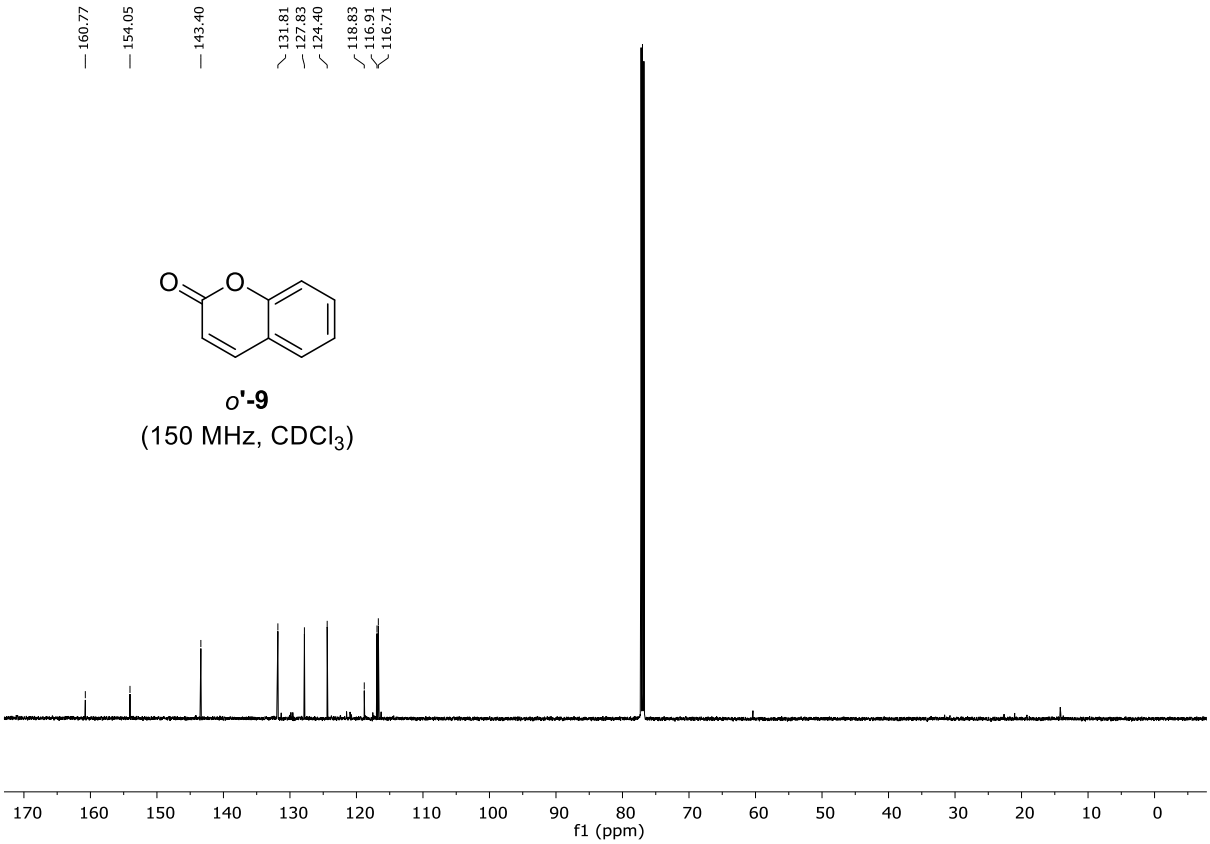

OH
CO2n-Bu
9 (o:p = 3:1)
(600 MHz, CDCl3)
2.03
1.18
1.00
6.7
6.5
6.3
1.00
0.65
0.67
0.64
0.68
1.84
0.63
0.36
2.00
2.02
2.01
2.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



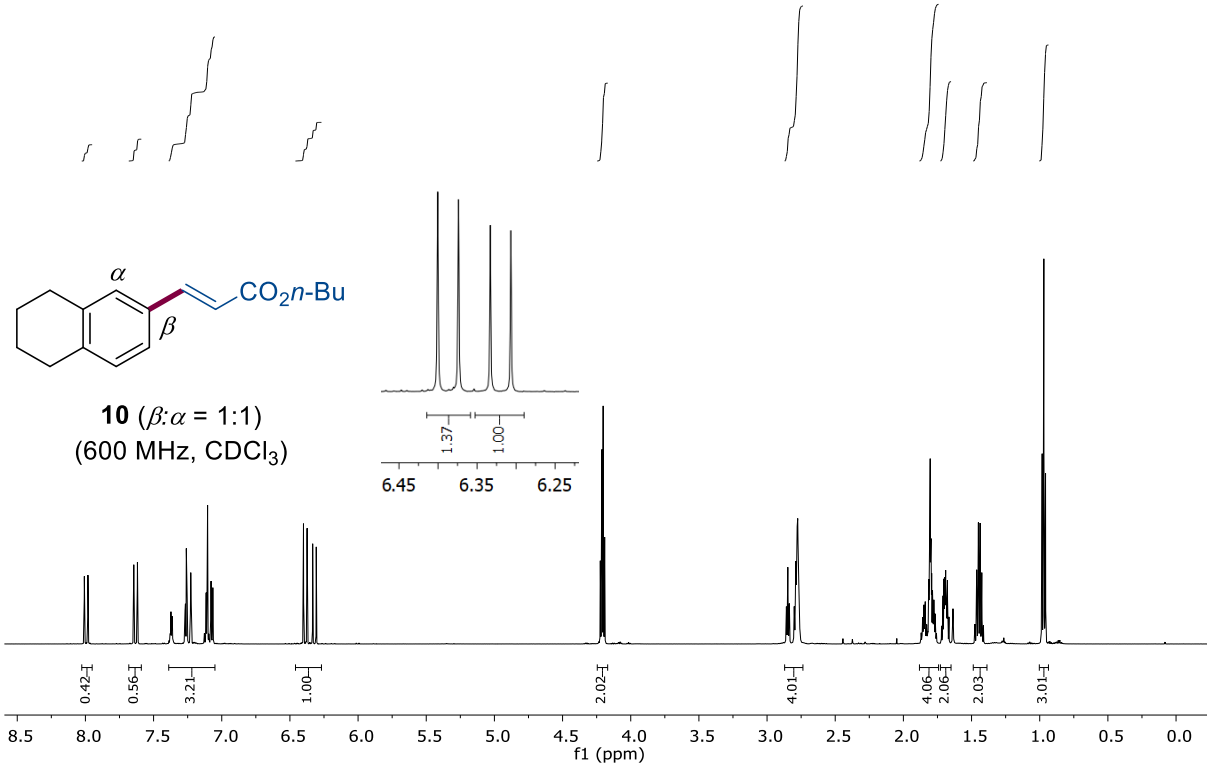
9 (*o*:*p* = 3:1)
(150 MHz, $CDCl_3$)



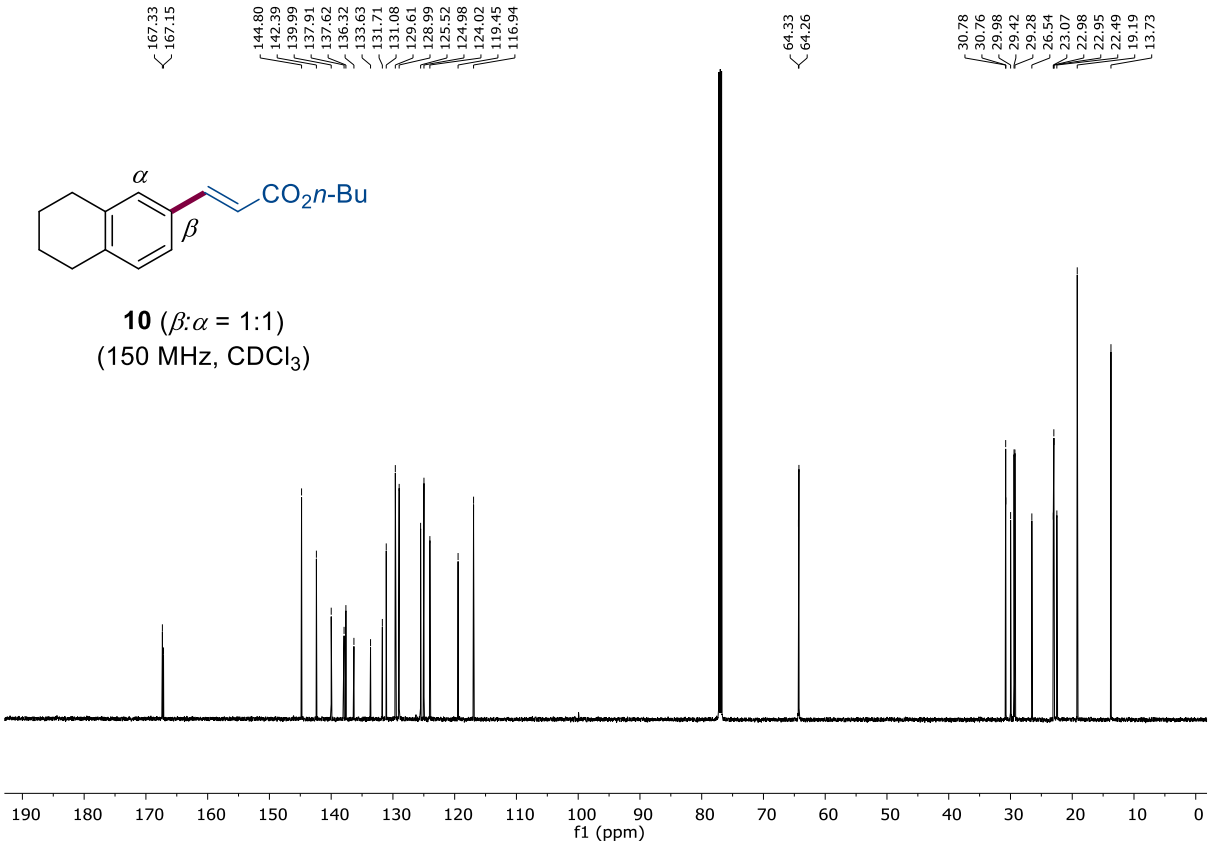
***o*'-9**
(600 MHz, $CDCl_3$)

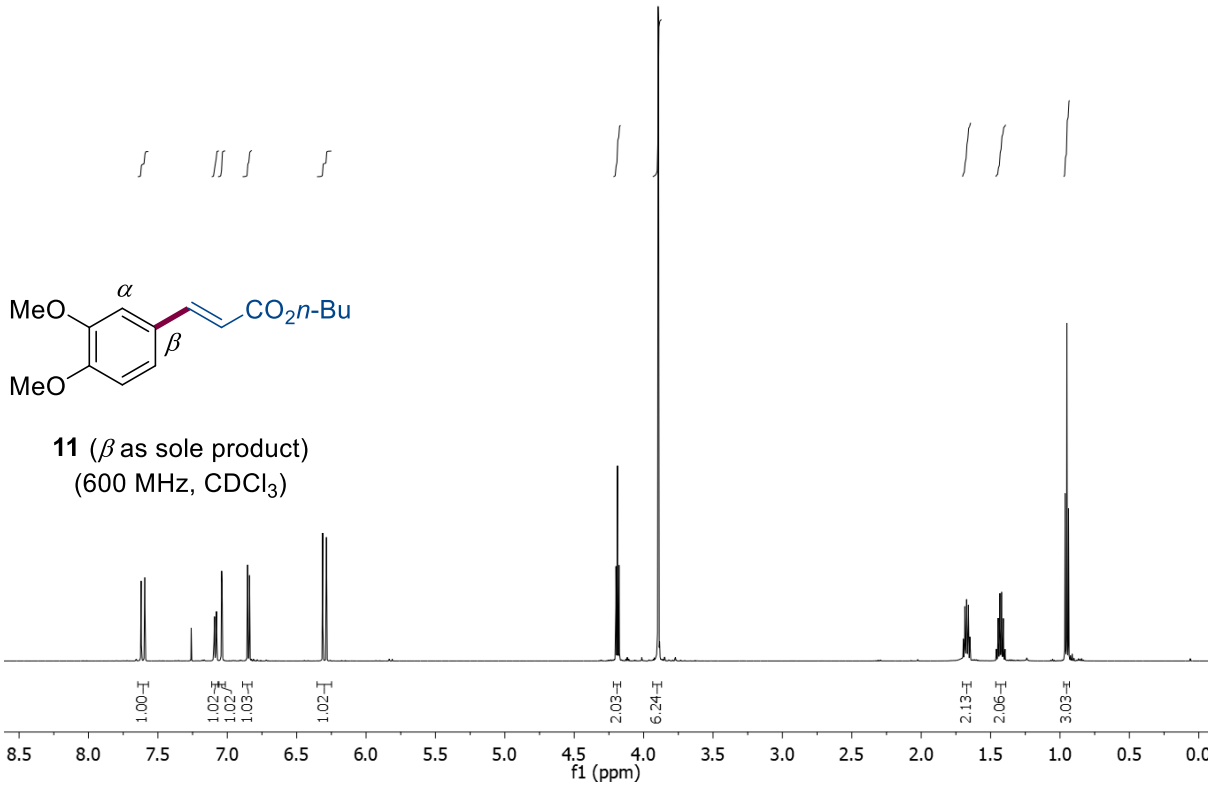


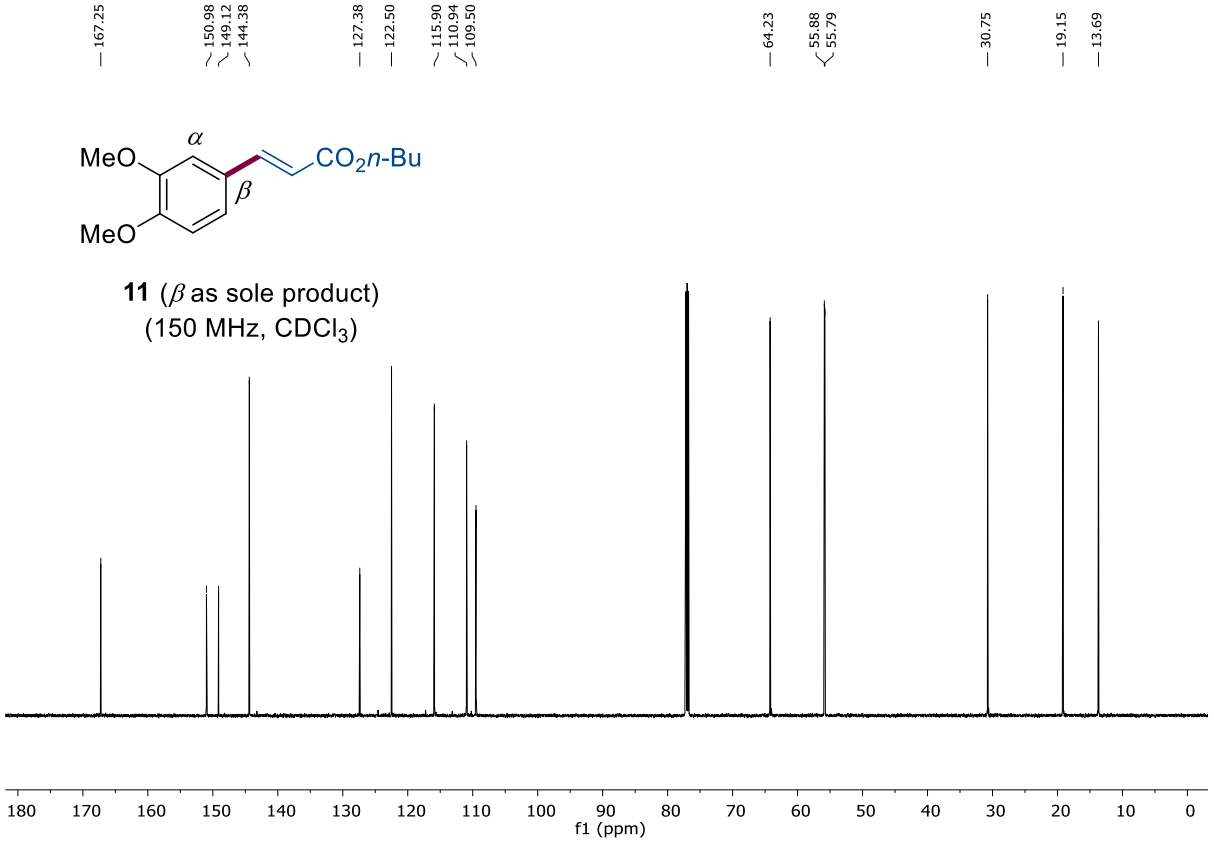
o'-**9**
(150 MHz, $CDCl_3$)

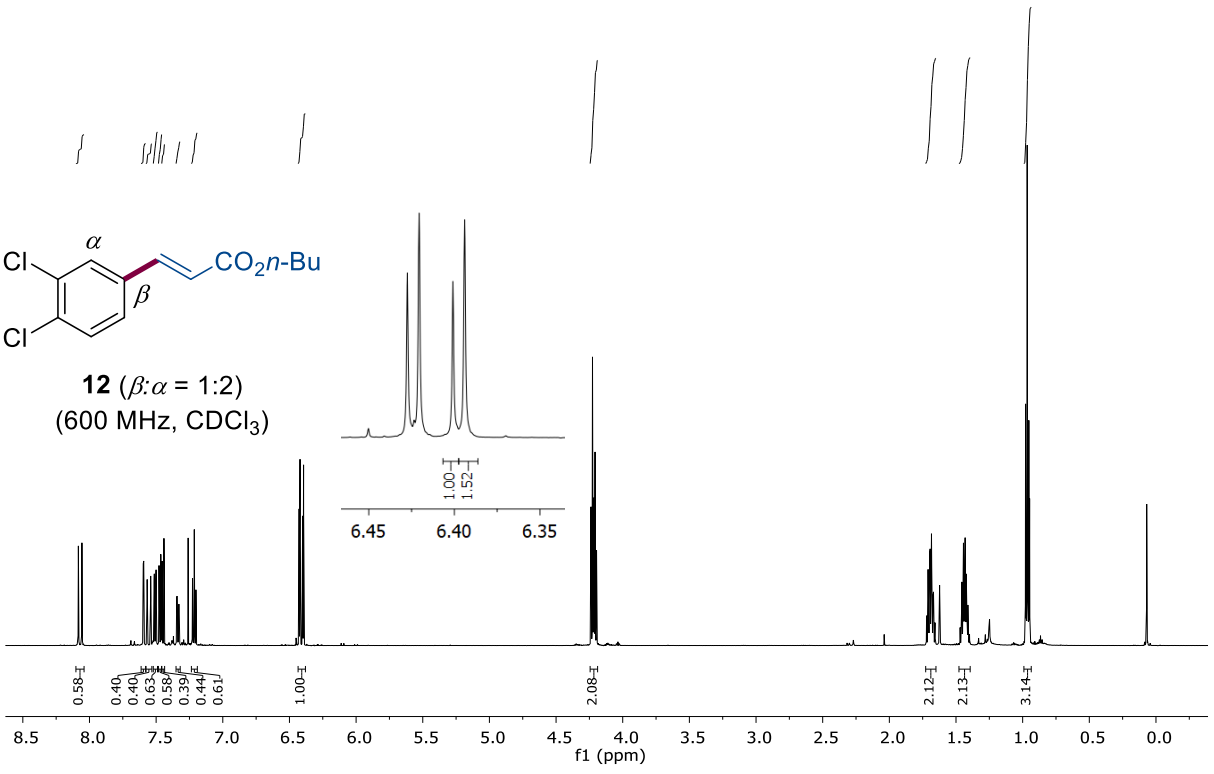


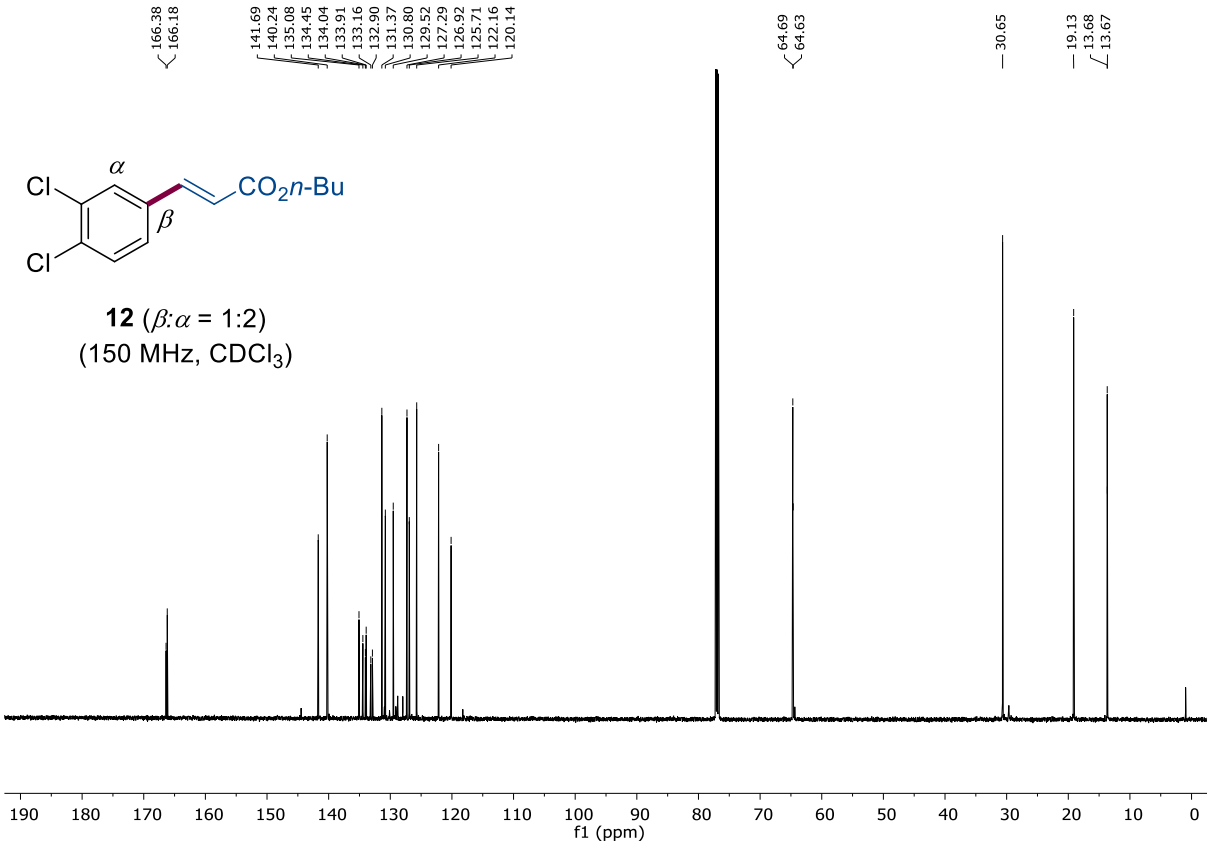
10 (*β*:*α* = 1:1)
(600 MHz, $CDCl_3$)

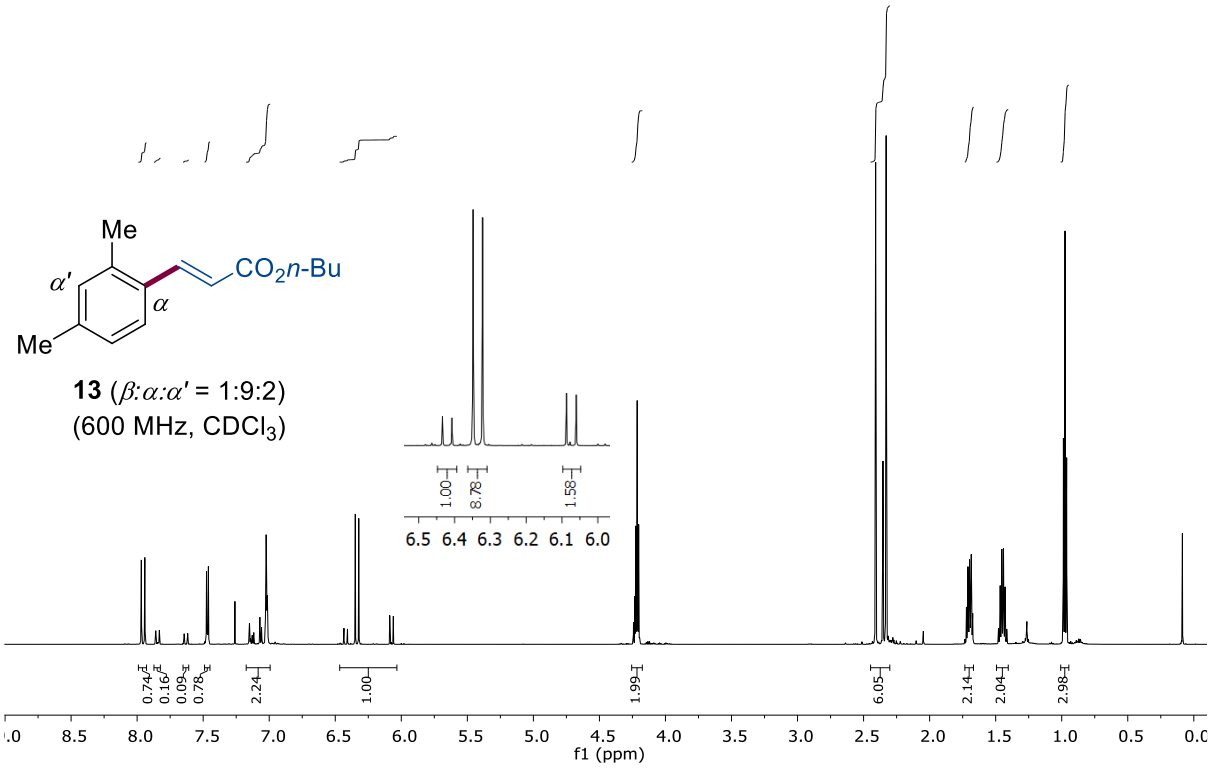

167.33
167.15
144.80
142.39
139.99
137.91
137.62
136.32
133.63
131.71
131.08
129.61
128.99
125.52
124.98
124.02
119.45
116.94
64.33
64.26
30.78
30.76
29.98
29.42
29.28
26.54
23.07
22.98
22.95
22.49
19.19
13.73
α
β
CO2n-Bu
10 (β:α = 1:1)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

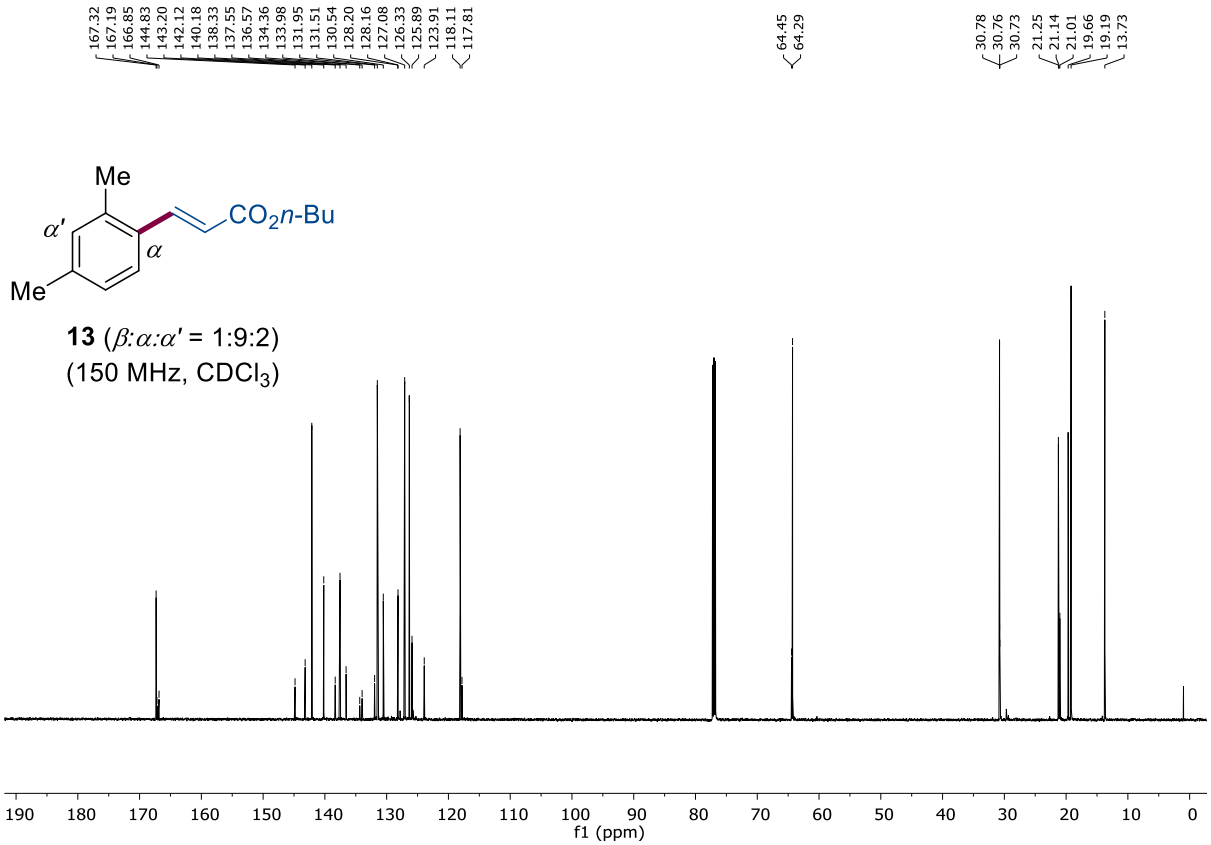

α
β
MeO
MeO
CO2n-Bu
11 (β as sole product)
(600 MHz, CDCl3)
1.00
1.02
1.02
1.03
1.02
2.03
6.24
2.13
2.06
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

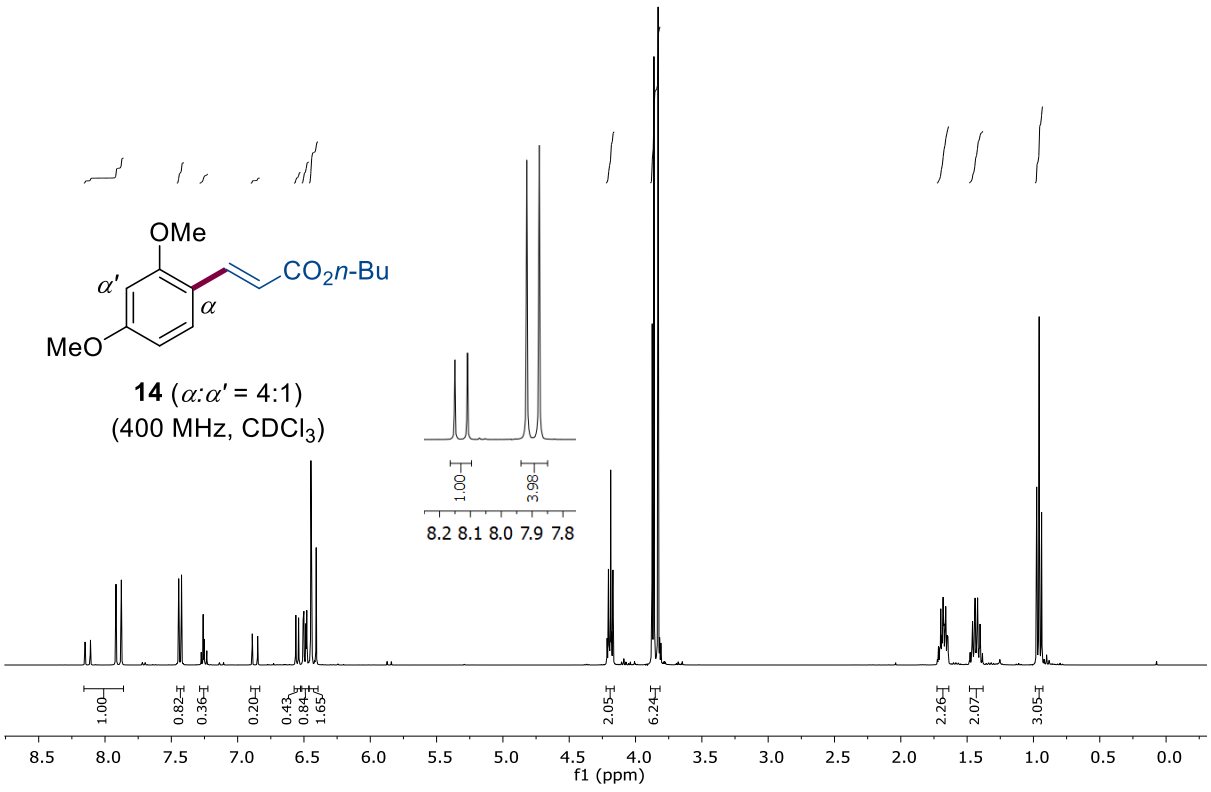

167.25
150.98
149.12
144.38
127.38
122.50
115.90
110.94
109.50
64.23
55.88
55.79
30.75
19.15
13.69
MeO
MeO
α
β
CO2n-Bu
11 (β as sole product)
(150 MHz, CDCl3)
f1 (ppm)

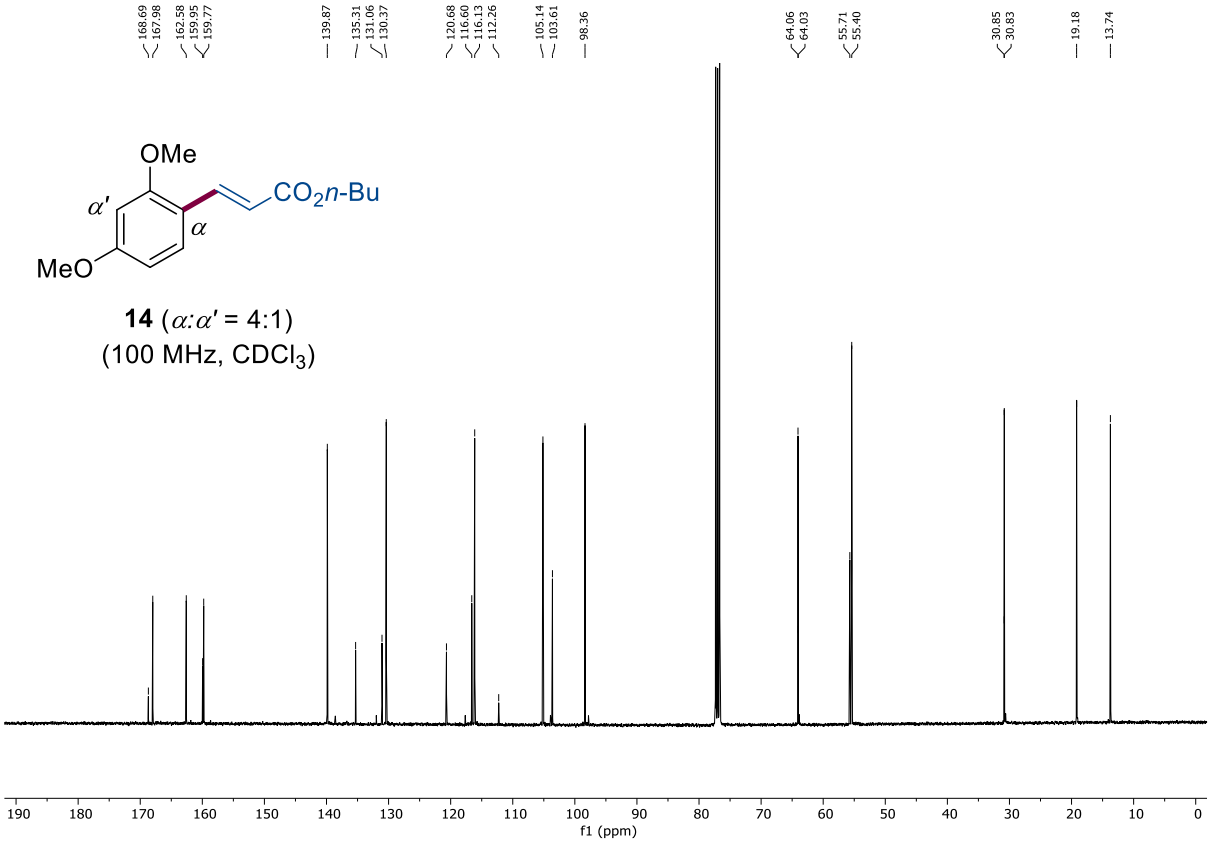

Cl
Cl
α
β
CO2n-Bu
12 (β:α = 1:2)
(600 MHz, CDCl3)
1.00
1.52
6.45
6.40
6.35
0.58
0.40
0.40
0.63
0.58
0.39
0.44
0.61
1.00
2.08
2.12
2.13
3.14
f1 (ppm)

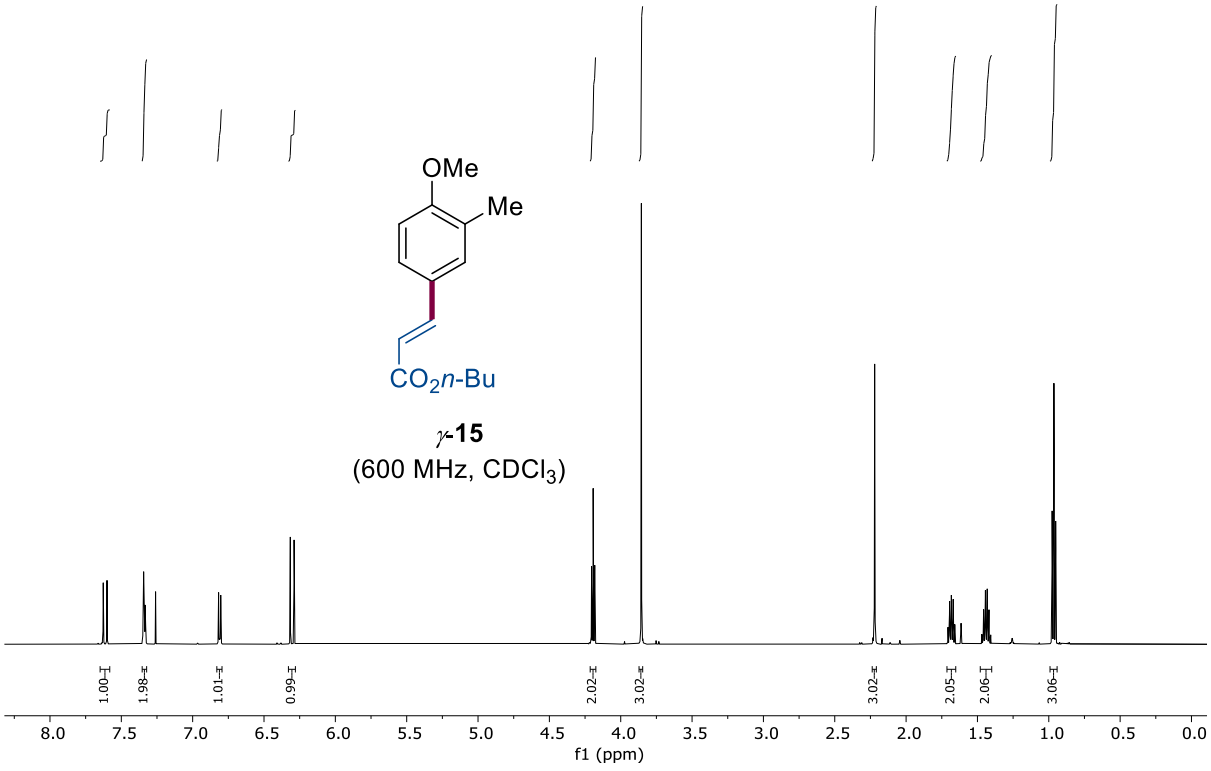

166.38
166.18
141.69
140.24
135.08
134.45
134.04
133.91
133.16
132.90
131.37
130.80
129.52
127.29
126.92
125.71
122.16
120.14
64.69
64.63
30.65
19.13
13.68
13.67
α
Cl
CO2n-Bu
β
Cl
12 (β:α = 1:2)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

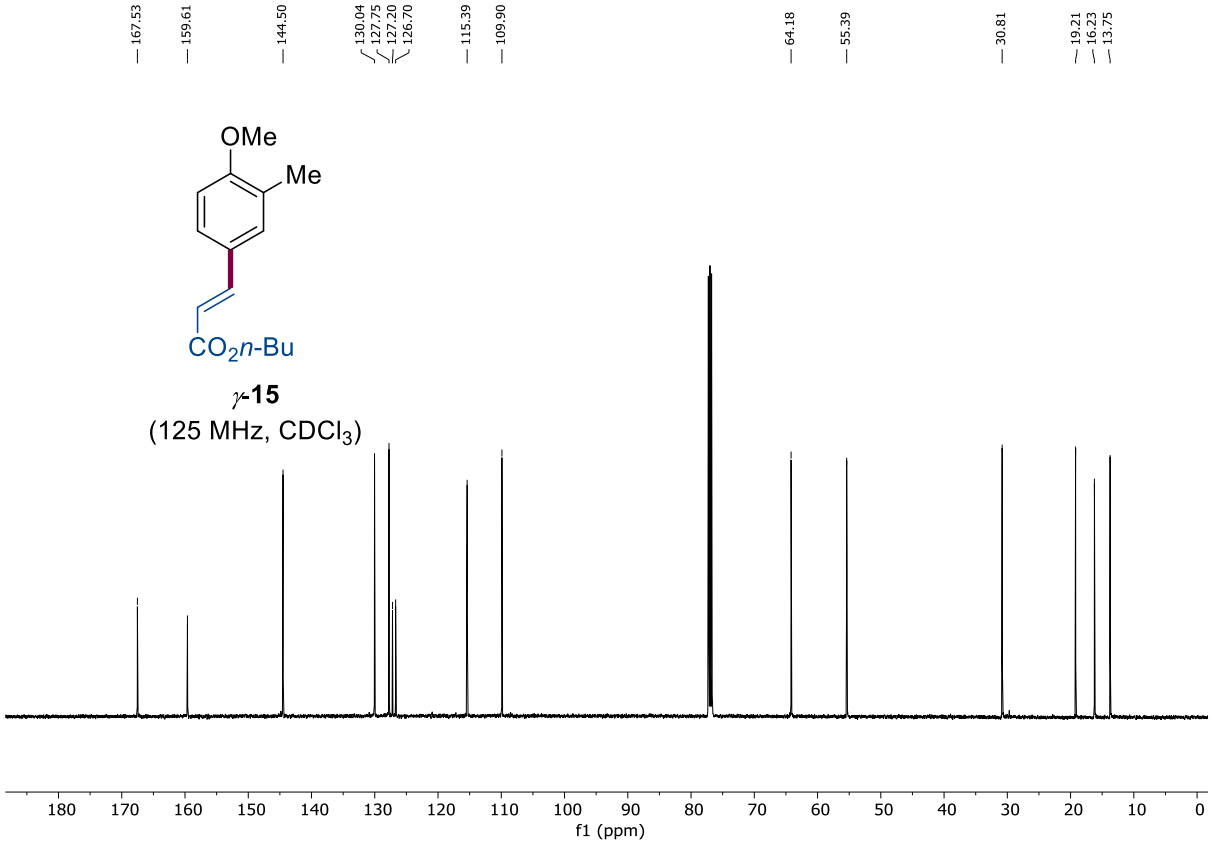

Me
α'
CO2n-Bu
α
Me
13 (β:α:α' = 1:9:2)
(600 MHz, CDCl3)
1.00
8.78
1.58
6.5 6.4 6.3 6.2 6.1 6.0
0.74
0.16
0.09
0.78
2.24
1.00
1.99
6.05
2.14
2.04
2.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

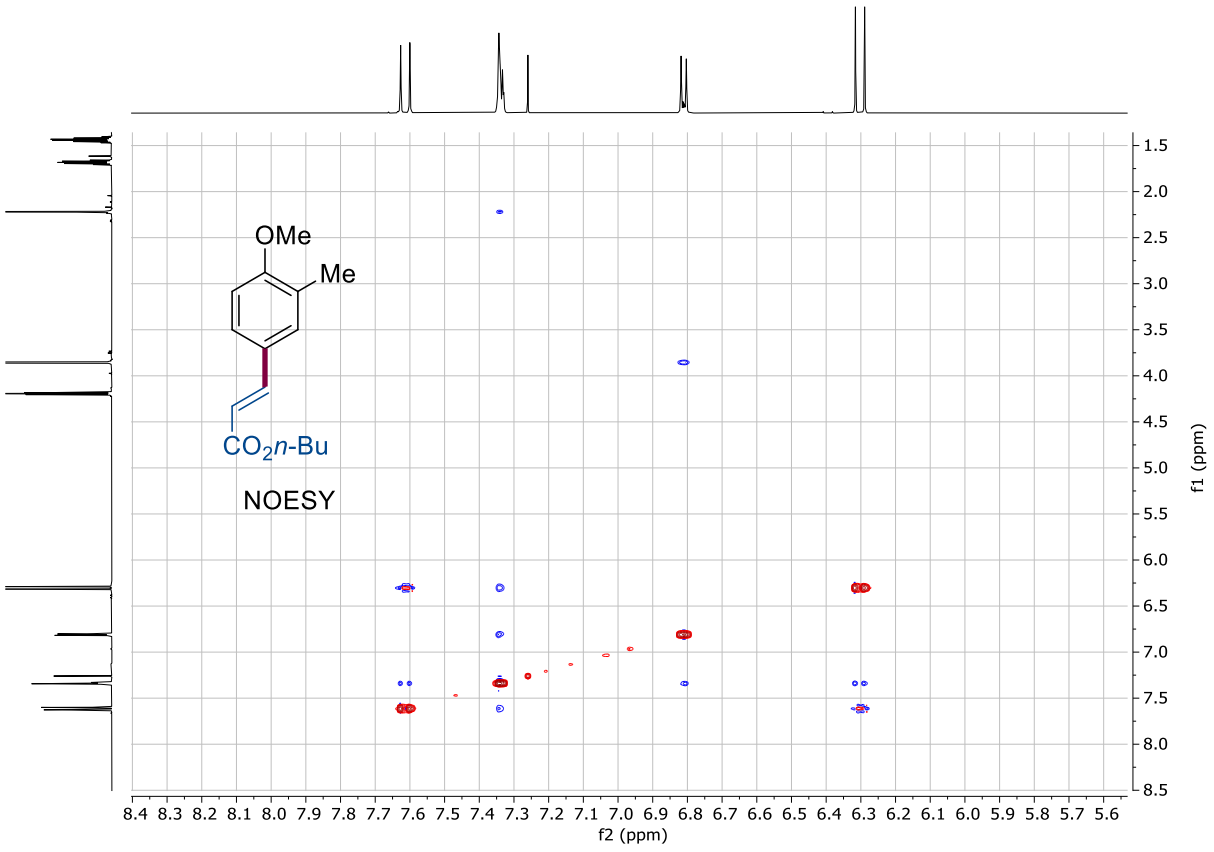

167.32
167.19
166.85
144.83
143.20
142.12
140.18
138.33
137.55
136.57
134.36
133.98
131.95
131.51
130.54
128.20
128.16
127.08
126.33
125.89
123.91
118.11
117.81
64.45
64.29
30.78
30.76
30.73
21.25
21.14
21.01
19.66
19.19
13.73
Me
α′
α
Me
CO2n-Bu
13 (β:α:α′ = 1:9:2)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

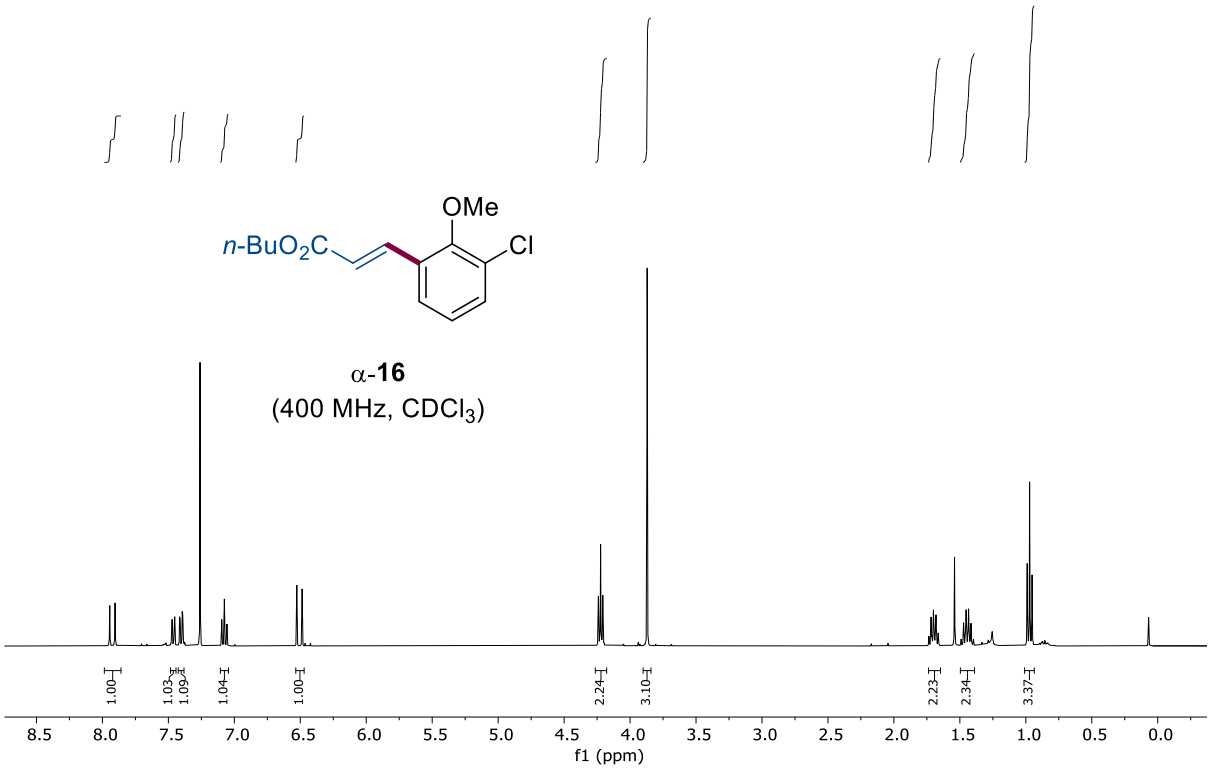

OMe
α′
α
MeO
CO2n-Bu
14 (α:α′ = 4:1)
(400 MHz, CDCl3)
1.00
3.98
8.2 8.1 8.0 7.9 7.8
1.00
0.82
0.36
0.20
0.43
0.84
1.65
2.05
6.24
2.26
2.07
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

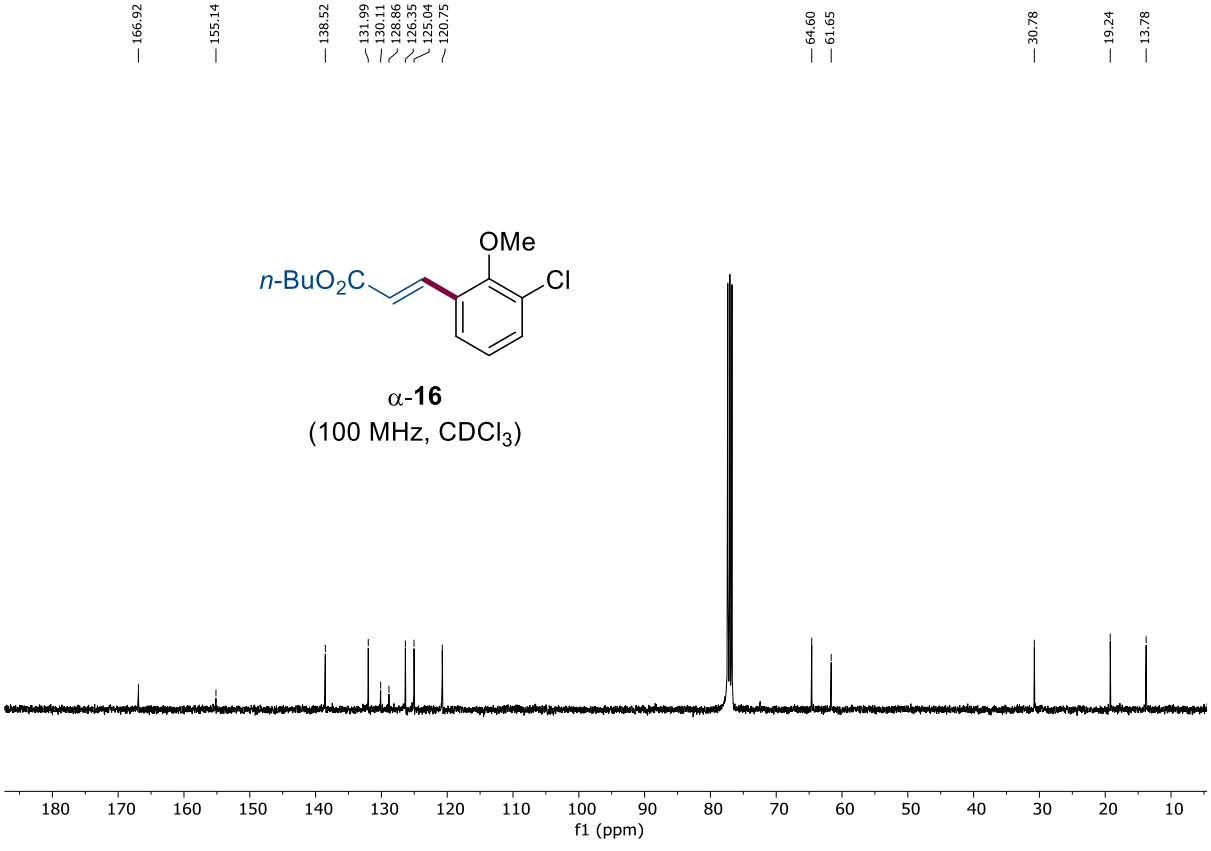

168.69
167.98
162.58
159.95
159.77
139.87
135.31
131.06
130.37
120.68
116.60
116.13
112.26
105.14
103.61
98.36
64.06
64.03
55.71
55.40
30.85
30.83
19.18
13.74
OMe
MeO
α′
α
CO2n-Bu
14 (α:α′ = 4:1)
(100 MHz, CDCl3)
f1 (ppm)

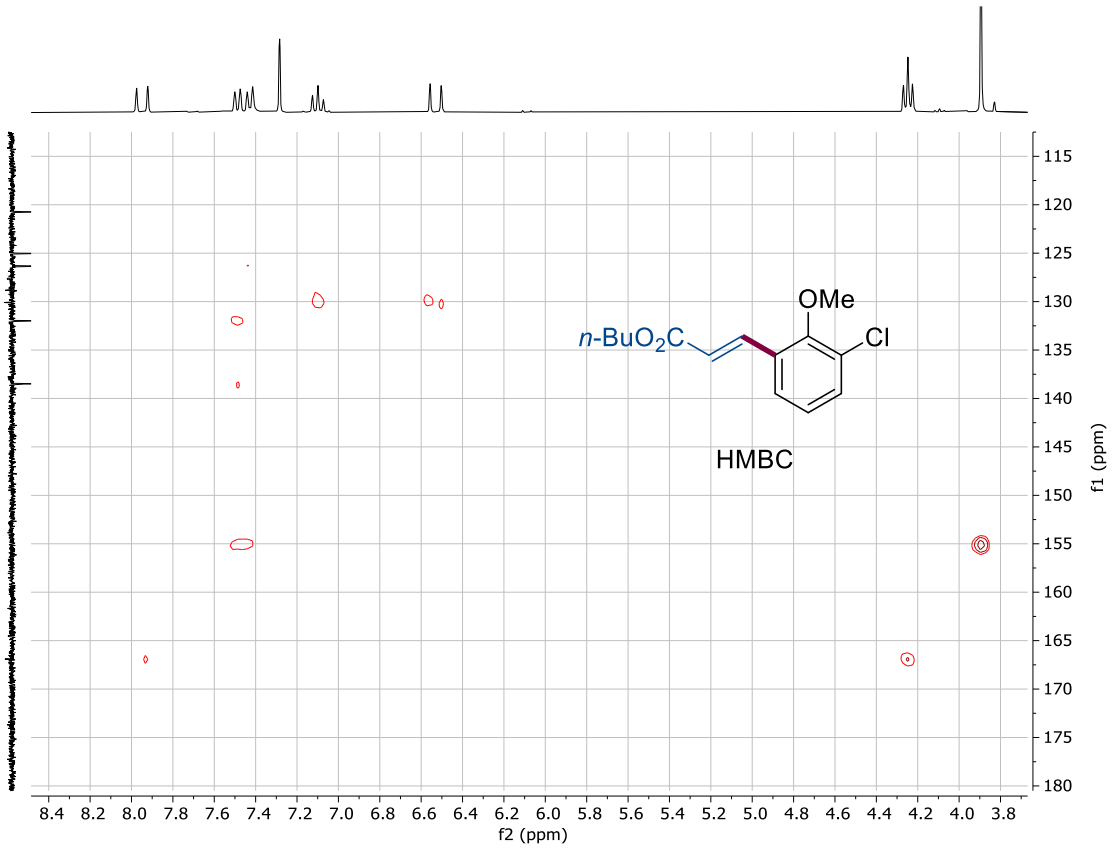

OMe
Me
CO2n-Bu
γ-15
(600 MHz, CDCl3)
1.00
1.98
1.01
0.99
2.02
3.02
3.02
2.05
2.06
3.06
f1 (ppm)

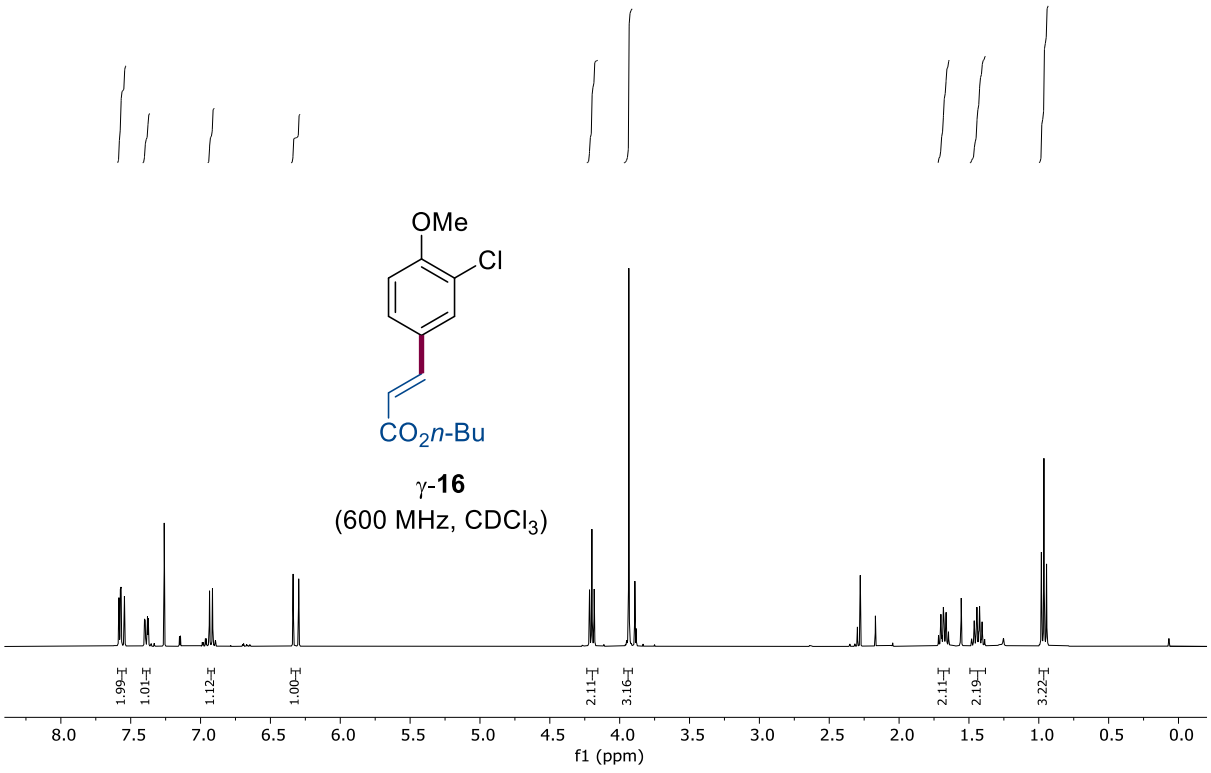

167.53
159.61
144.50
130.04
127.75
127.20
126.70
115.39
109.90
64.18
55.39
30.81
19.21
16.23
13.75
OMe
Me
CO2n-Bu
γ-15
(125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

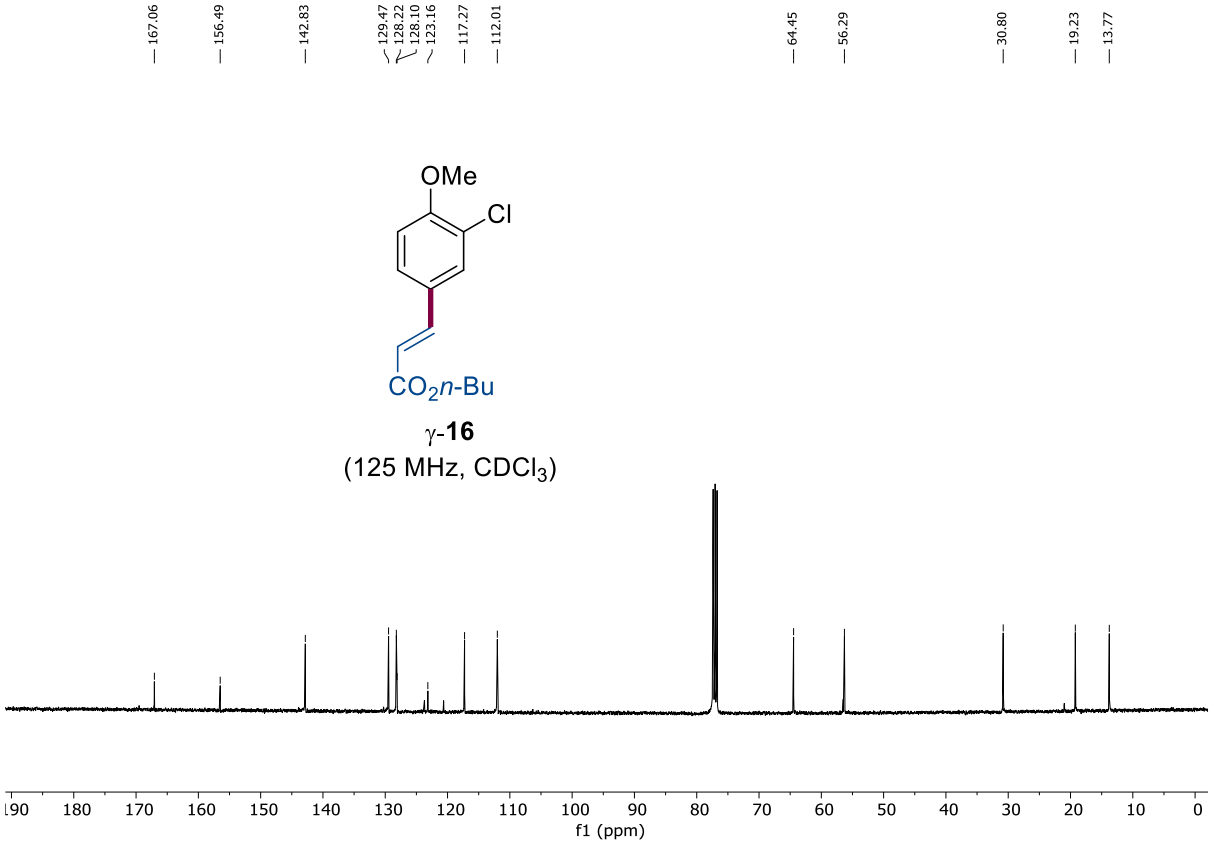

OMe
Me
CO2n-Bu
NOESY
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5
f1 (ppm)
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6
f2 (ppm)

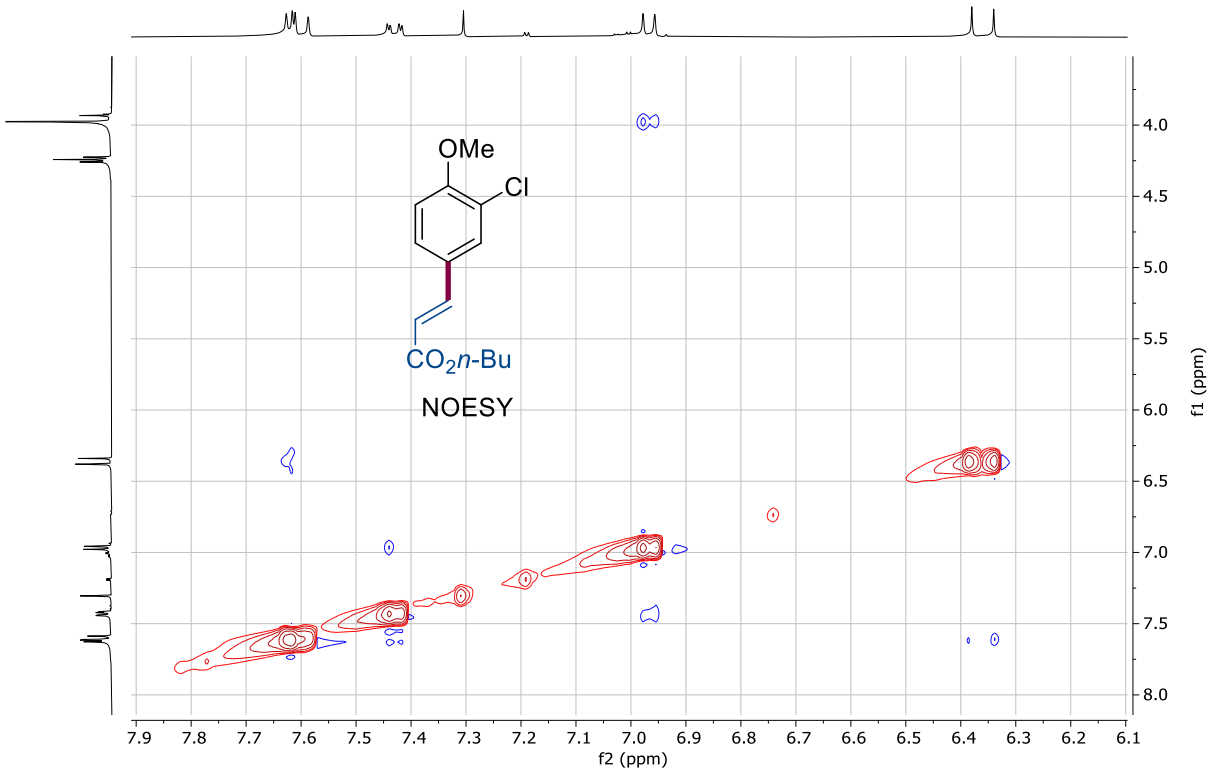

OMe
n-BuO2C
Cl
α-16
(400 MHz, CDCl3)
1.00
1.03
1.09
1.04
1.00
2.24
3.10
2.23
2.34
3.37
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

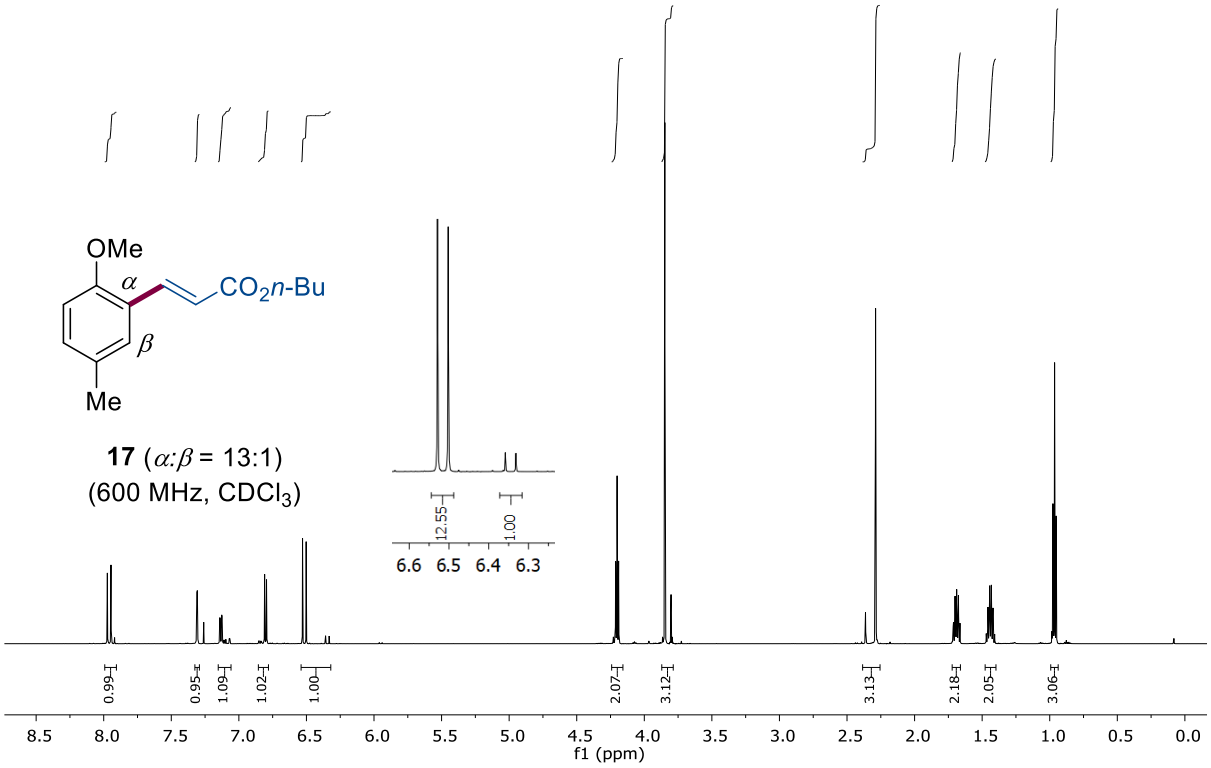

166.92
155.14
138.52
131.99
130.11
128.86
126.35
125.04
120.75
64.60
61.65
30.78
19.24
13.78
OMe
n-BuO2C
Cl
α-16
(100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

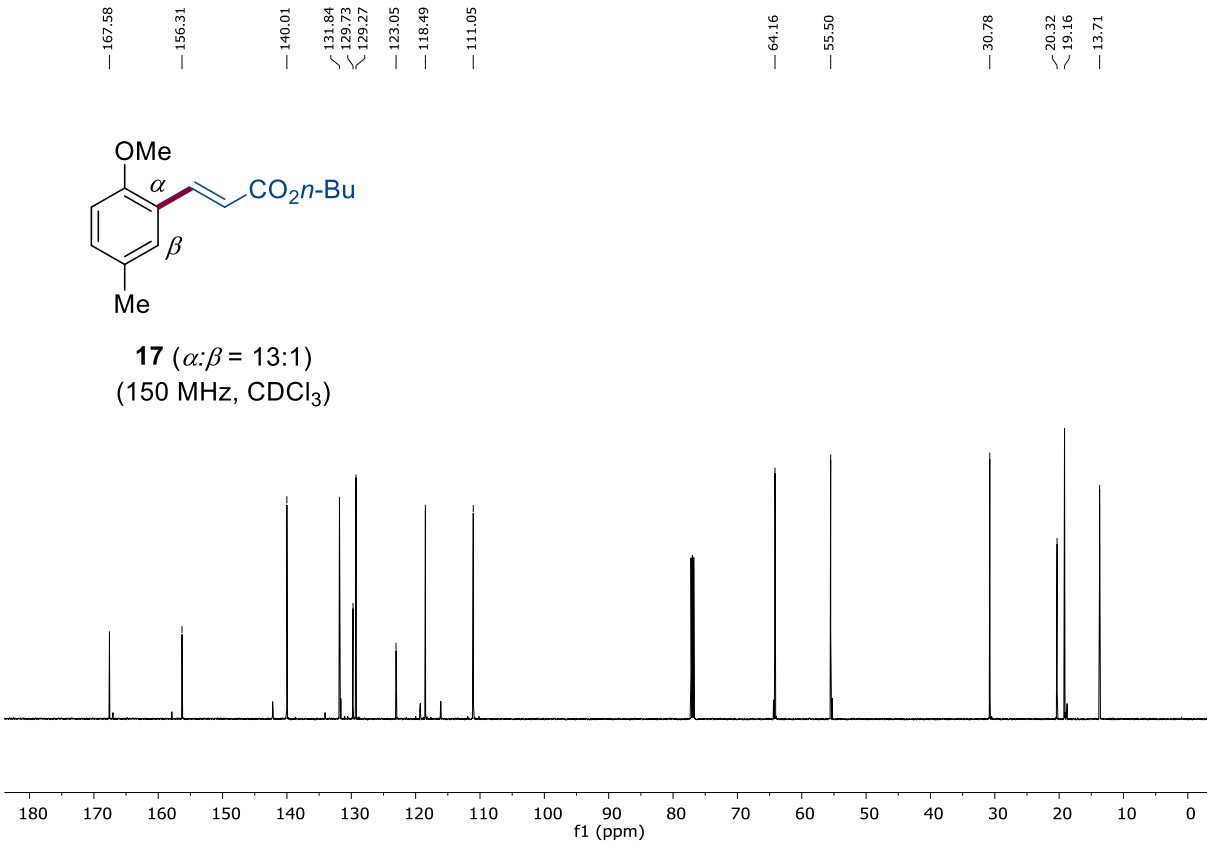

OMe
Cl
n-BuO2C
HMBC
f1 (ppm)
f2 (ppm)

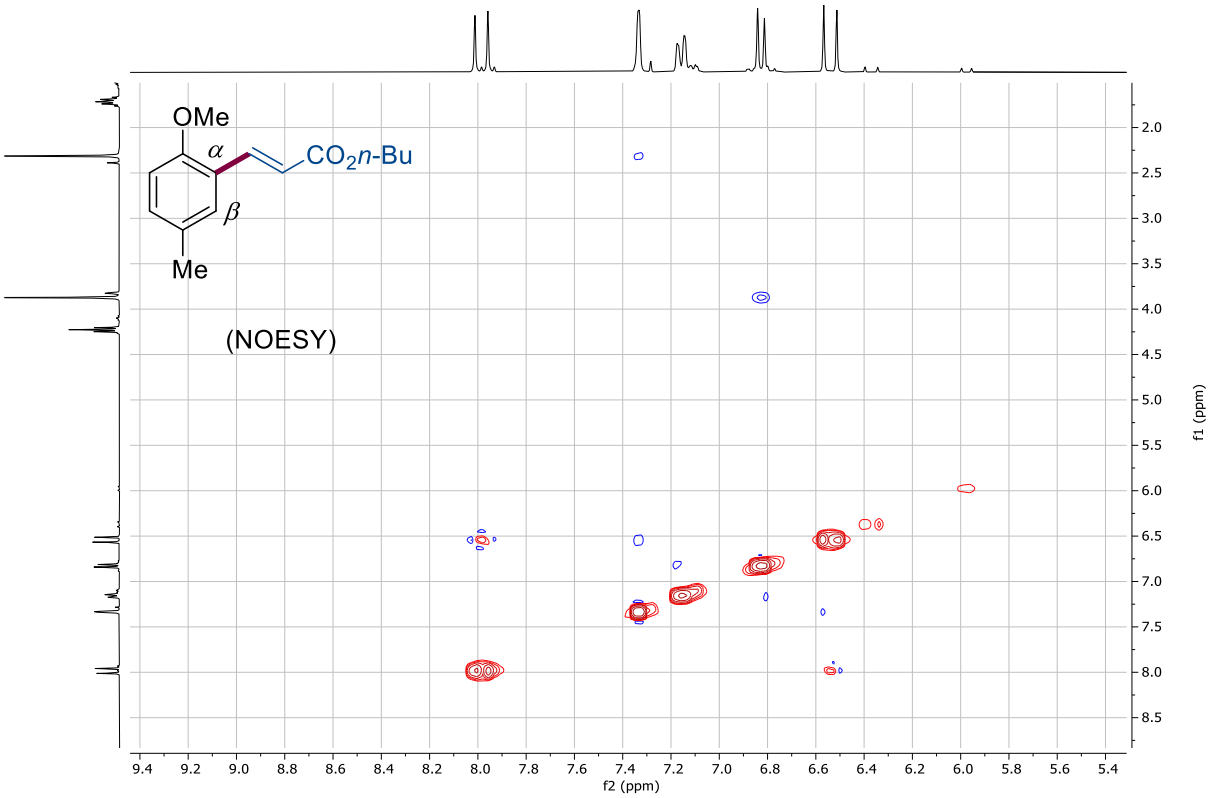

OMe
Cl
CO2n-Bu
γ-16
(600 MHz, CDCl3)
1.99
1.01
1.12
1.00
2.11
3.16
2.11
2.19
3.22
f1 (ppm)

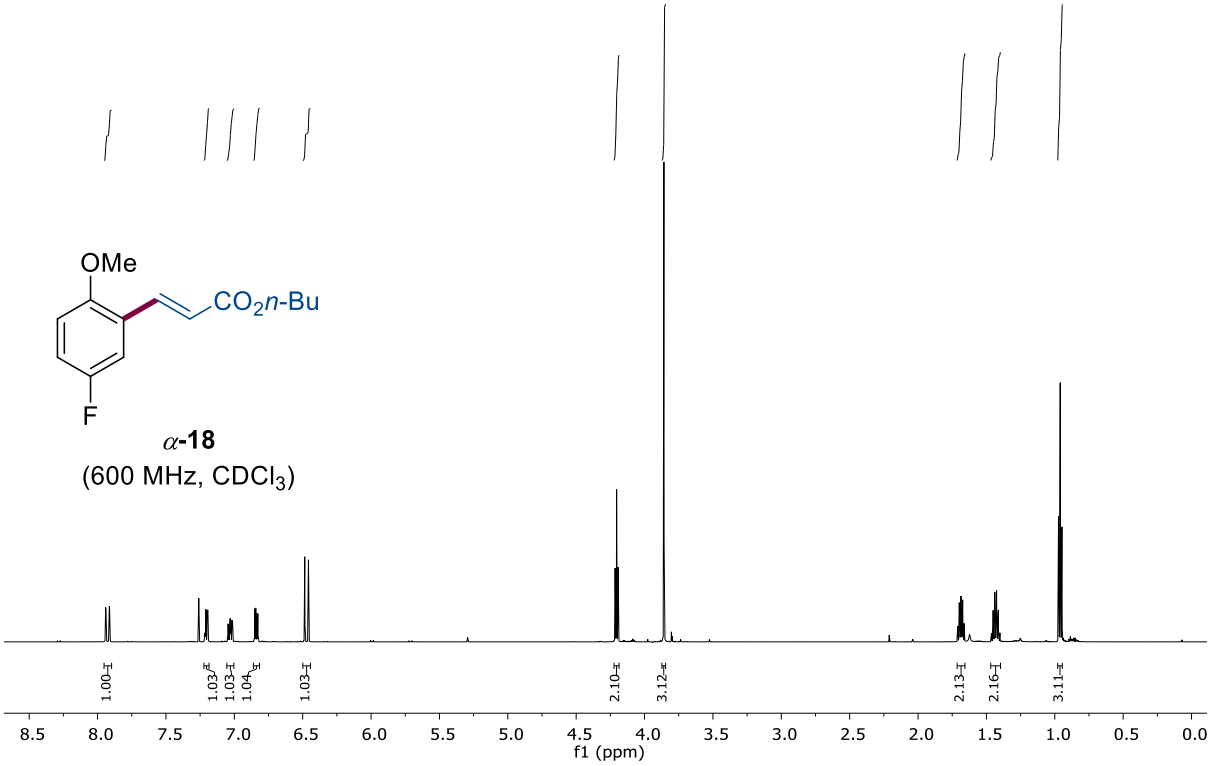

167.06
156.49
142.83
129.47
128.22
128.10
123.16
117.27
112.01
64.45
56.29
30.80
19.23
13.77
OMe
Cl
CO2n-Bu
γ-16
(125 MHz, CDCl3)
f1 (ppm)

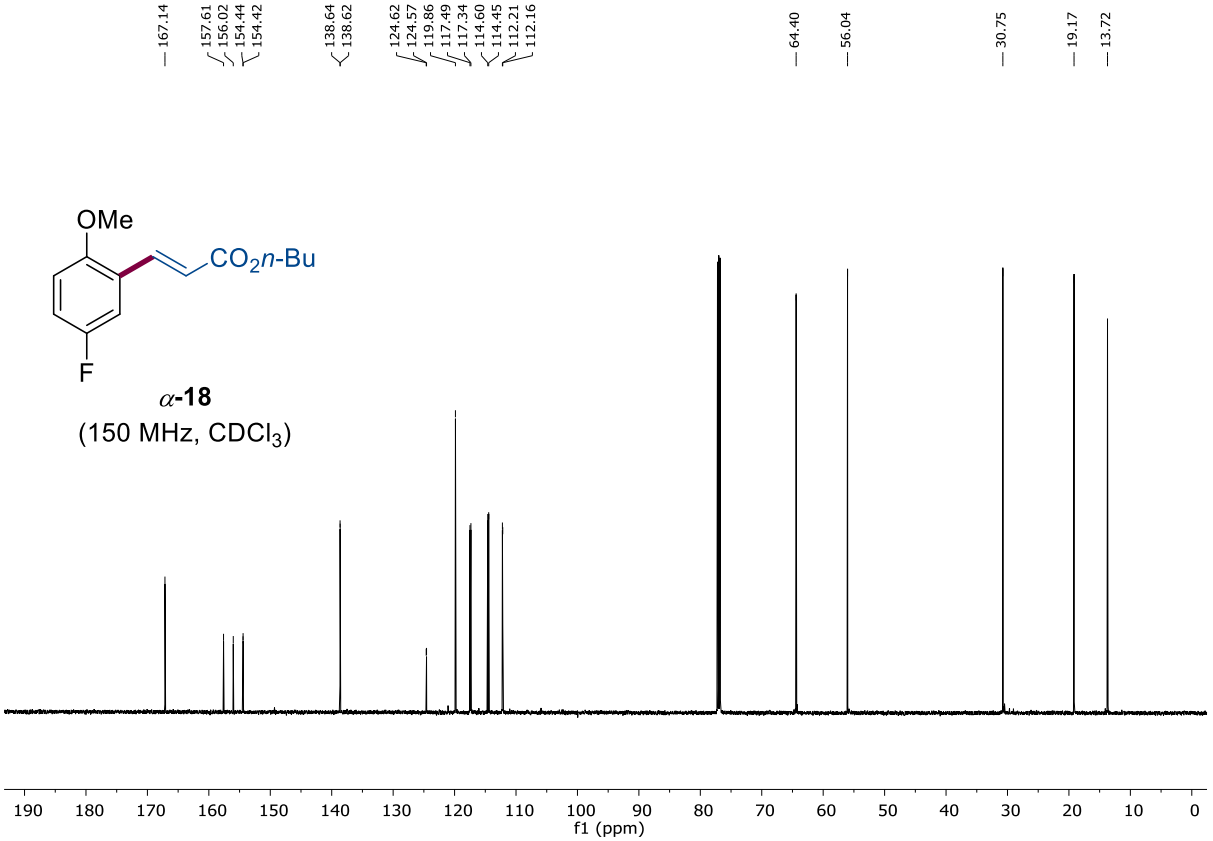

OMe
Cl
CO2n-Bu
NOESY
f1 (ppm)
f2 (ppm)

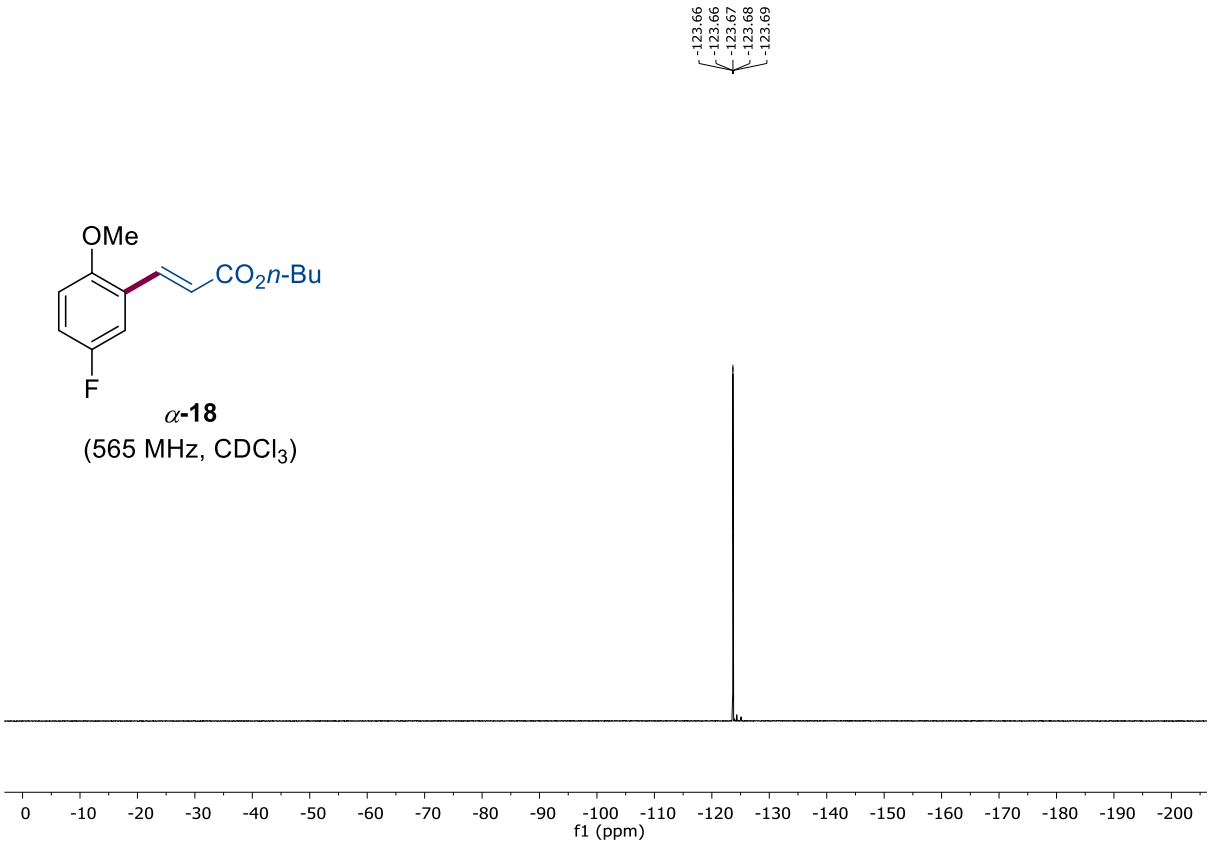

OMe
α
CO2n-Bu
β
Me
17 (α:β = 13:1)
(600 MHz, CDCl3)
12.55
1.00
6.6 6.5 6.4 6.3
0.99
0.95
1.09
1.02
1.00
2.07
3.12
3.13
2.18
2.05
3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

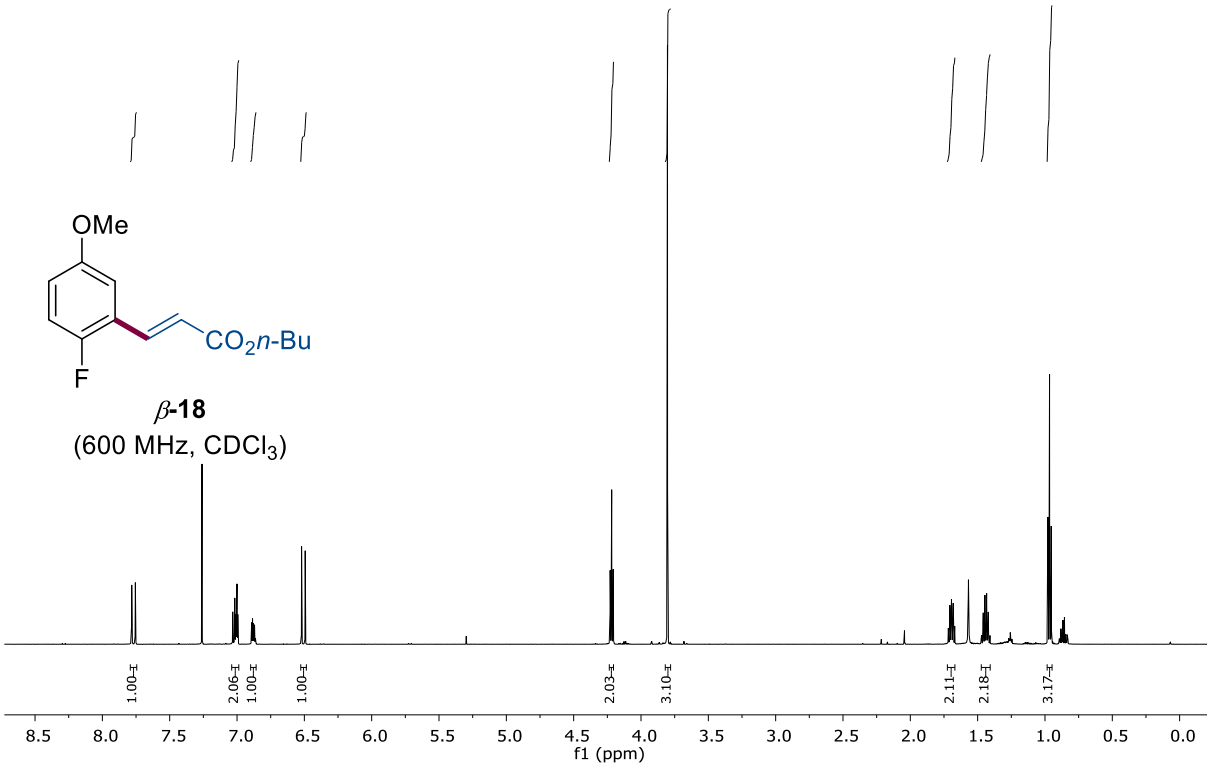

167.58
156.31
140.01
131.84
129.73
129.27
123.05
118.49
111.05
64.16
55.50
30.78
20.32
19.16
13.71
OMe
α
CO2n-Bu
β
Me
17 (α:β = 13:1)
(150 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

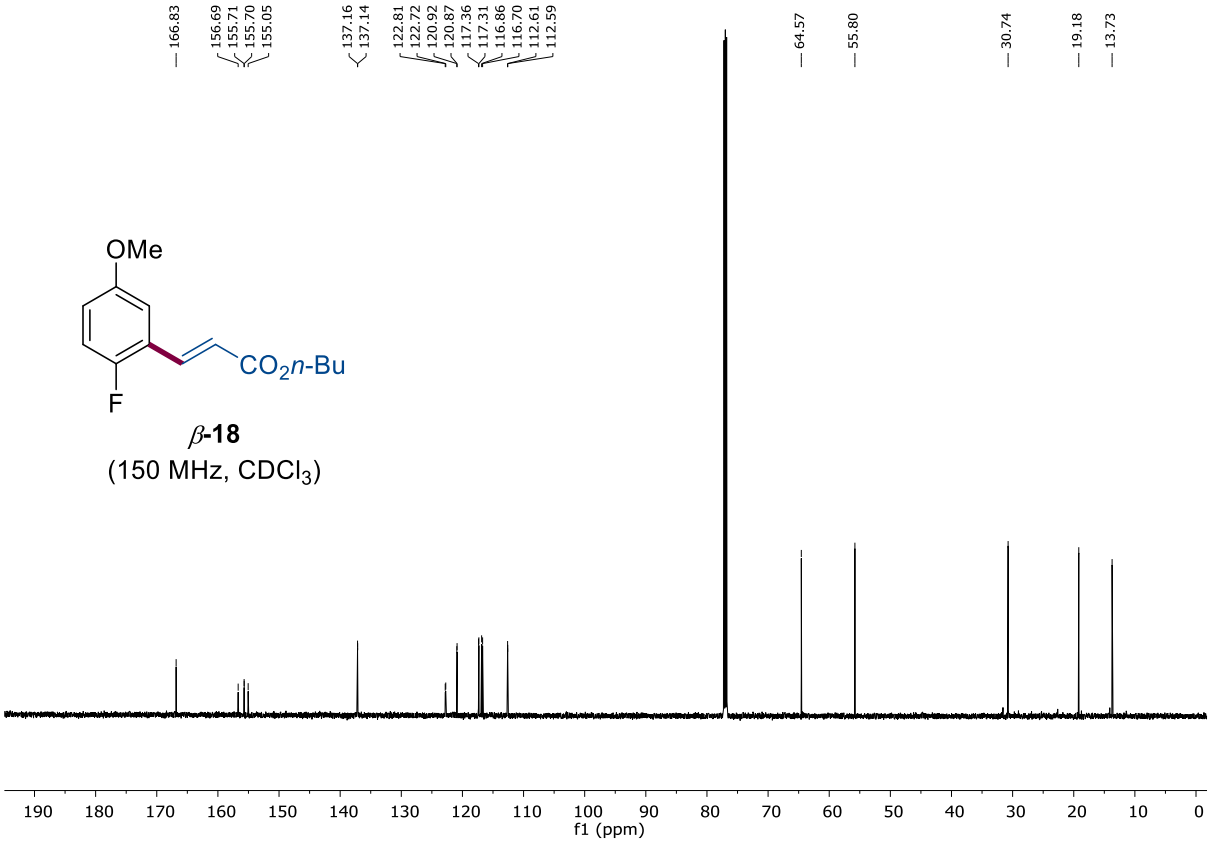

OMe
α
CO2n-Bu
β
Me
(NOESY)
f2 (ppm)
f1 (ppm)

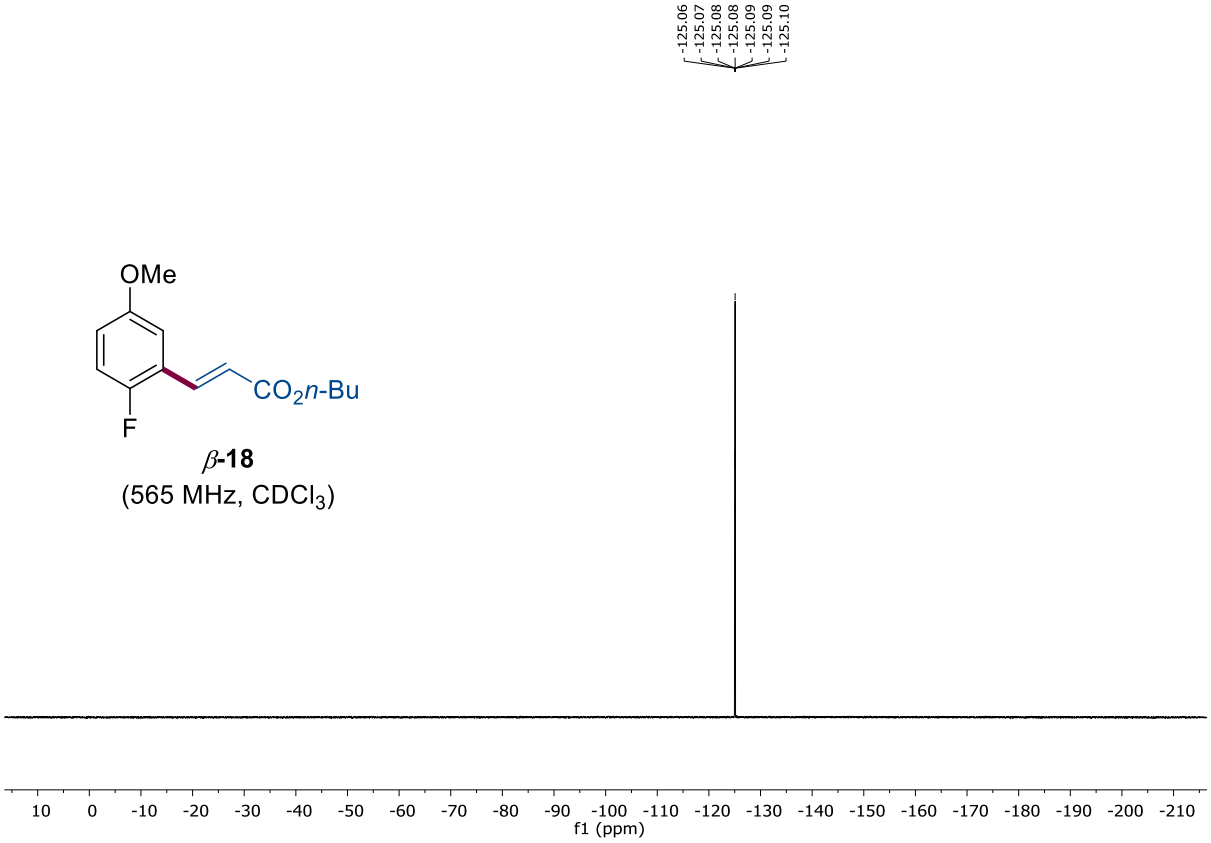

OMe
CO2n-Bu
F
α-18
(600 MHz, CDCl3)
f1 (ppm)

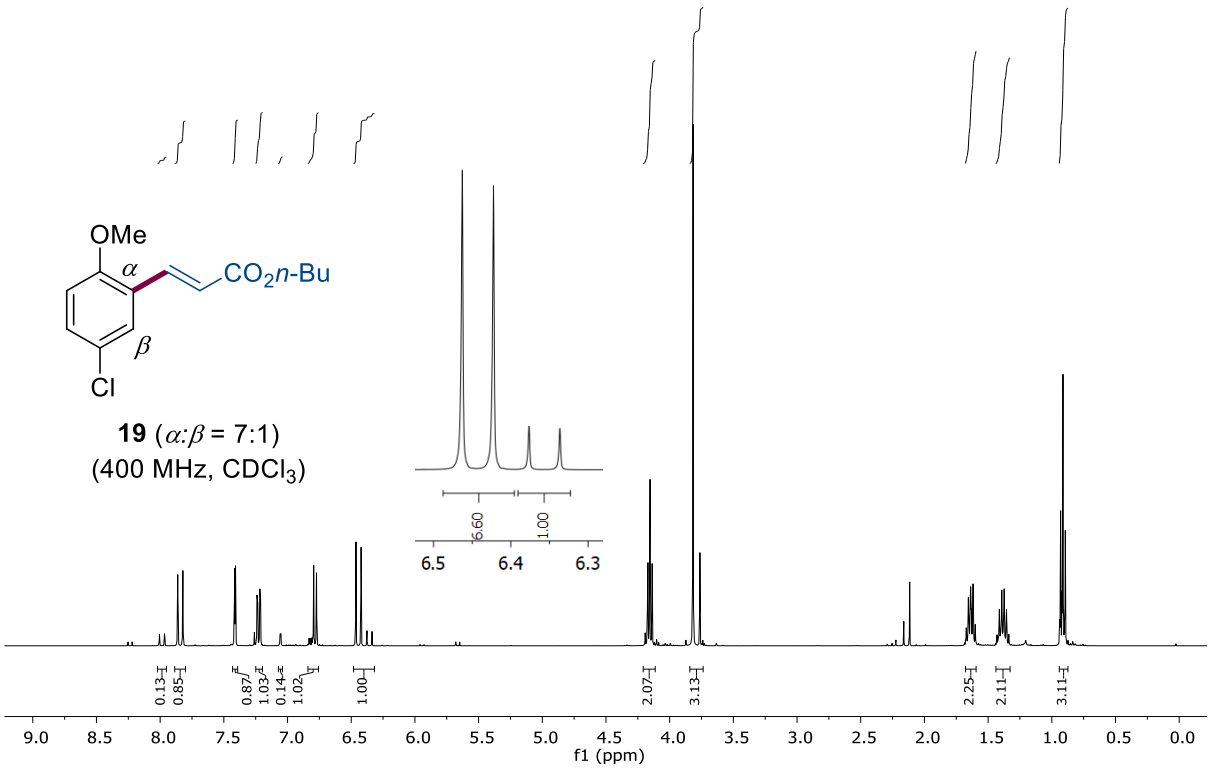

167.14
157.61
156.02
154.44
154.42
138.64
138.62
124.62
124.57
119.86
117.49
117.34
114.60
114.45
112.21
112.16
64.40
56.04
30.75
19.17
13.72
OMe
CO2n-Bu
F
α-18
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

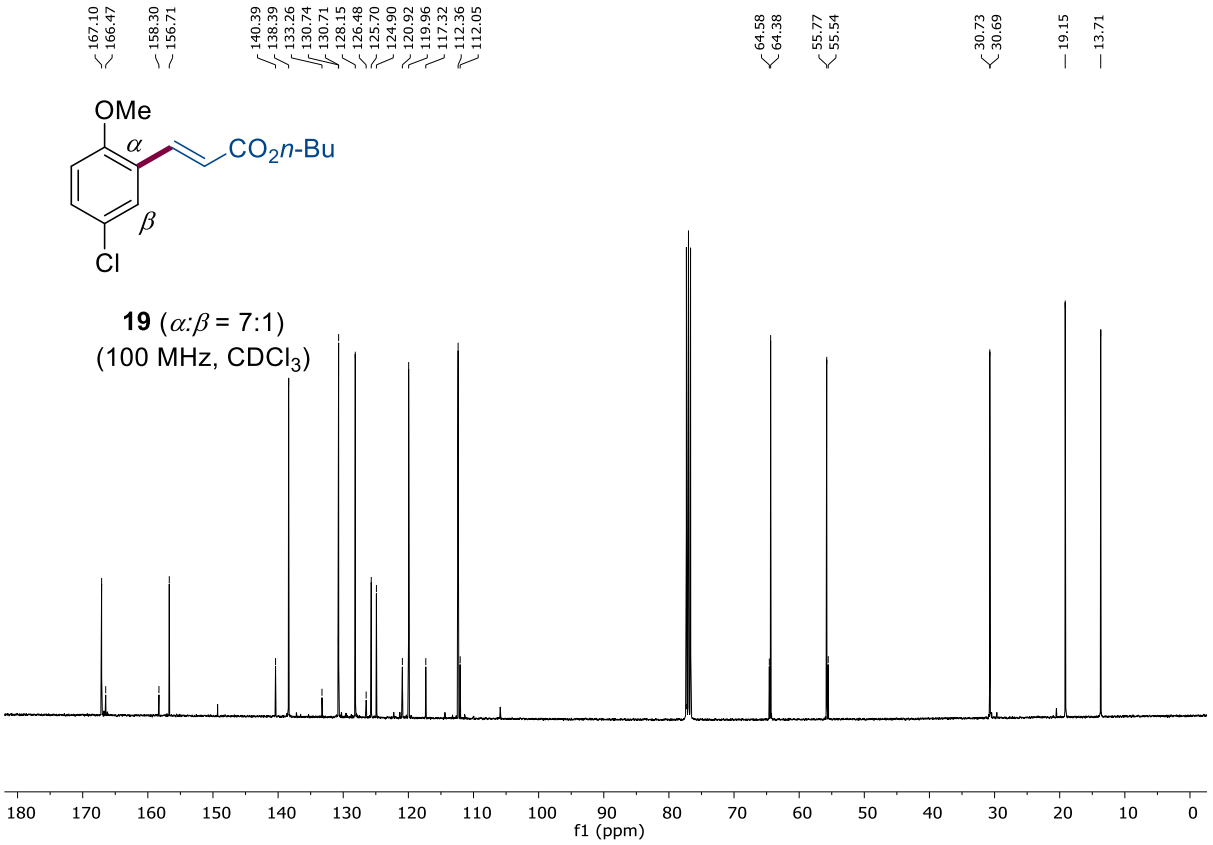

-123.66
-123.66
-123.67
-123.68
-123.69
OMe
CO2n-Bu
F
α-18
(565 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

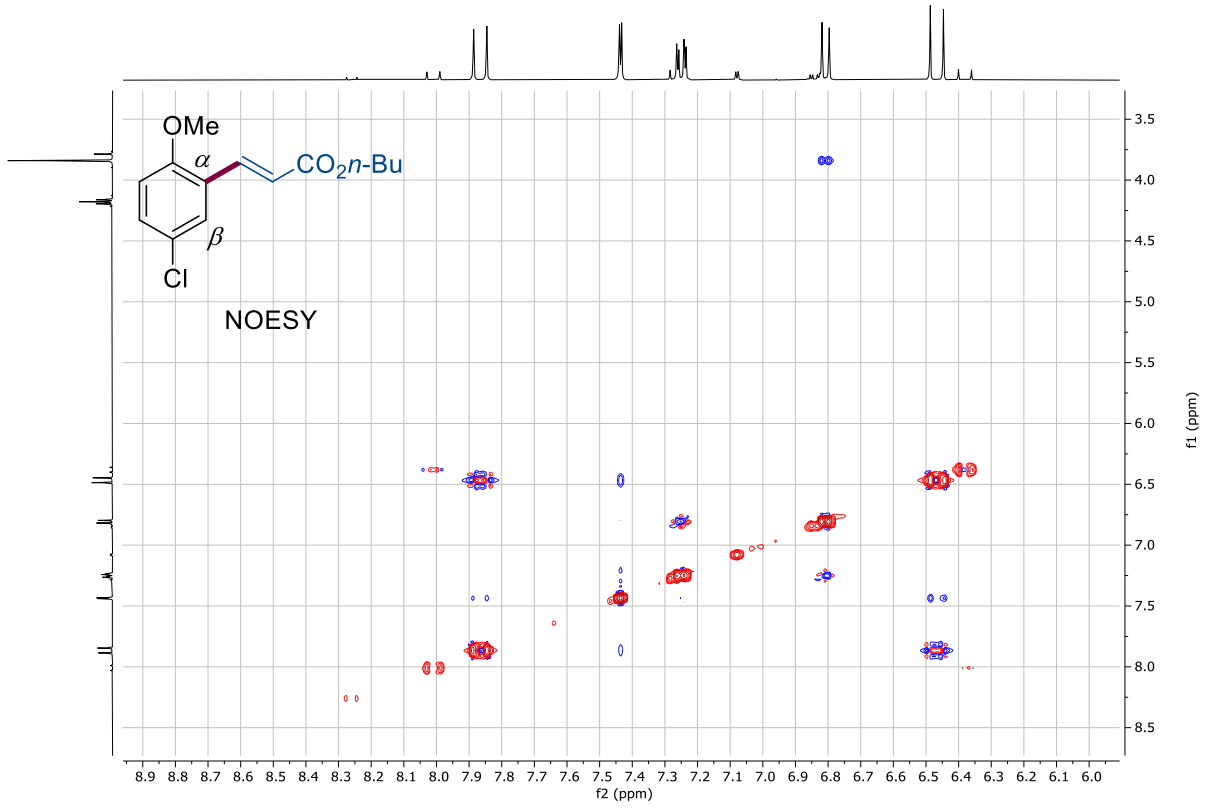

OMe
CO2n-Bu
F
β-18
(600 MHz, CDCl3)
1.00
2.06
1.00
1.00
2.03
3.10
2.11
2.18
3.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

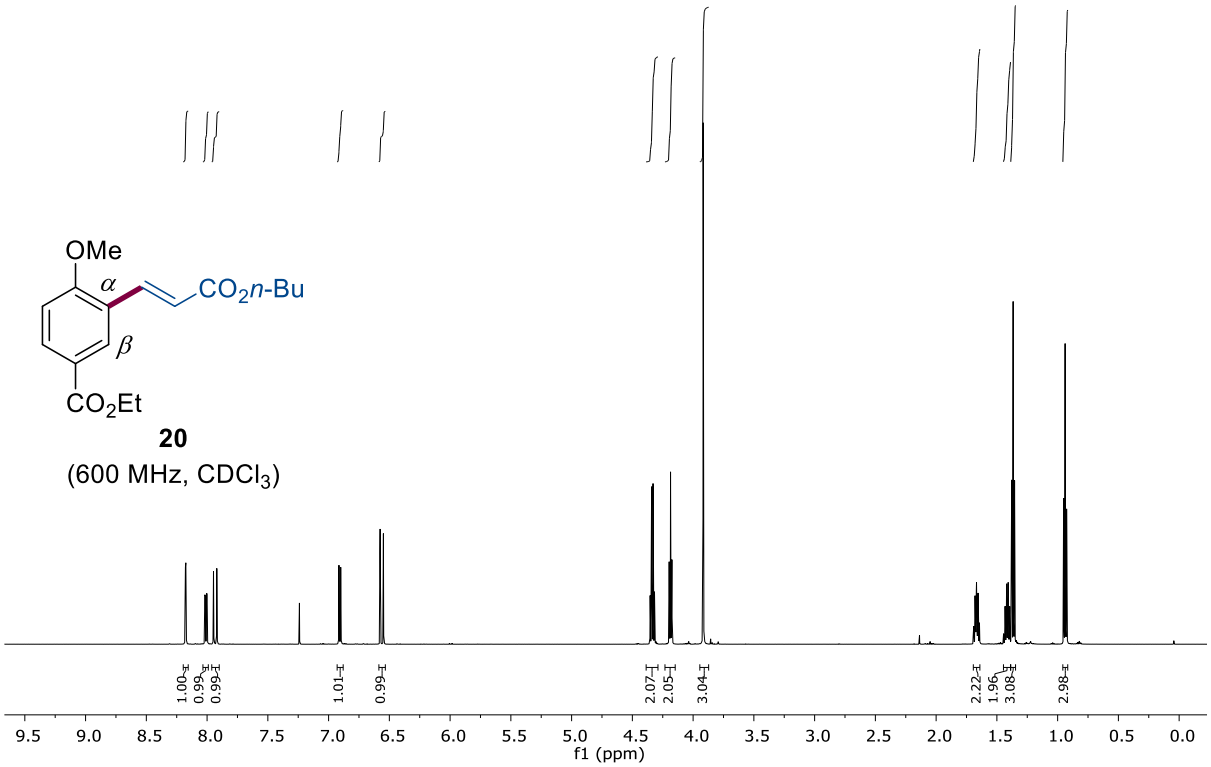

166.83
156.69
155.71
155.70
155.05
137.16
137.14
122.81
122.72
120.92
120.87
117.36
117.31
116.86
116.70
112.61
112.59
64.57
55.80
30.74
19.18
13.73
OMe
CO2n-Bu
F
β-18
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

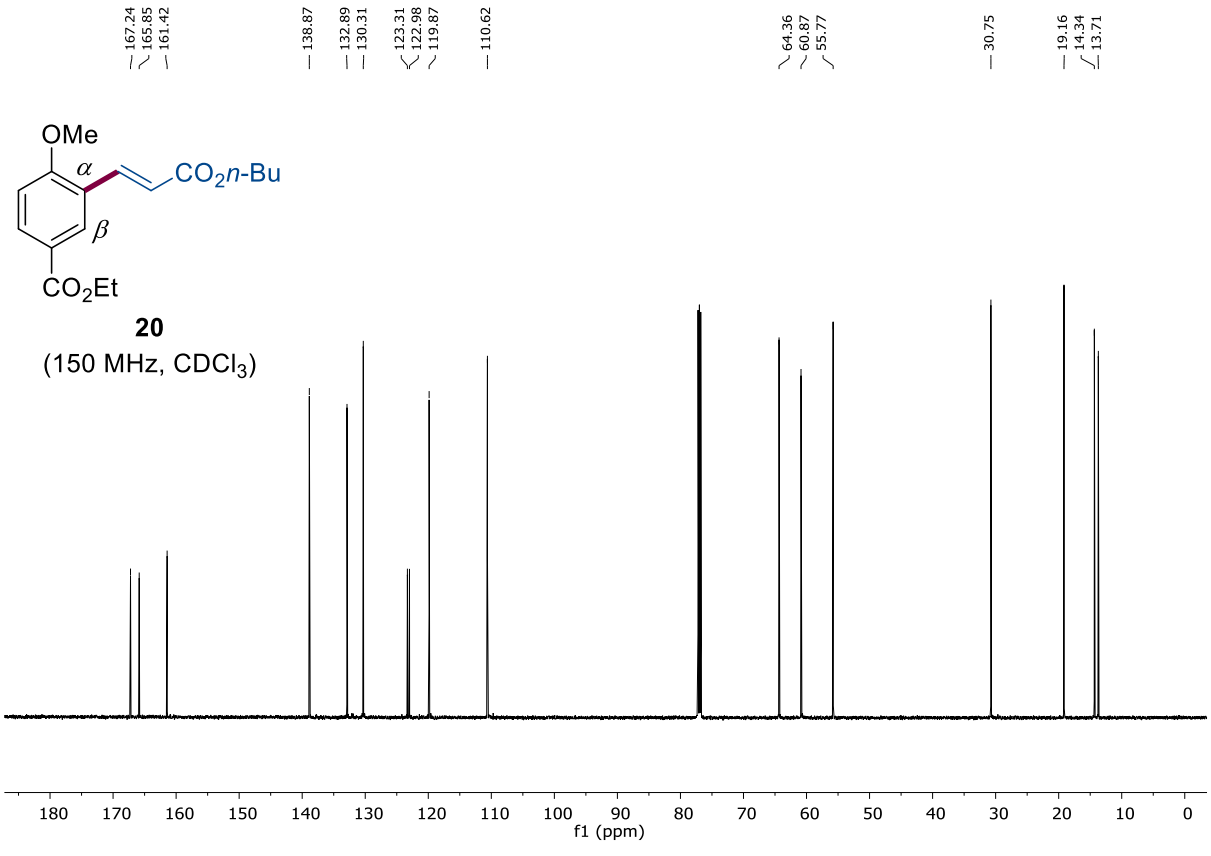

-125.06
-125.07
-125.08
-125.08
-125.09
-125.09
-125.10
OMe
CO2n-Bu
F
β-18
(565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

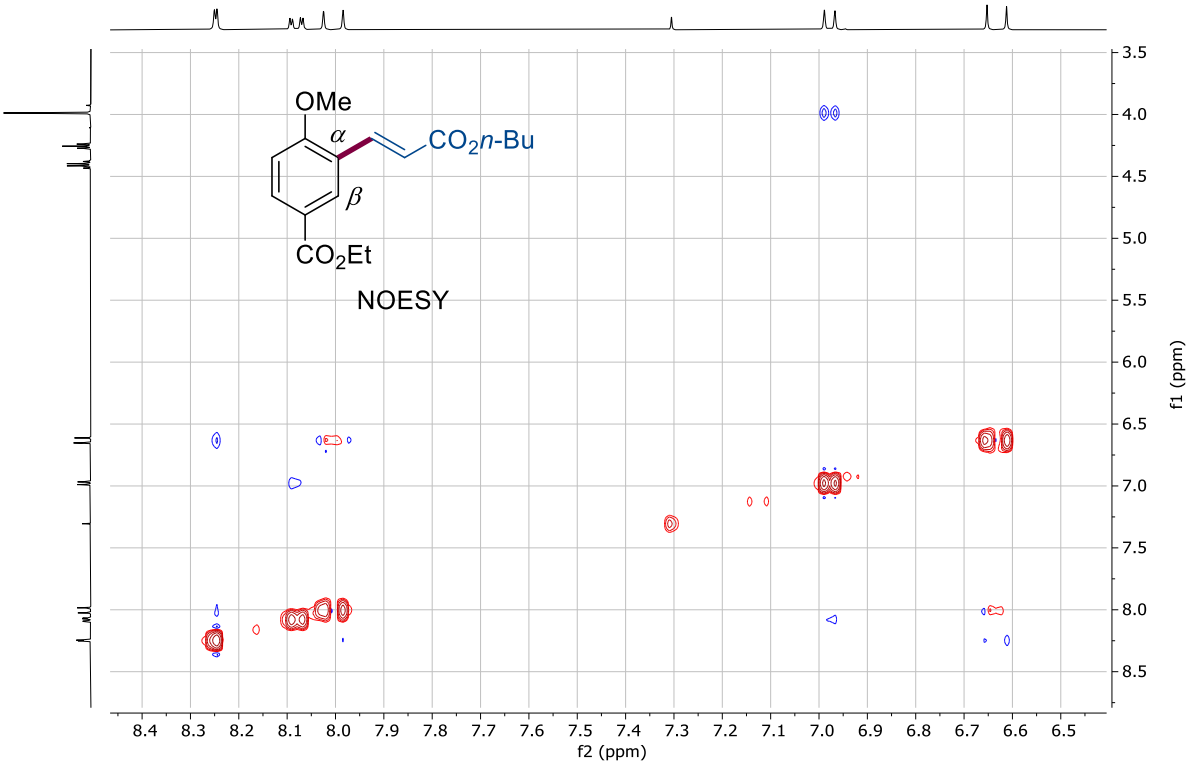

OMe
α
CO2n-Bu
β
Cl
19 (α:β = 7:1)
(400 MHz, CDCl3)
6.60
1.00
6.5 6.4 6.3
0.13
0.85
0.87
1.03
0.14
1.02
1.00
2.07
3.13
2.25
2.11
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

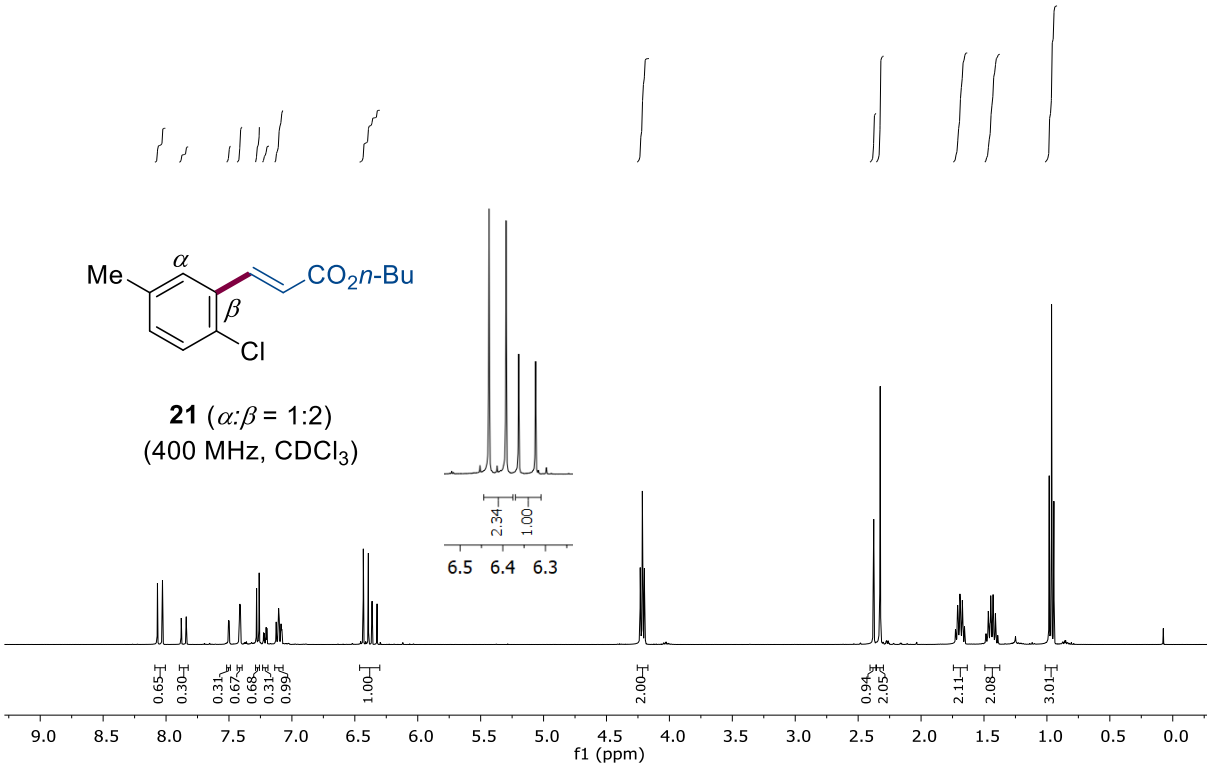

167.10
166.47
158.30
156.71
140.39
138.39
133.26
130.74
130.71
128.15
126.48
125.70
124.90
120.92
119.96
117.32
112.36
112.05
64.58
64.38
55.77
55.54
30.73
30.69
19.15
13.71
OMe
α
CO2n-Bu
β
Cl
19 (α:β = 7:1)
(100 MHz, CDCl3)
f1 (ppm)

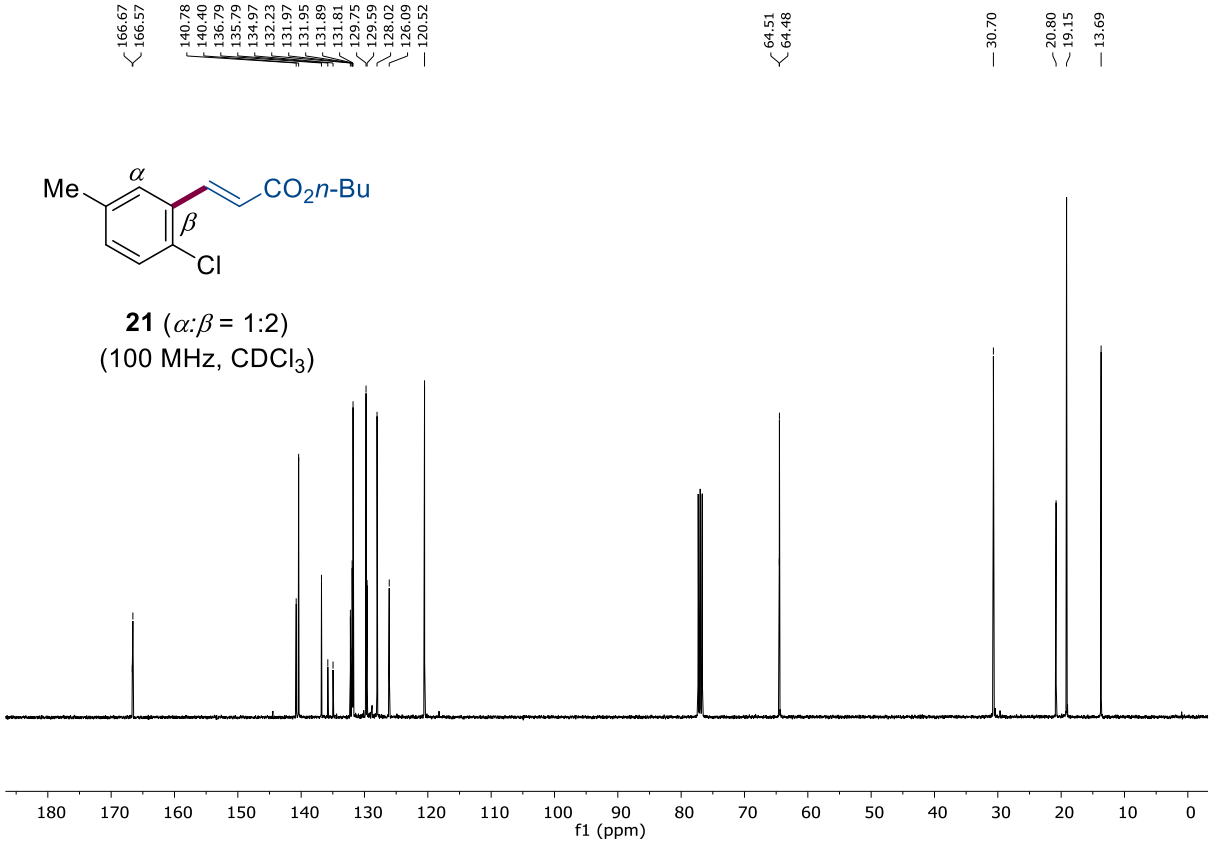

OMe
α
CO2n-Bu
β
Cl
NOESY
f1 (ppm)
f2 (ppm)

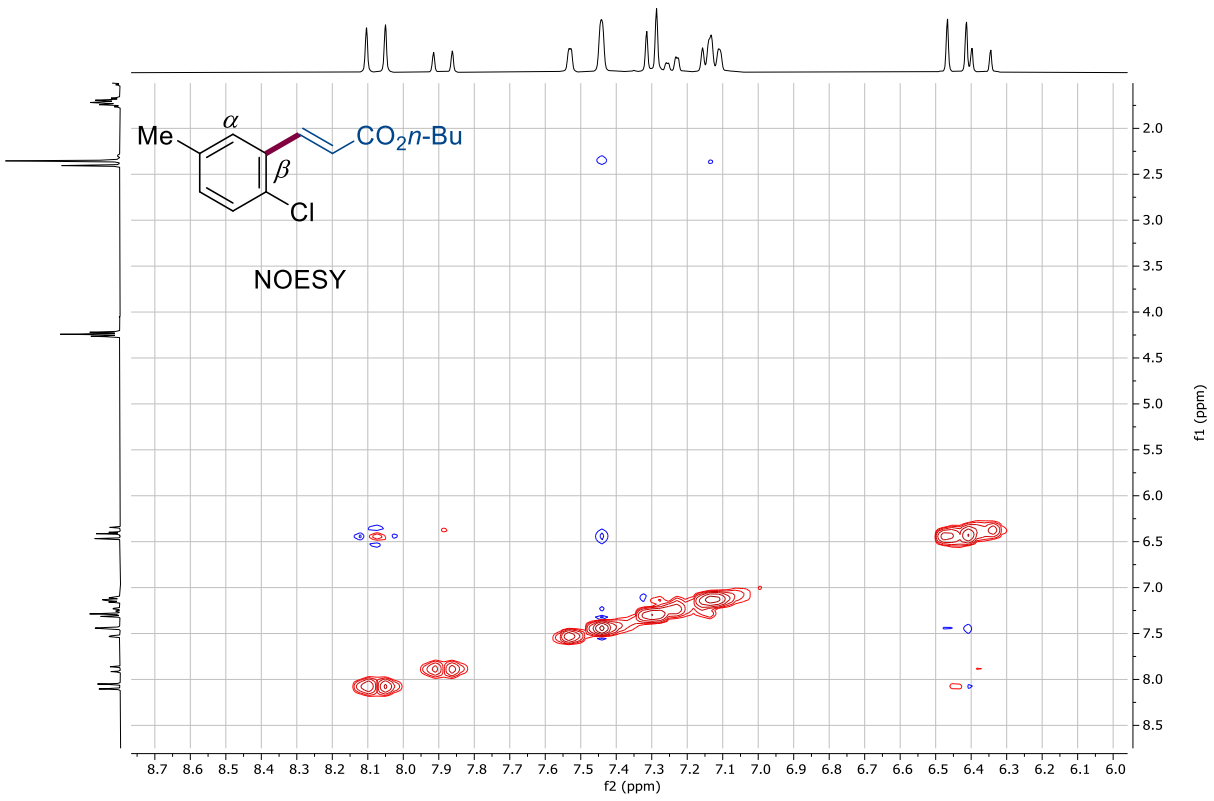

OMe
α
CO2n-Bu
β
CO2Et
20
(600 MHz, CDCl3)
1.00
0.99
0.99
1.01
0.99
2.07
2.05
3.04
2.22
1.96
3.08
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

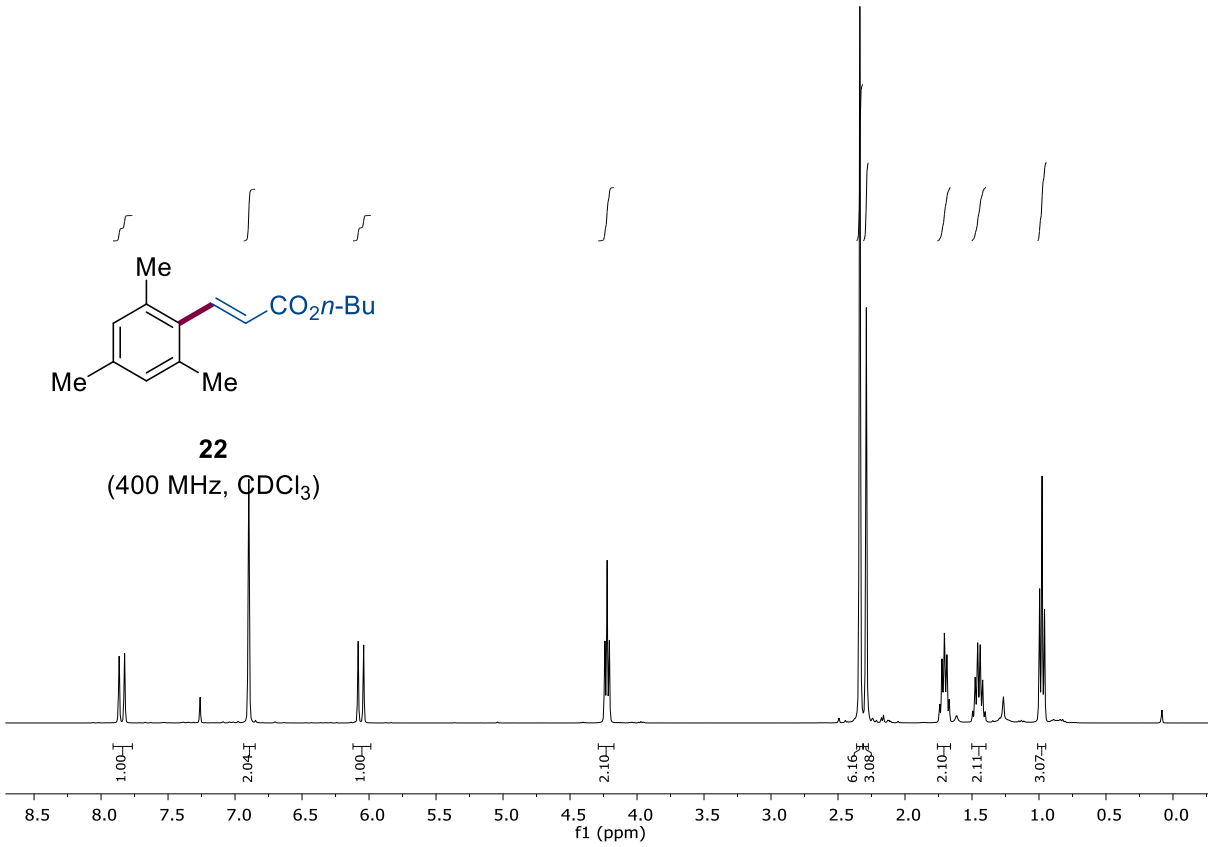

167.24
165.85
161.42
138.87
132.89
130.31
123.31
122.98
119.87
110.62
64.36
60.87
55.77
30.75
19.16
14.34
13.71
OMe
α
CO2n-Bu
β
CO2Et
20
(150 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
α
CO2n-Bu
β
CO2Et
NOESY
f2 (ppm)
f1 (ppm)


Me
α
CO2n-Bu
β
Cl
21 (α:β = 1:2)
(400 MHz, CDCl3)
f1 (ppm)

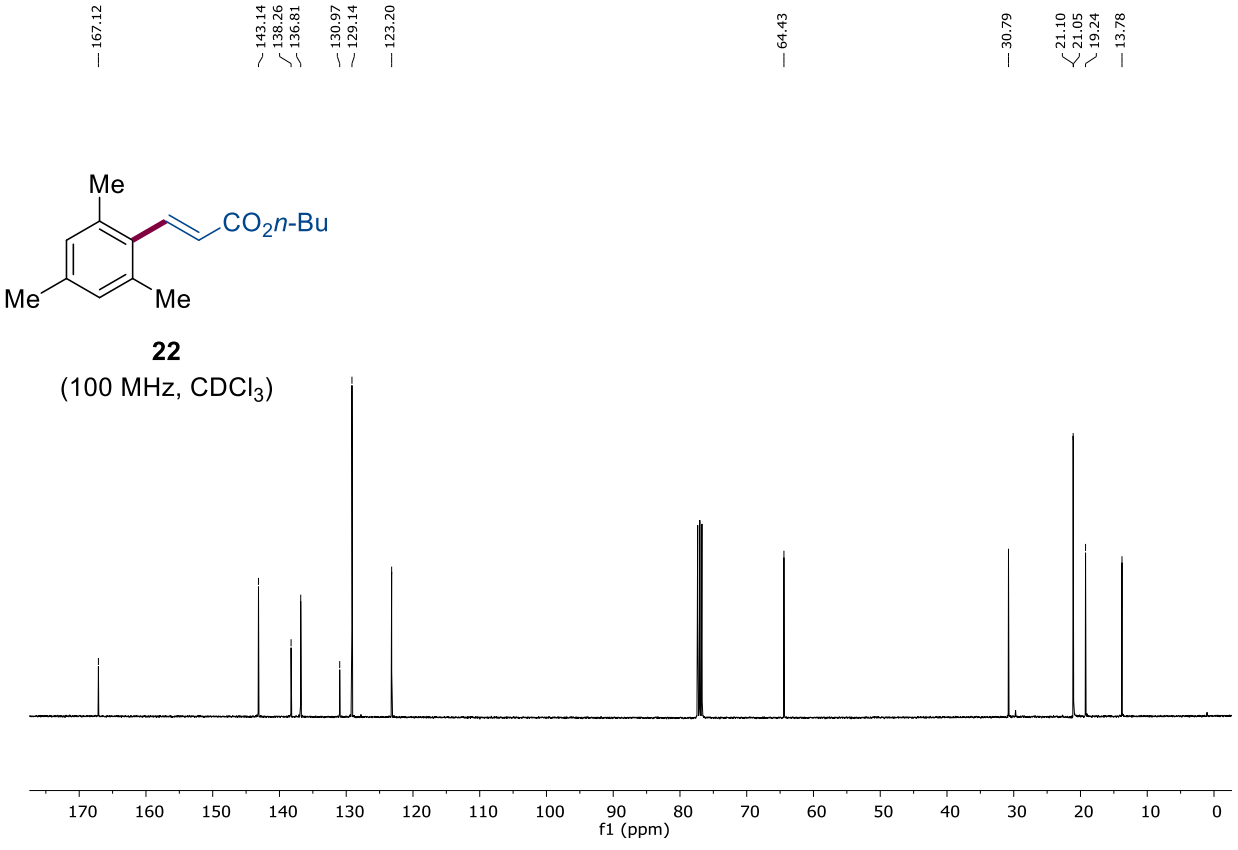

166.67
166.57
140.78
140.40
136.79
135.79
134.97
132.23
131.97
131.95
131.89
131.81
129.75
129.59
128.02
126.09
120.52
64.51
64.48
30.70
20.80
19.15
13.69
Me
α
β
Cl
CO2n-Bu
21 (α:β = 1:2)
(100 MHz, CDCl3)
f1 (ppm)


Me
α
β
Cl
CO2n-Bu
NOESY
f2 (ppm)
f1 (ppm)



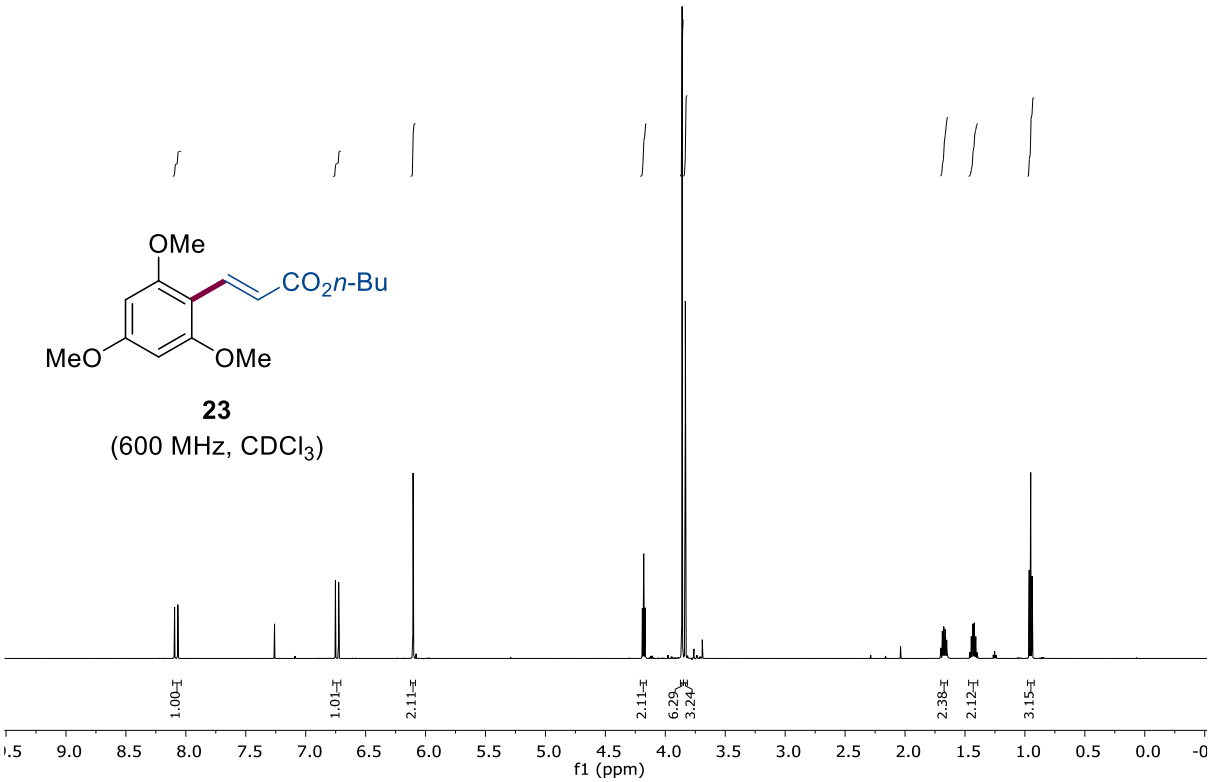
22

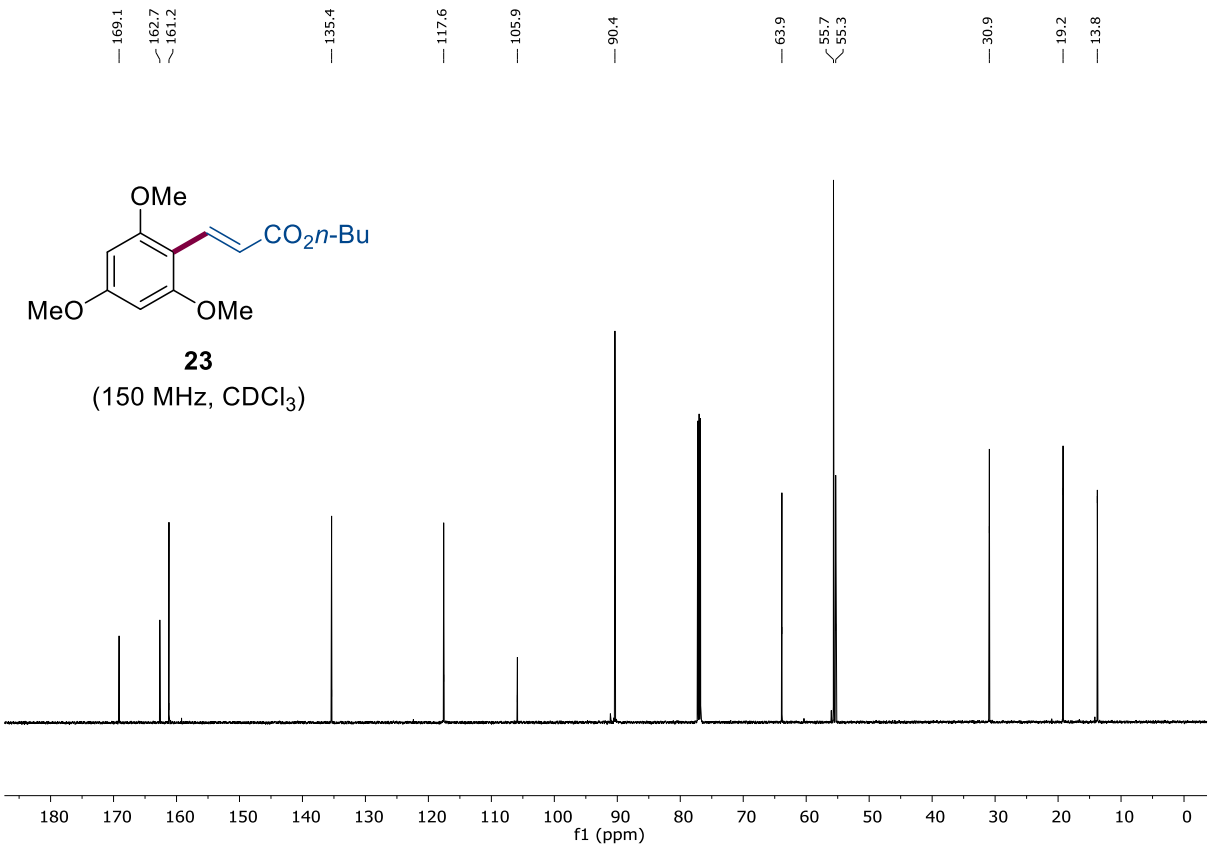
(400 MHz, $CDCl_3$)

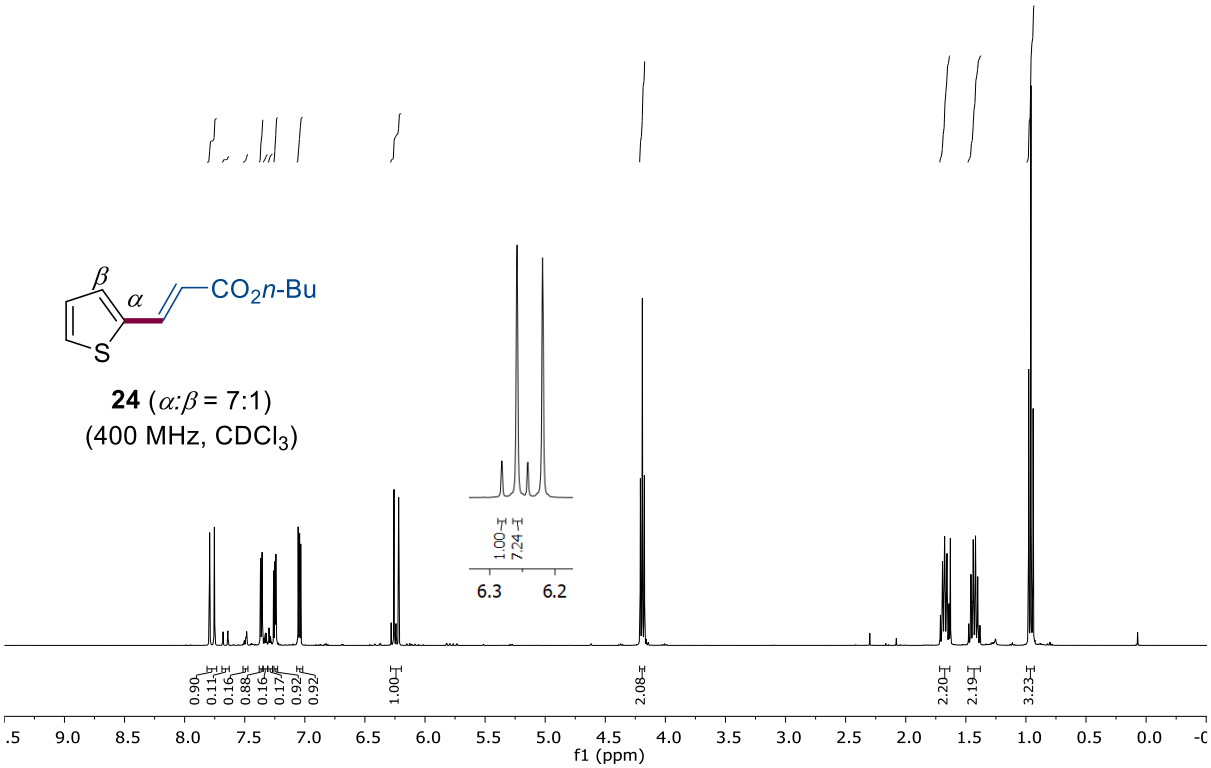


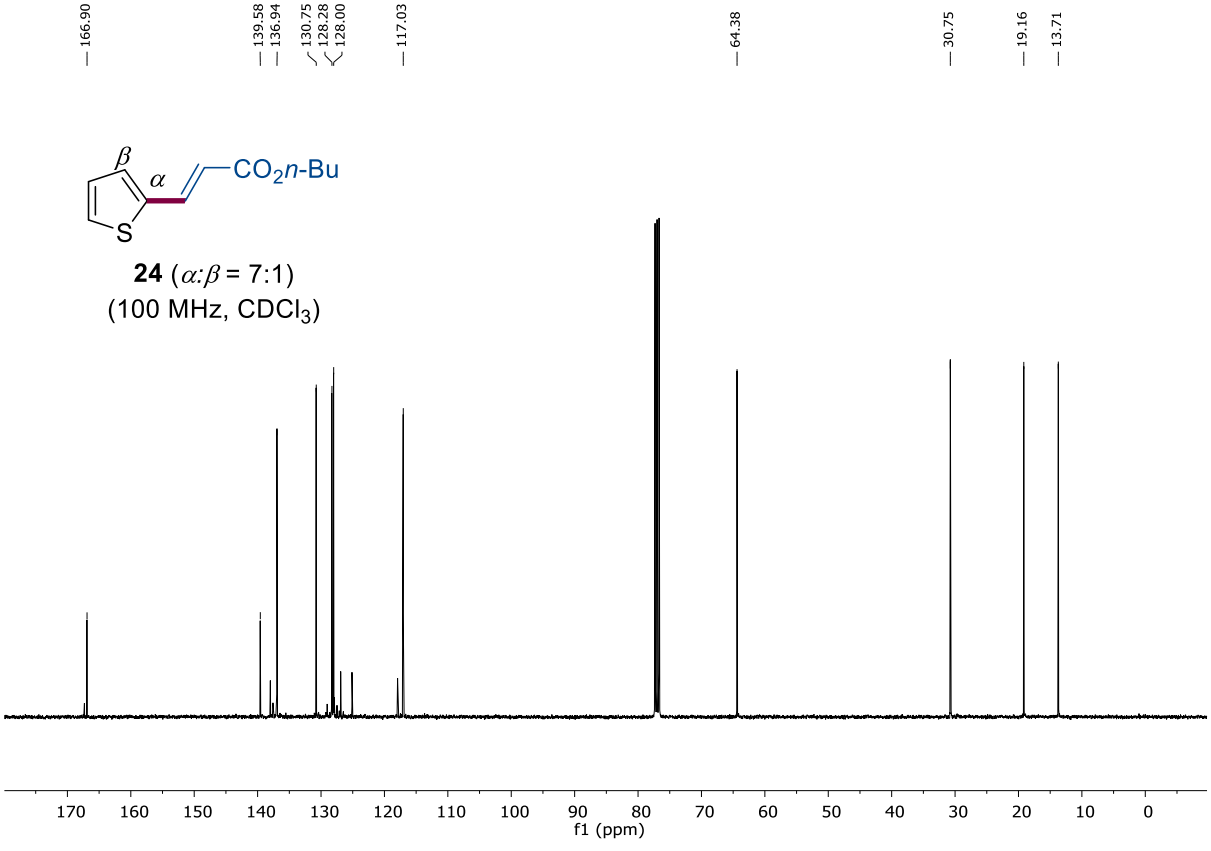
22

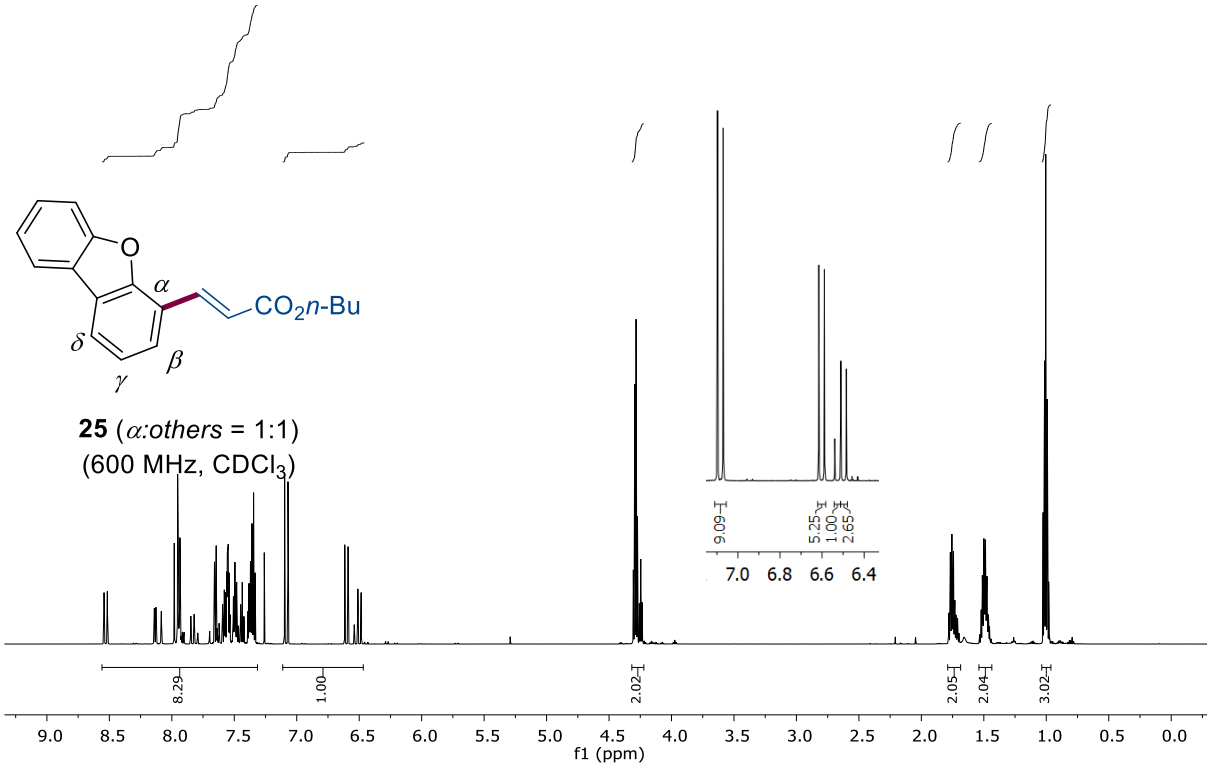
(100 MHz, $CDCl_3$)

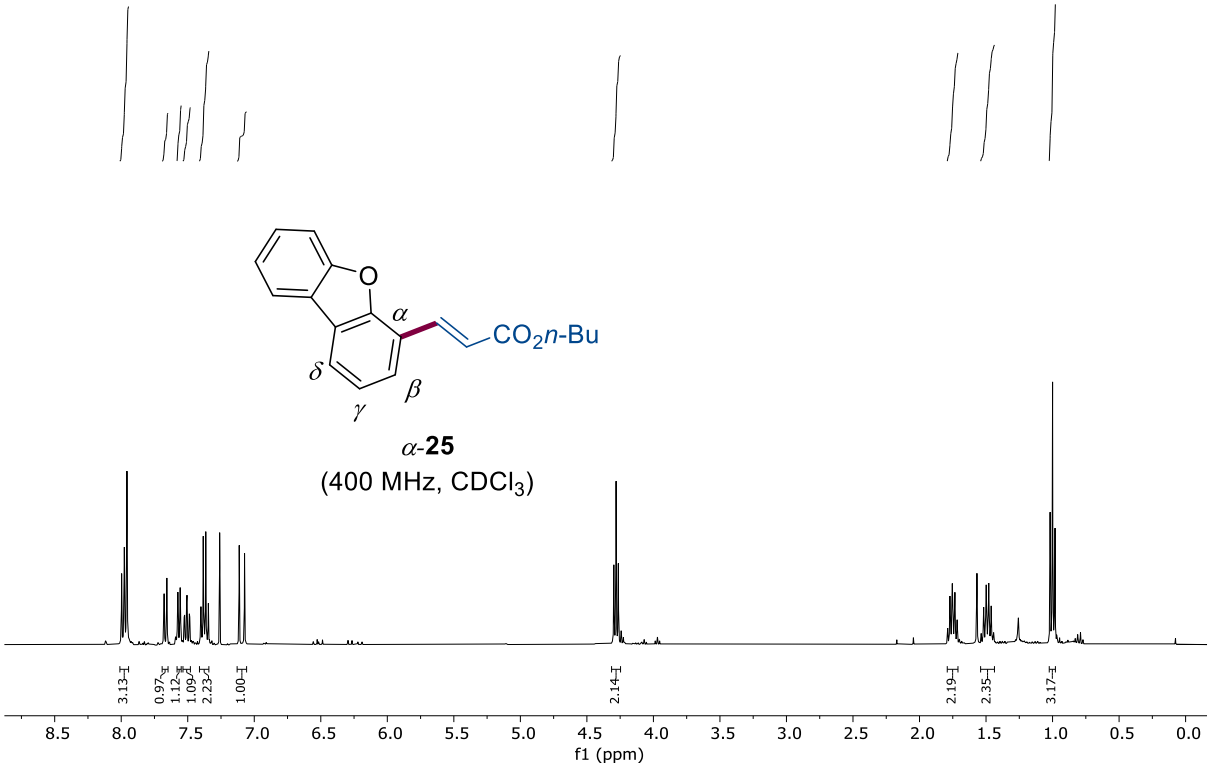

OMe
CO2n-Bu
MeO
OMe
23
(600 MHz, CDCl3)
1.00
1.01
2.11
2.11
6.29
3.24
2.38
2.12
3.15
f1 (ppm)

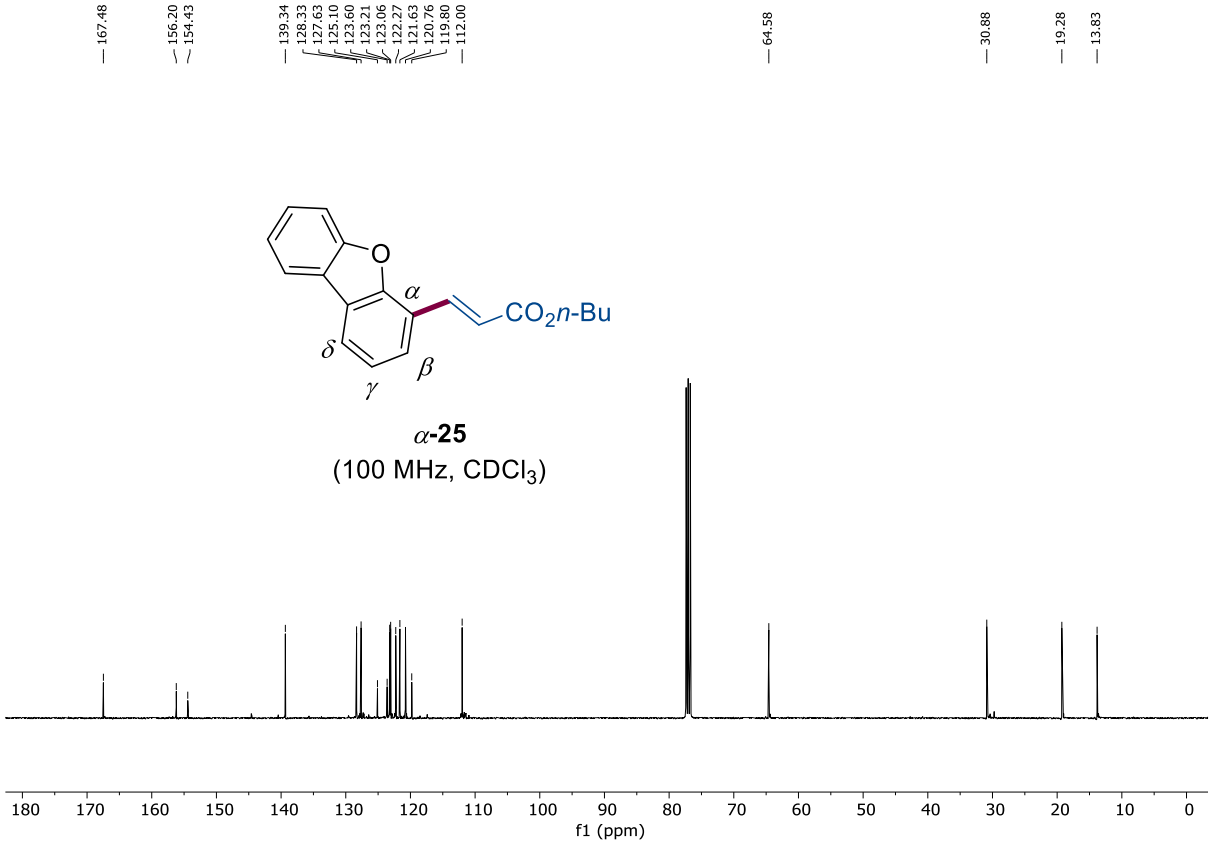

169.1
162.7
161.2
135.4
117.6
105.9
90.4
63.9
55.7
55.3
30.9
19.2
13.8
OMe
CO2n-Bu
MeO
OMe
23
(150 MHz, CDCl3)
f1 (ppm)

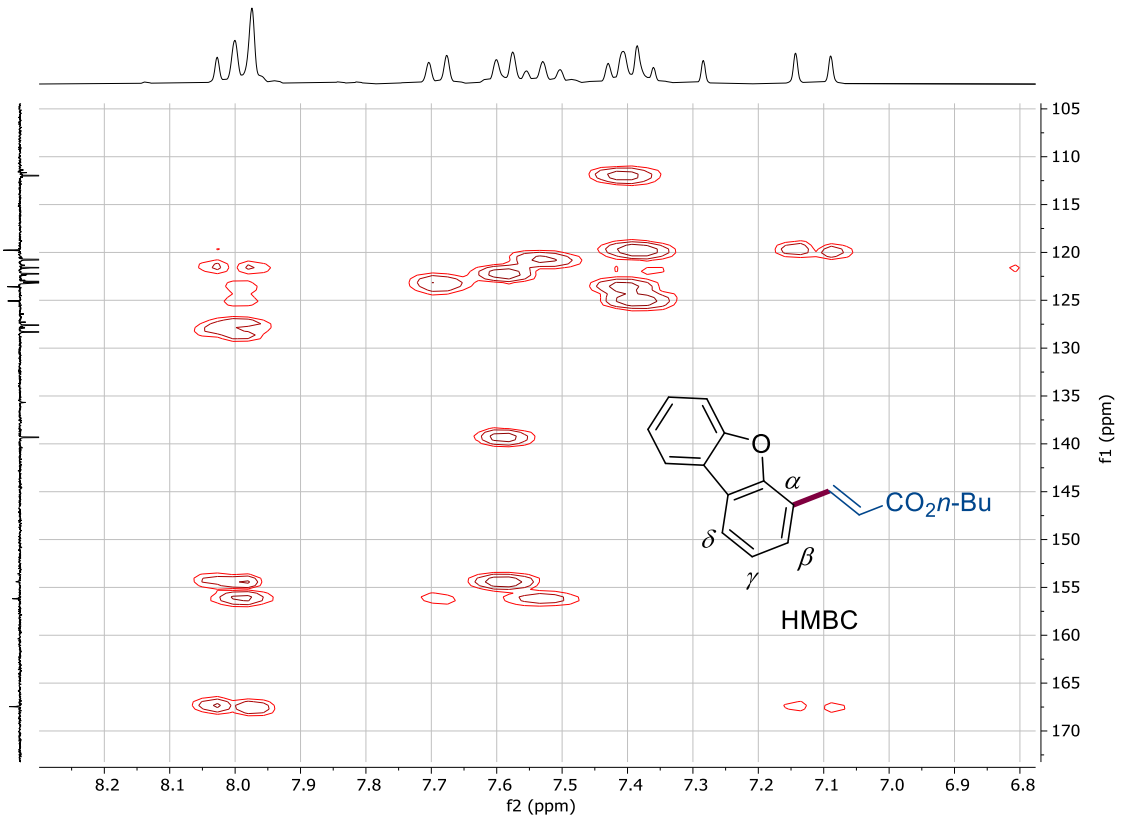

β
α
CO2n-Bu
S
24 (α:β = 7:1)
(400 MHz, CDCl3)
1.00
7.24
6.3
6.2
0.90
0.11
0.16
0.88
0.16
0.17
0.92
0.92
1.00
2.08
2.20
2.19
3.23
f1 (ppm)

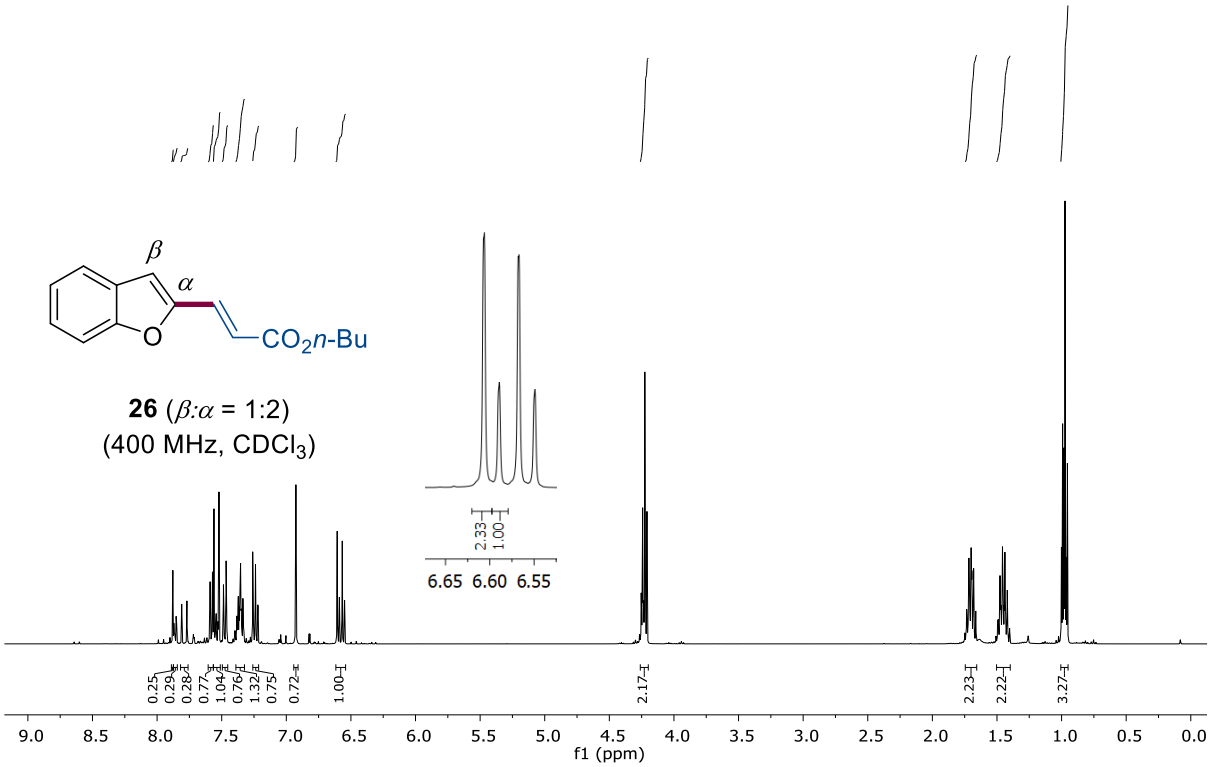

166.90
139.58
136.94
130.75
128.28
128.00
117.03
64.38
30.75
19.16
13.71
β
α
CO2n-Bu
S
24 (α:β = 7:1)
(100 MHz, CDCl3)
f1 (ppm)

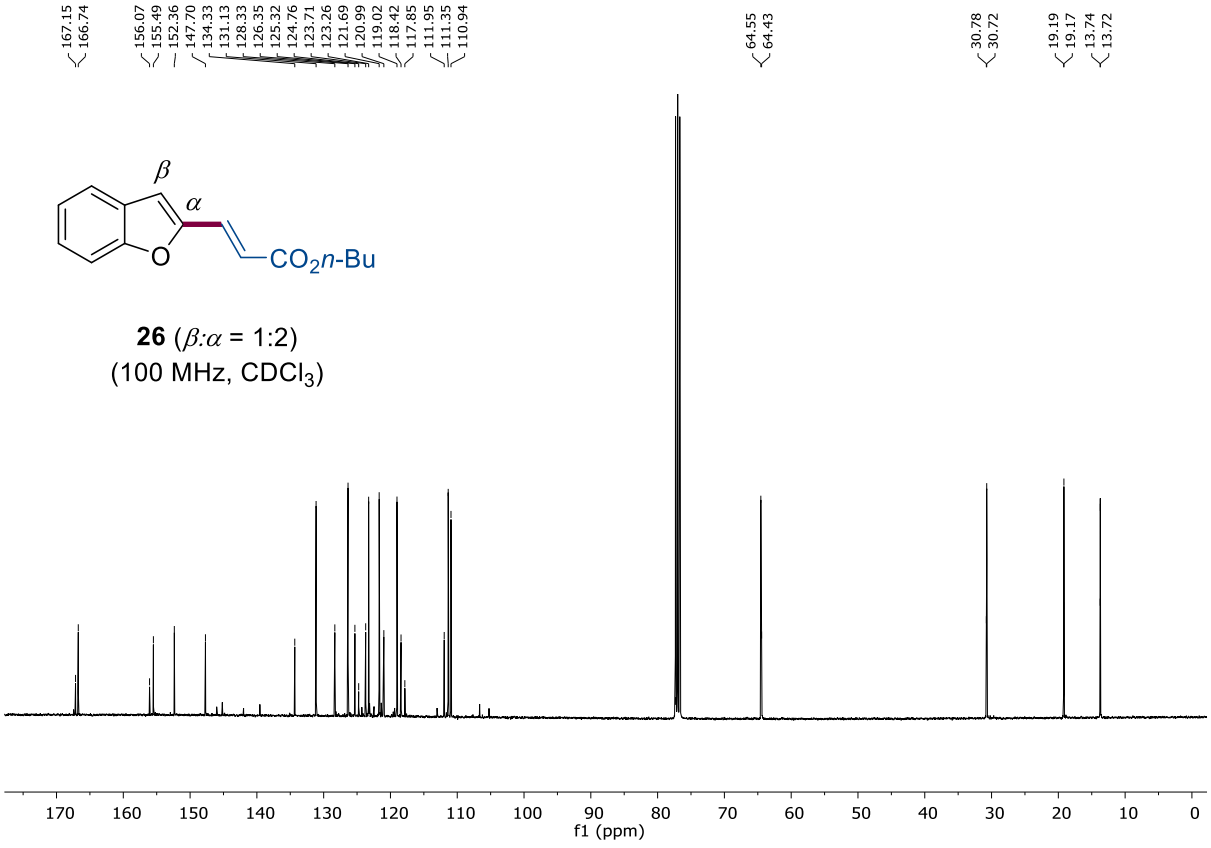

O
α
CO2n-Bu
δ
β
γ
25 (α:others = 1:1)
(600 MHz, CDCl3)
9.09
5.25
1.00
2.65
7.0 6.8 6.6 6.4
8.29
1.00
2.02
2.05
2.04
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

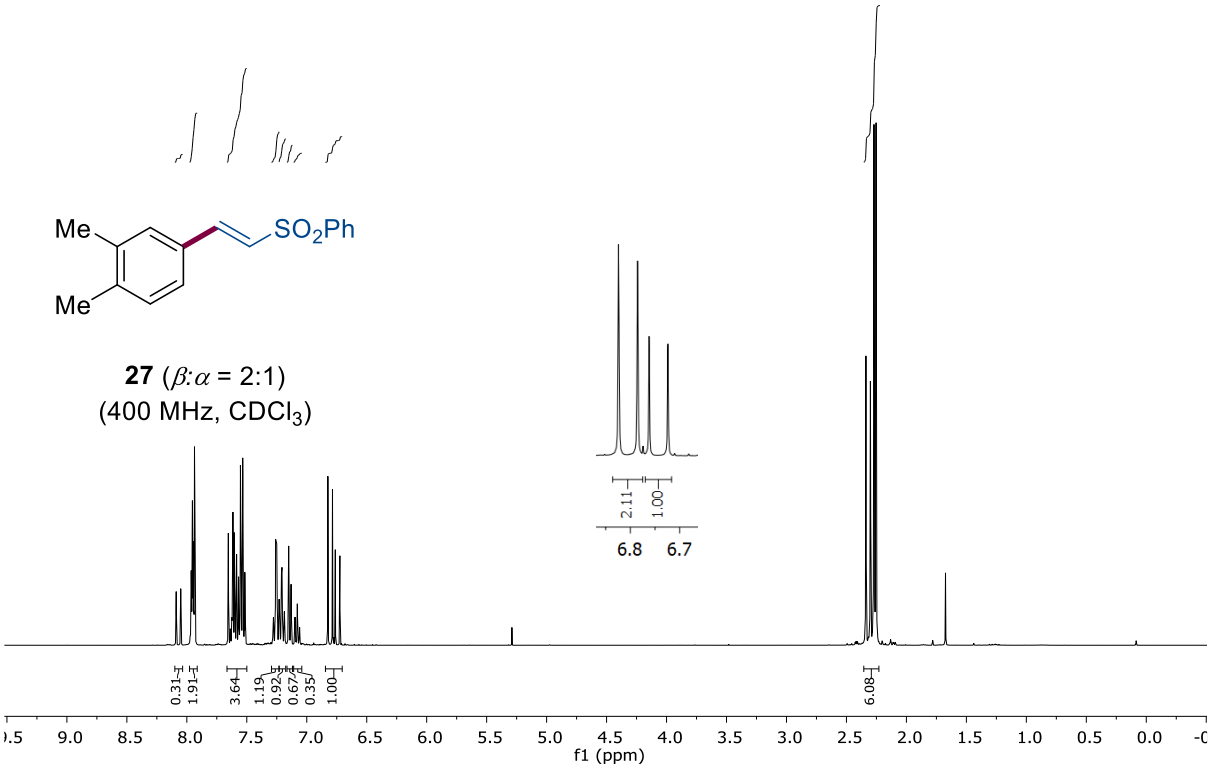

O
α
CO2n-Bu
δ
β
γ
α-25
(400 MHz, CDCl3)
3.13
0.97
1.12
1.09
2.23
1.00
2.14
2.19
2.35
3.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.48
156.20
154.43
139.34
128.33
127.63
125.10
123.60
123.21
123.06
122.27
121.63
120.76
119.80
112.00
64.58
30.88
19.28
13.83
O
α
CO2n-Bu
δ
β
γ
α-25
(100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

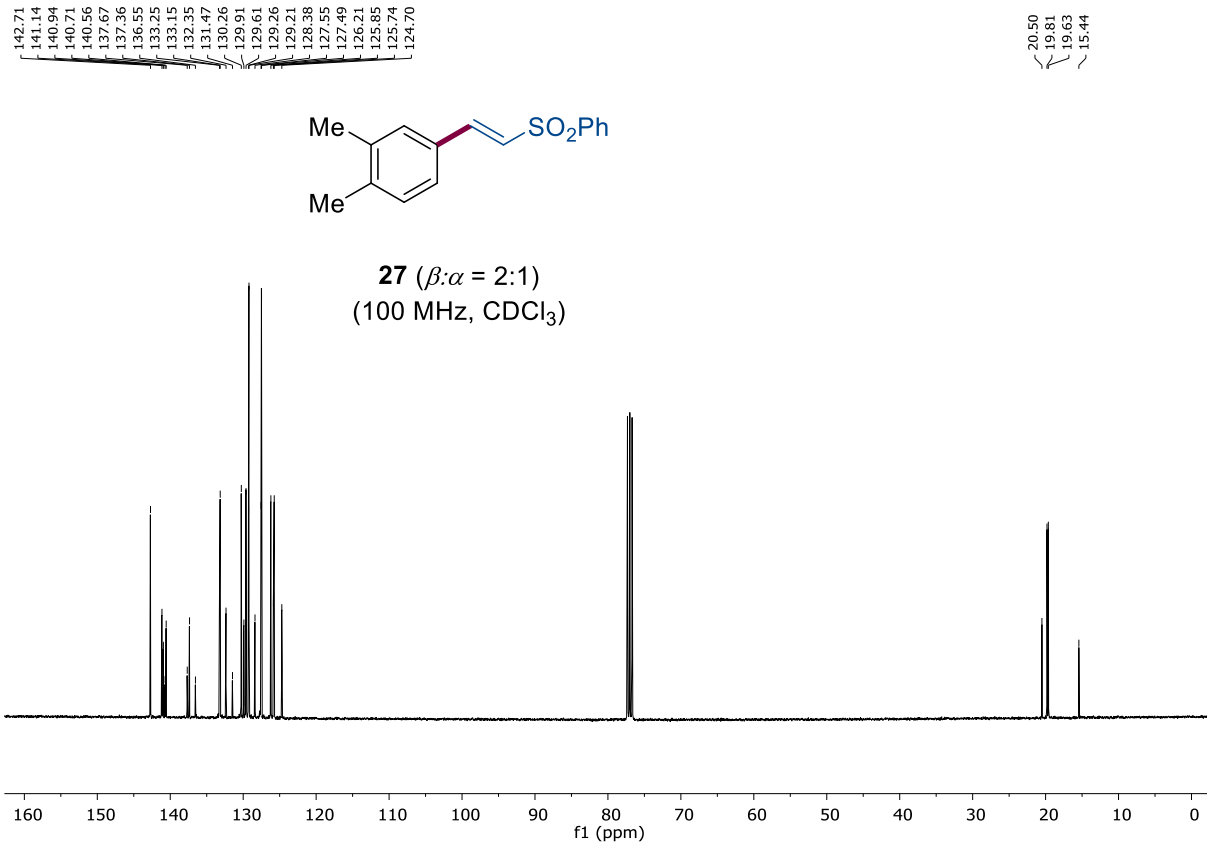

105 110 115 120 125 130 135 140 145 150 155 160 165 170
f1 (ppm)
O
α
CO2n-Bu
δ
β
γ
HMBC
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f2 (ppm)


β
α
O
CO2n-Bu
26 (β:α = 1:2)
(400 MHz, CDCl3)
6.65 6.60 6.55
2.33
1.00
0.25
0.29
0.28
0.77
1.04
0.76
1.32
0.75
0.72
1.00
2.17
2.23
2.22
3.27
f1 (ppm)

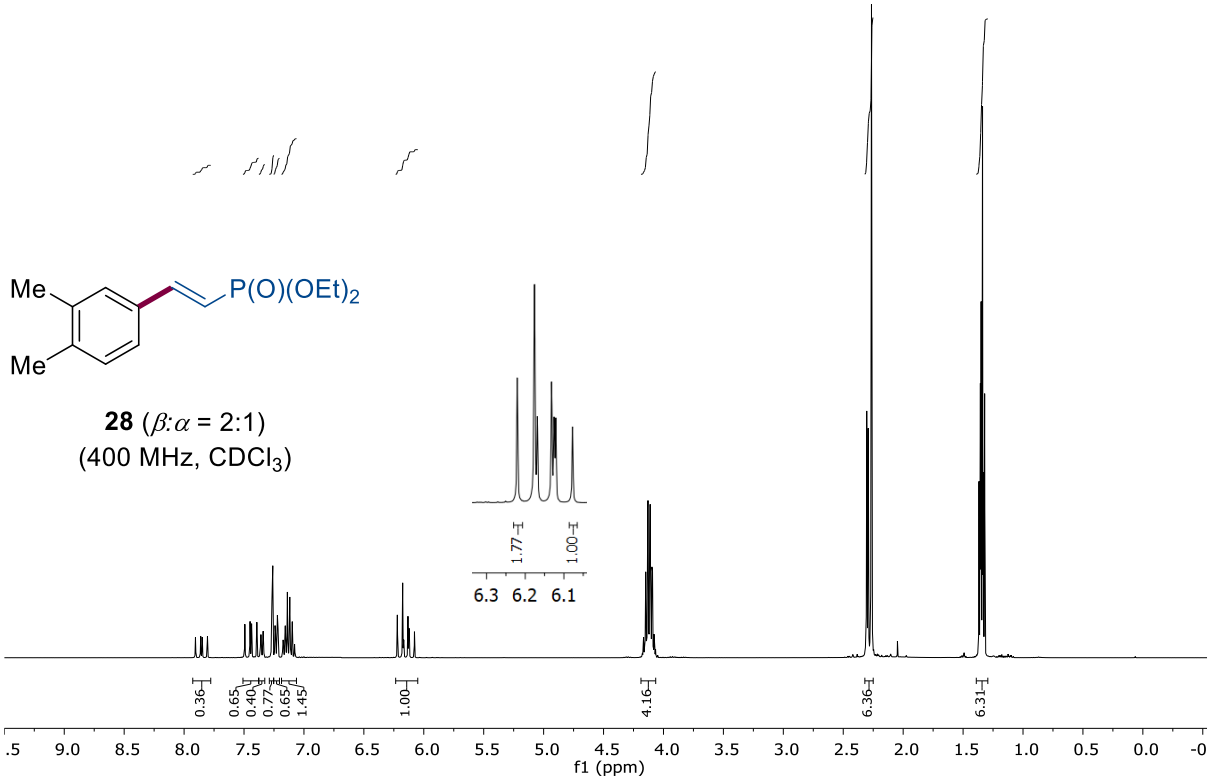

167.15
166.74
156.07
155.49
152.36
147.70
134.33
131.13
128.33
126.35
125.32
124.76
123.71
123.26
121.69
120.99
119.02
118.42
117.85
111.95
111.35
110.94
64.55
64.43
30.78
30.72
19.19
19.17
13.74
13.72
β
α
O
CO2n-Bu
26 (β:α = 1:2)
(100 MHz, CDCl3)
f1 (ppm)

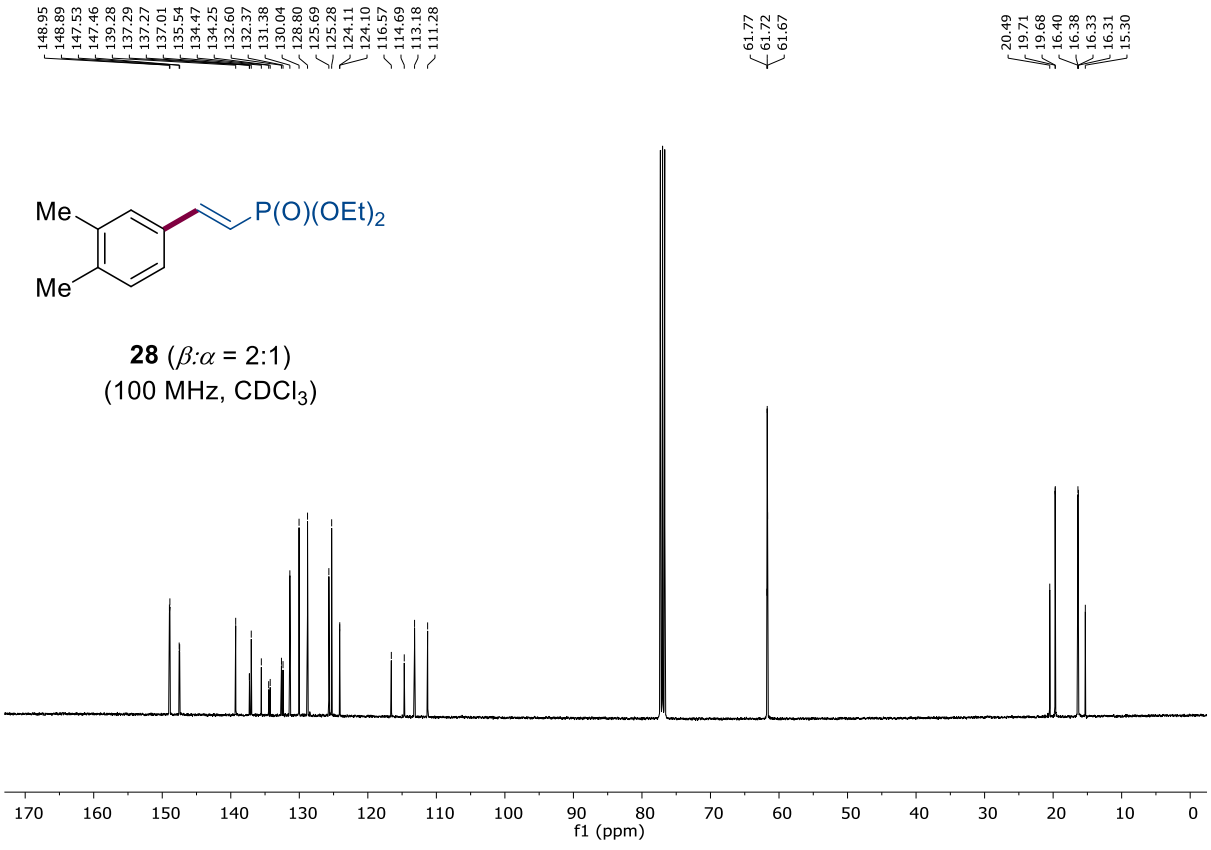


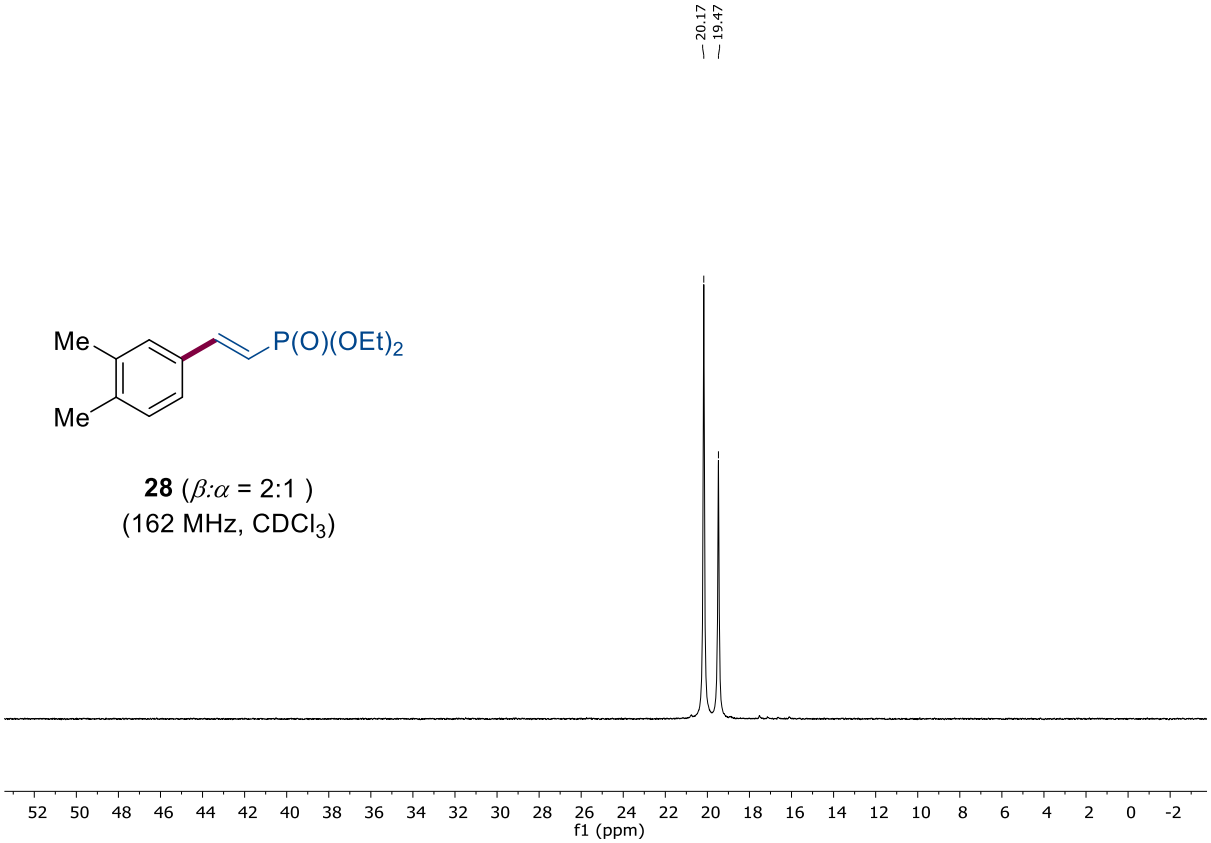
27 (β:α = 2:1)
(400 MHz, $CDCl_3$)

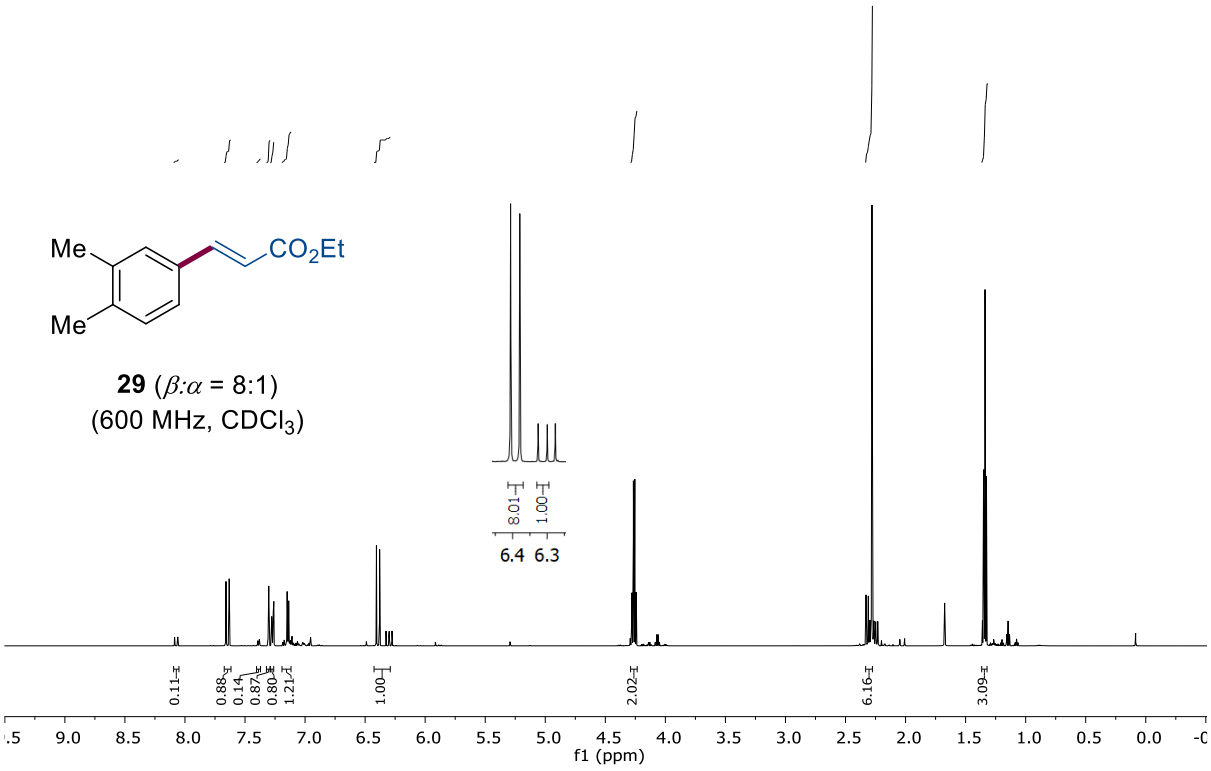


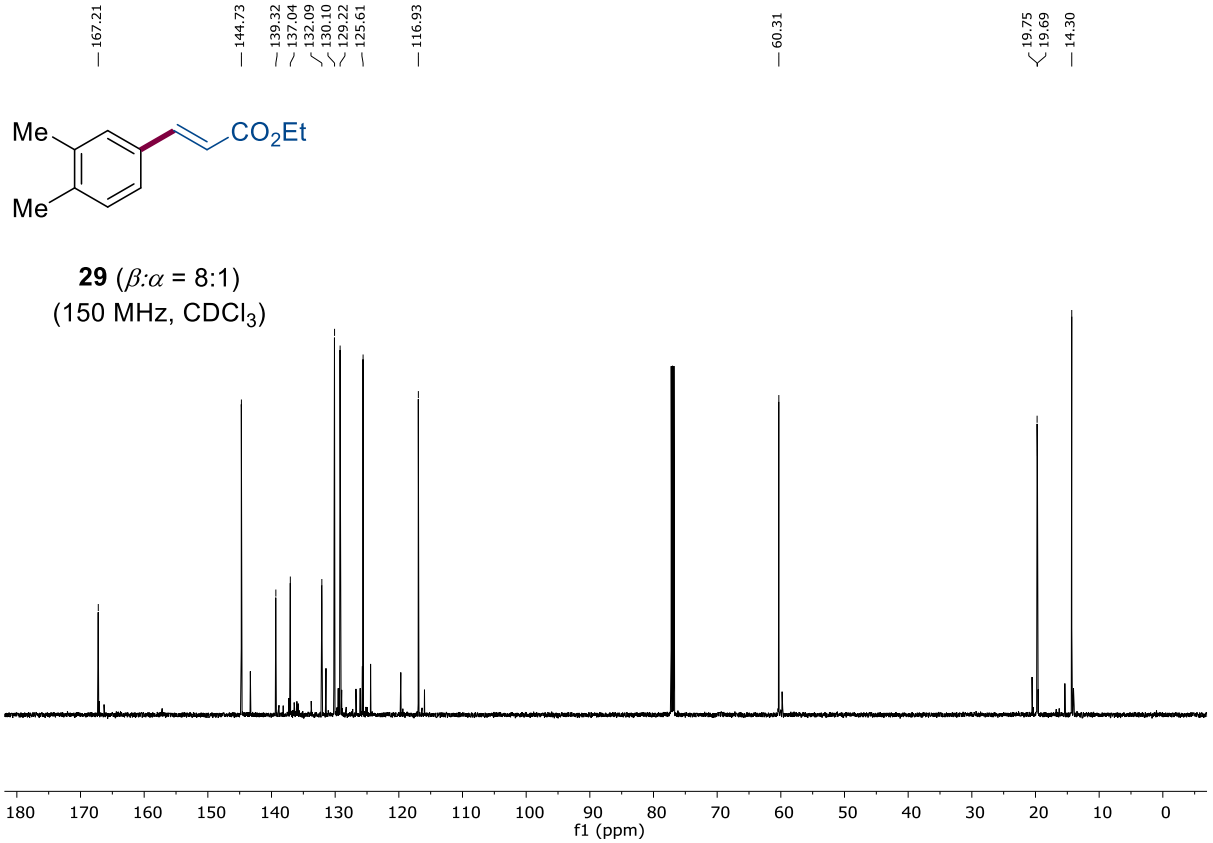
27 (β:α = 2:1)
(100 MHz, $CDCl_3$)

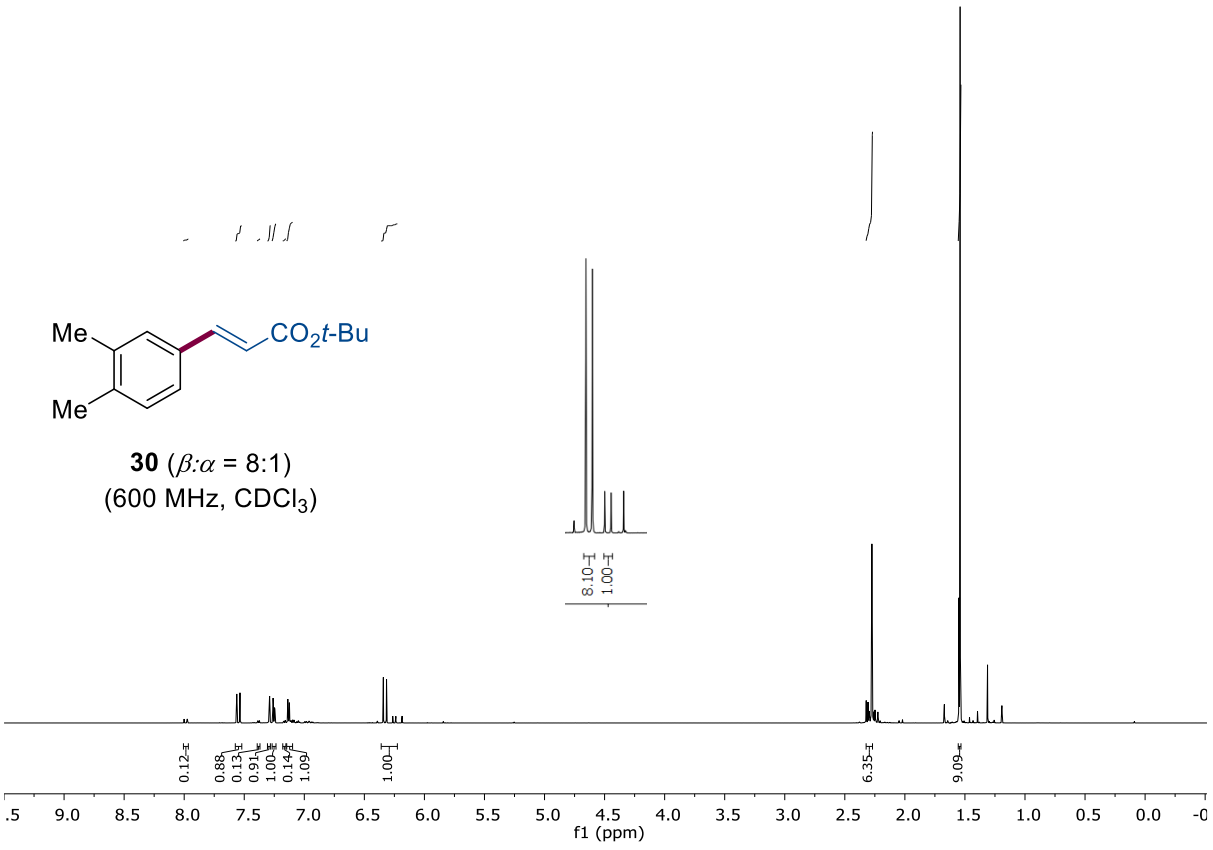

Me
Me
P(O)(OEt)2
28 (β:α = 2:1)
(400 MHz, CDCl3)
1.77
1.00
6.3 6.2 6.1
0.36
0.65
0.40
0.77
0.65
1.45
1.00
4.16
6.36
6.31
f1 (ppm)

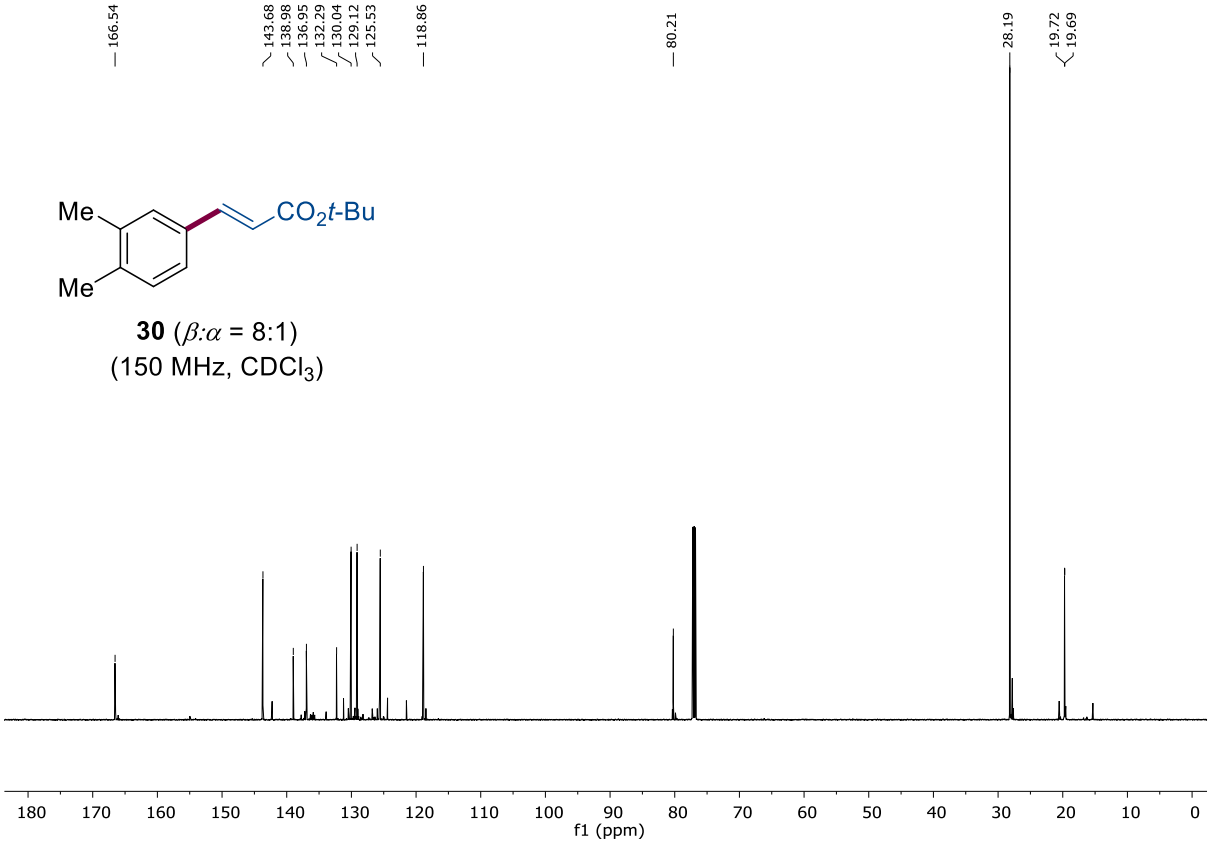

148.95
148.89
147.53
147.46
139.28
137.29
137.27
137.01
135.54
134.47
134.25
132.60
132.37
131.38
130.04
128.80
125.69
125.28
124.11
124.10
116.57
114.69
113.18
111.28
61.77
61.72
61.67
20.49
19.71
19.68
16.40
16.38
16.33
16.31
15.30
Me
Me
P(O)(OEt)2
28 (β:α = 2:1)
(100 MHz, CDCl3)
f1 (ppm)


20.17
19.47
Me
Me
P(O)(OEt)2
28 (β:α = 2:1)
(162 MHz, CDCl3)
52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2
f1 (ppm)

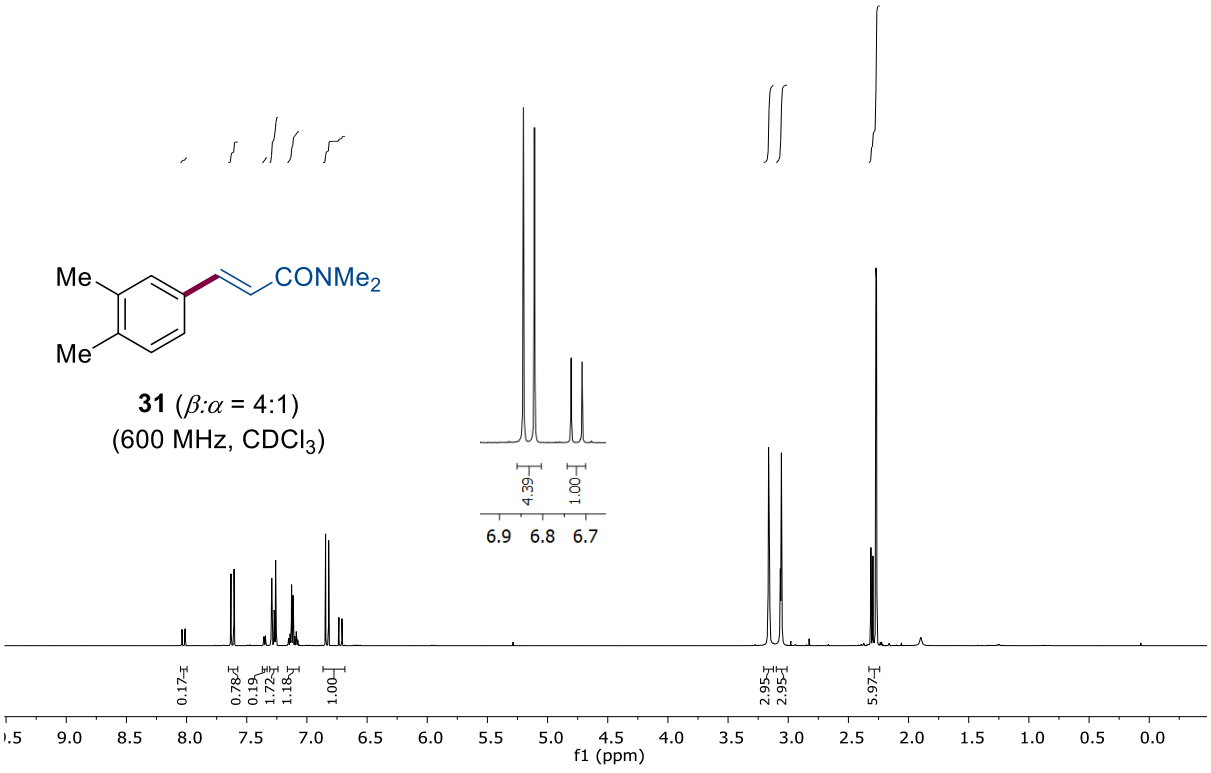

Me
Me
CO2Et
29 (β:α = 8:1)
(600 MHz, CDCl3)
8.01
1.00
6.4 6.3
0.11
0.88
0.14
0.87
0.80
1.21
1.00
2.02
6.16
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.21
144.73
139.32
137.04
132.09
130.10
129.22
125.61
116.93
60.31
19.75
19.69
14.30
Me
Me
CO2Et
29 (β:α = 8:1)
(150 MHz, CDCl3)
f1 (ppm)

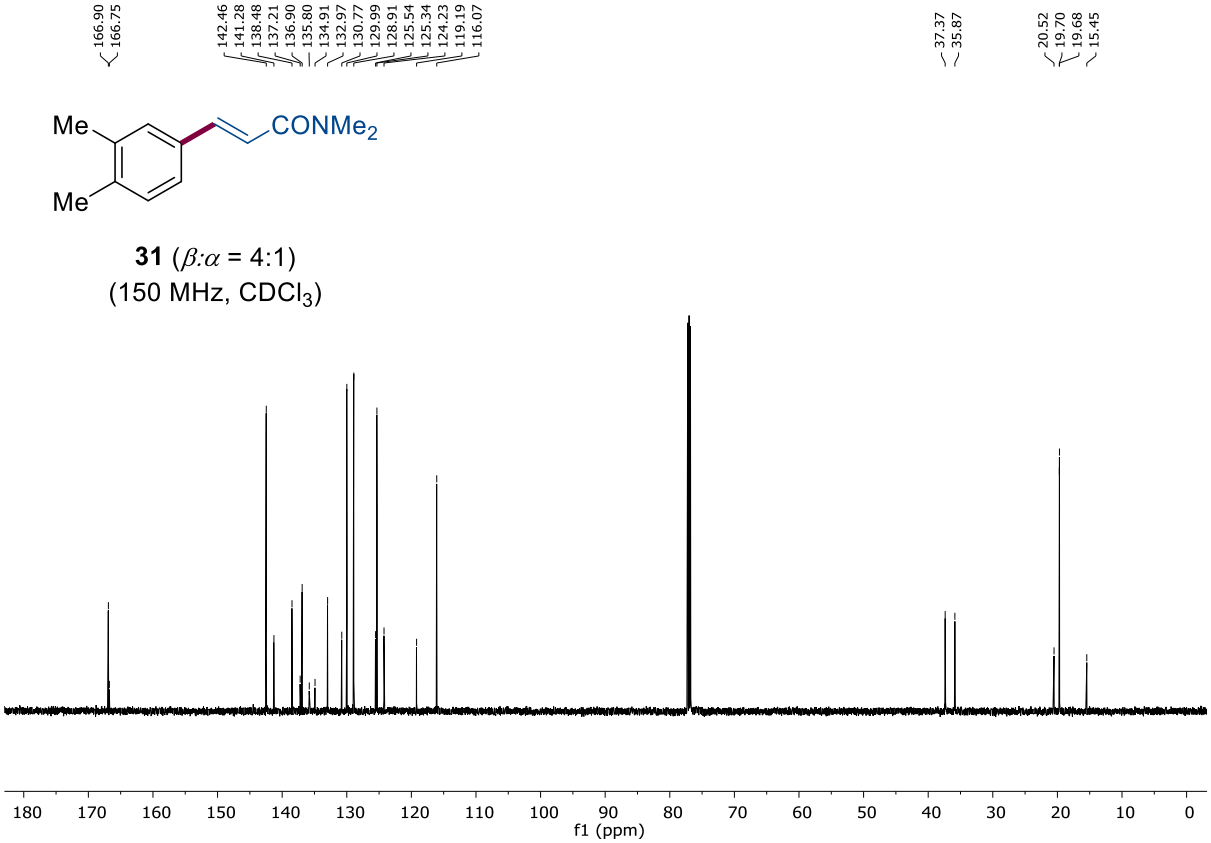

Me
Me
CO2t-Bu
30 (β:α = 8:1)
(600 MHz, CDCl3)
8.10
1.00
0.12
0.88
0.13
0.91
1.00
0.14
1.09
1.00
6.35
9.09
f1 (ppm)



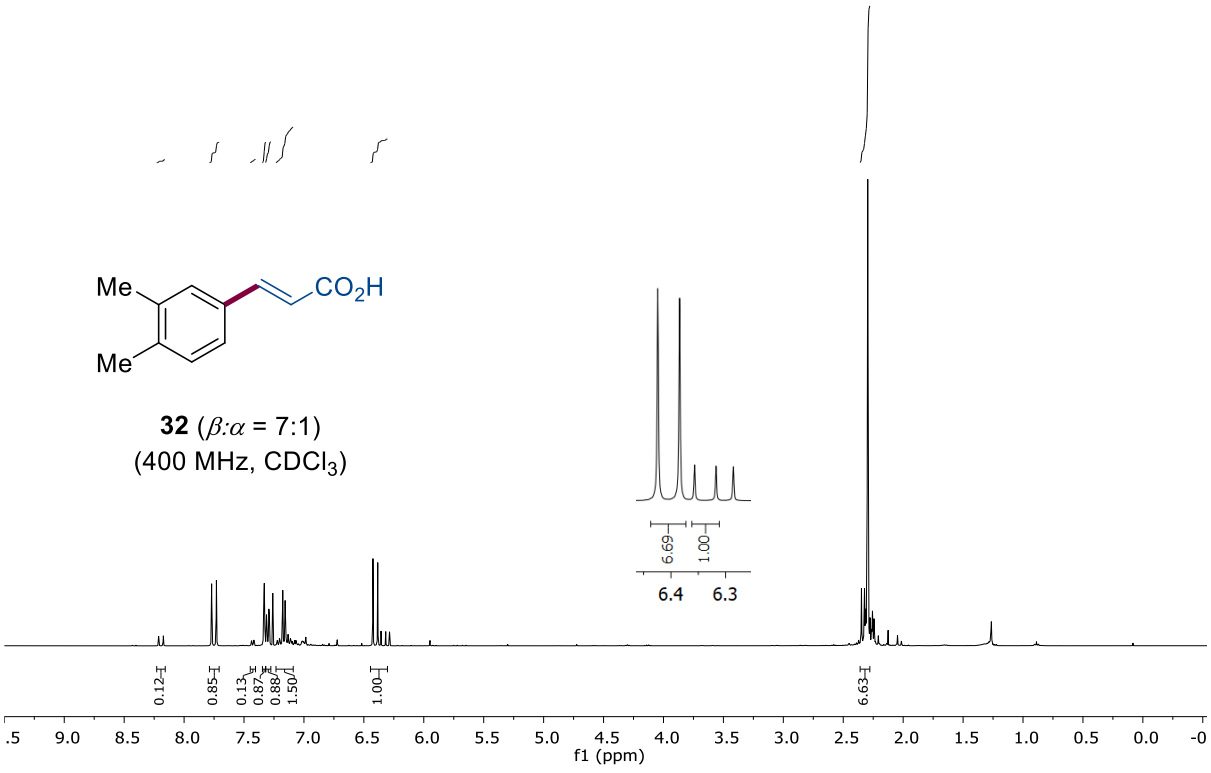
30 (β:α = 8:1)
(150 MHz, $CDCl_3$)



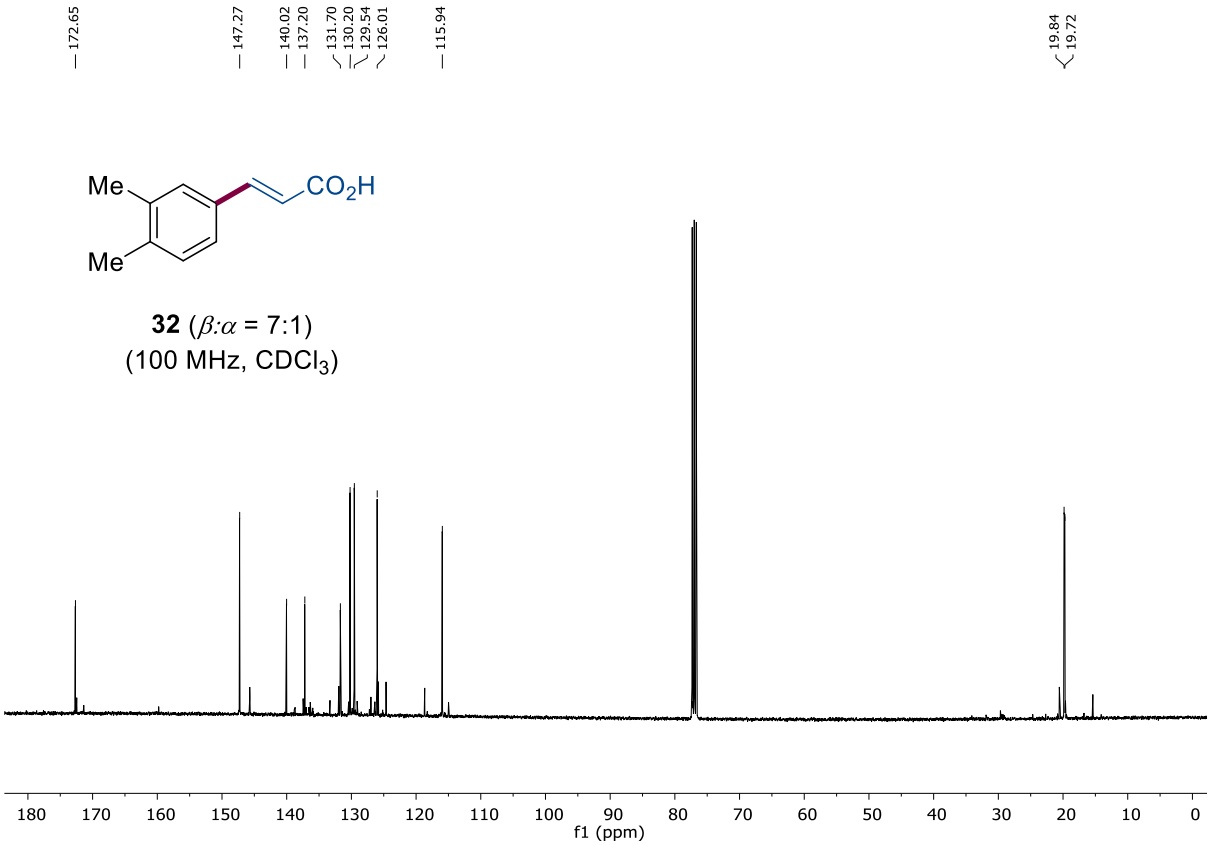
31 (β:α = 4:1)
(600 MHz, $CDCl_3$)

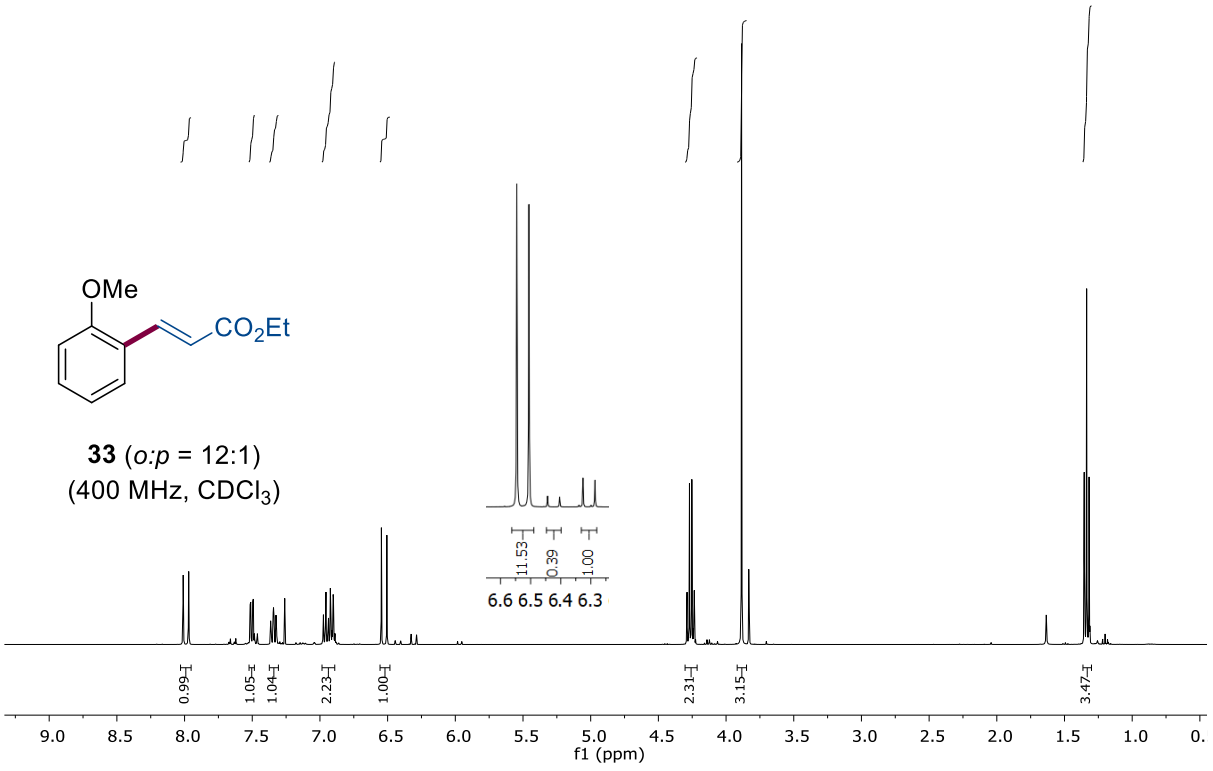


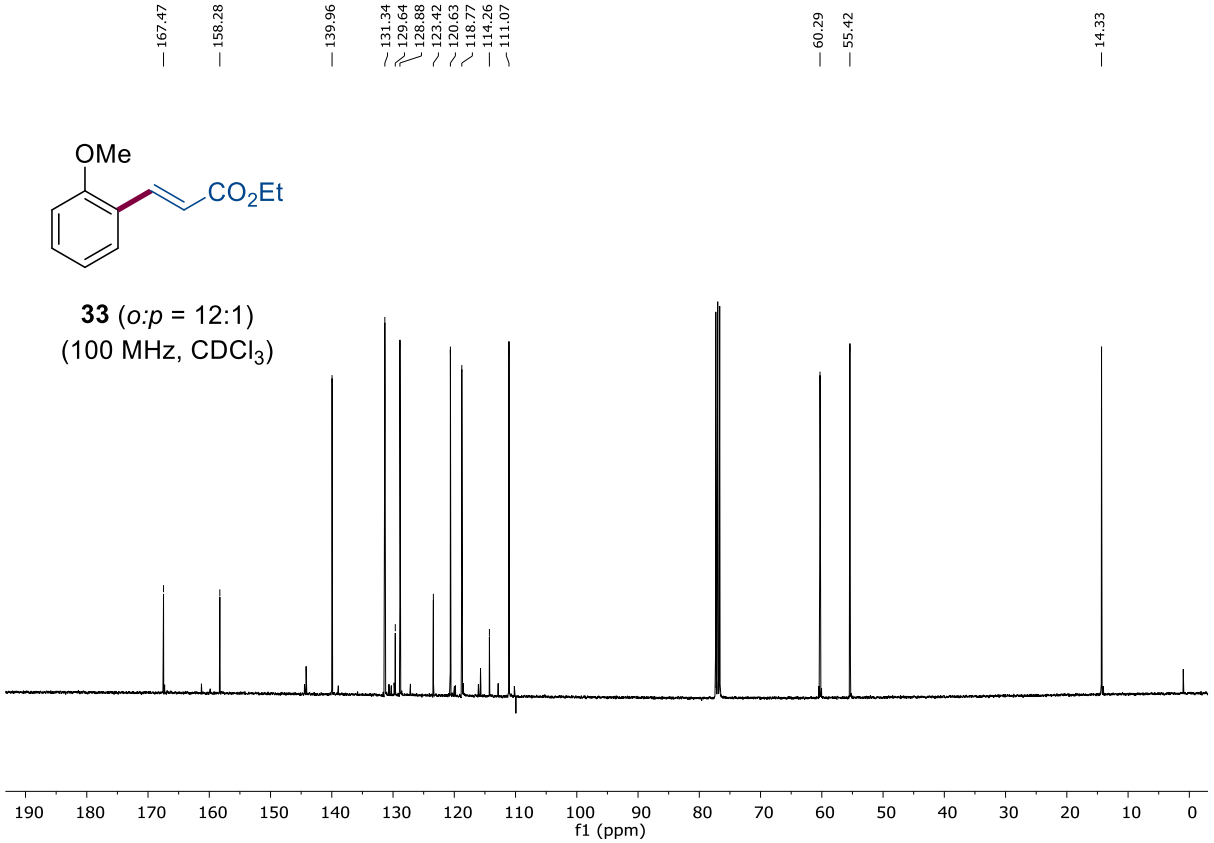
31 (β:α = 4:1)
(150 MHz, $CDCl_3$)

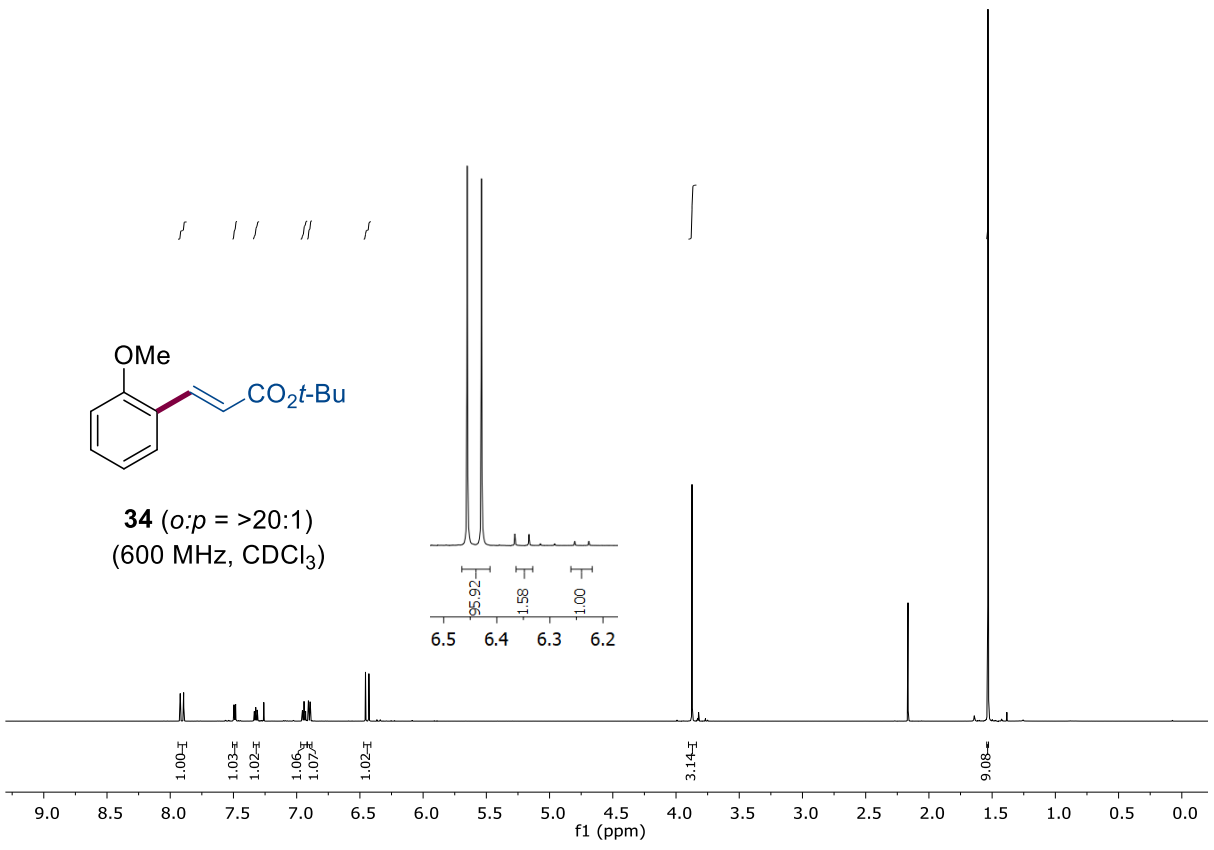


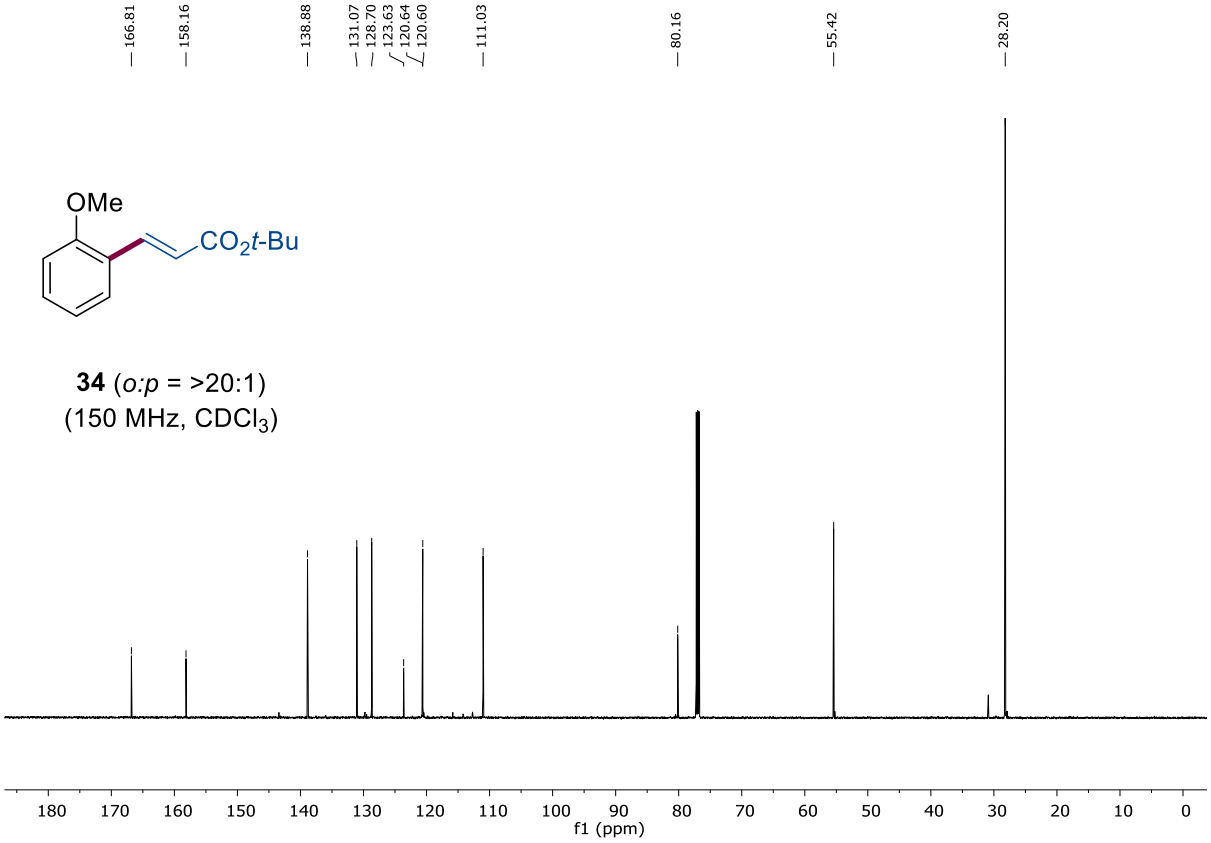
32 (β:α = 7:1)
(400 MHz, $CDCl_3$)

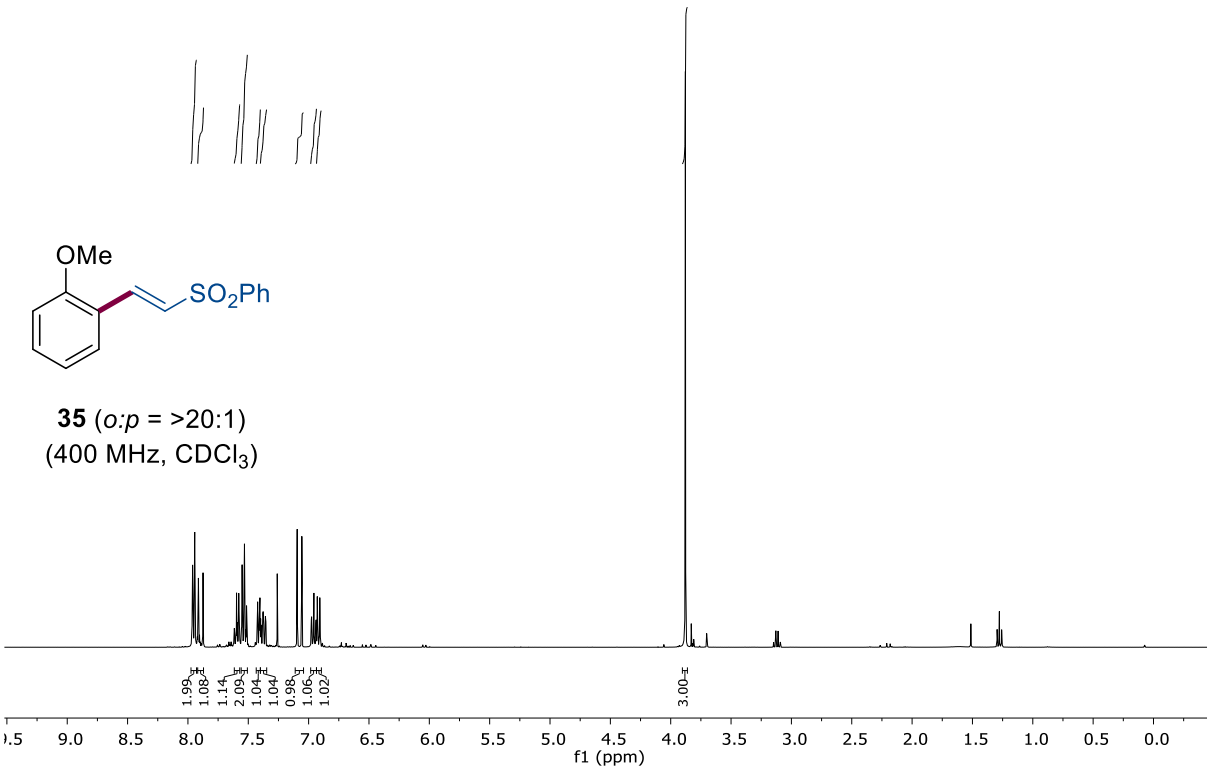

172.65
147.27
140.02
137.20
131.70
130.20
129.54
126.01
115.94
19.84
19.72
Me
Me
CO2H
32 (β:α = 7:1)
(100 MHz, CDCl3)
f1 (ppm)

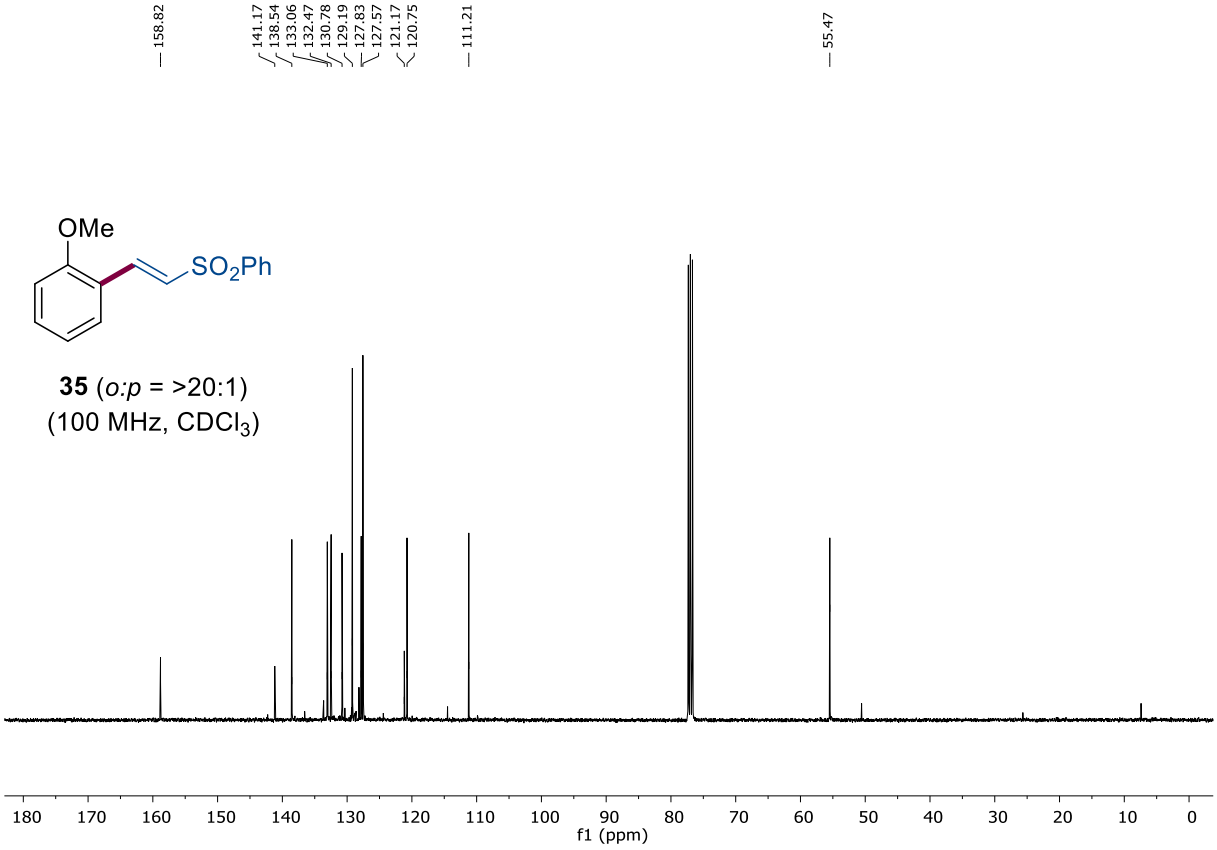

OMe
CO2Et
33 (o:p = 12:1)
(400 MHz, CDCl3)
11.53
0.39
1.00
6.6 6.5 6.4 6.3
0.99
1.05
1.04
2.23
1.00
2.31
3.15
3.47
f1 (ppm)

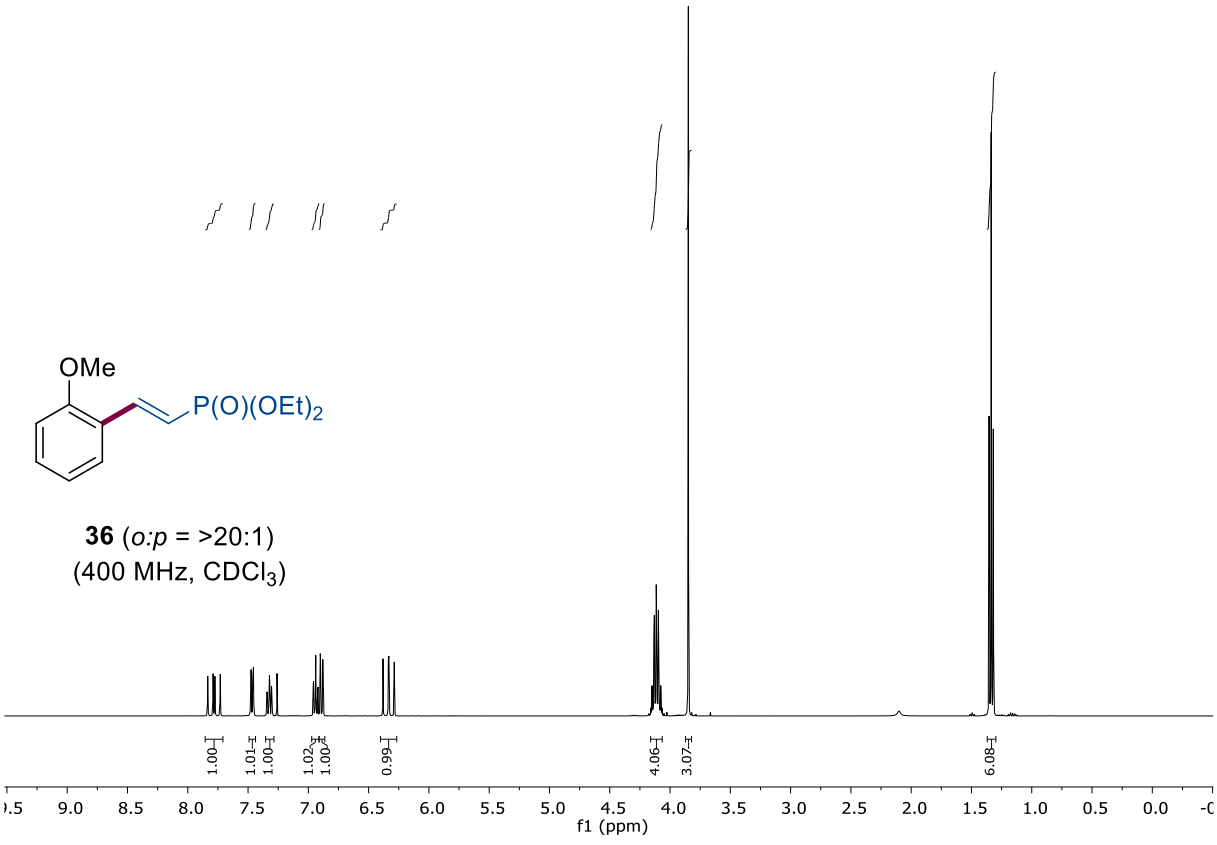

167.47
158.28
139.96
131.34
129.64
128.88
123.42
120.63
118.77
114.26
111.07
60.29
55.42
14.33
OMe
CO2Et
33 (o:p = 12:1)
(100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

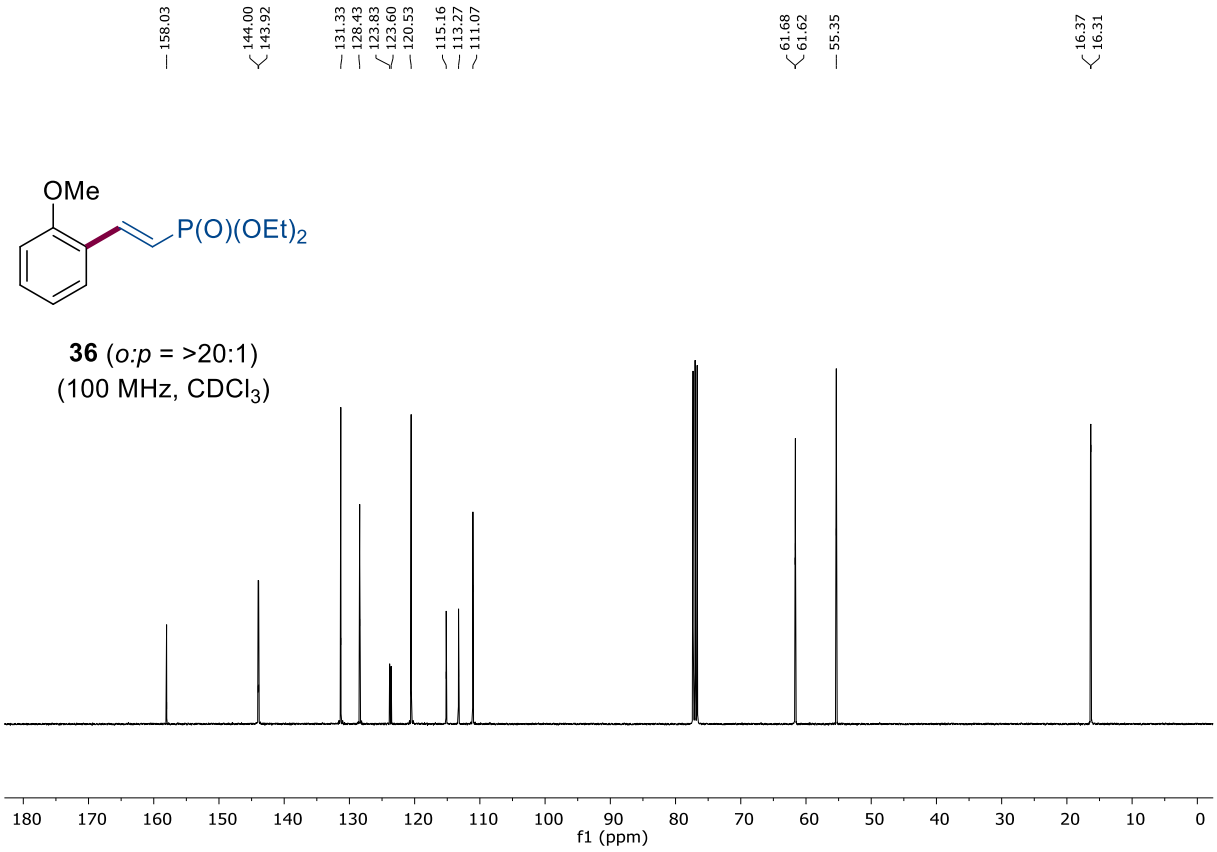

OMe
CO2t-Bu
34 (o:p = >20:1)
(600 MHz, CDCl3)
5.92
1.58
1.00
6.5 6.4 6.3 6.2
1.00
1.03
1.02
1.06
1.07
1.02
3.14
9.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

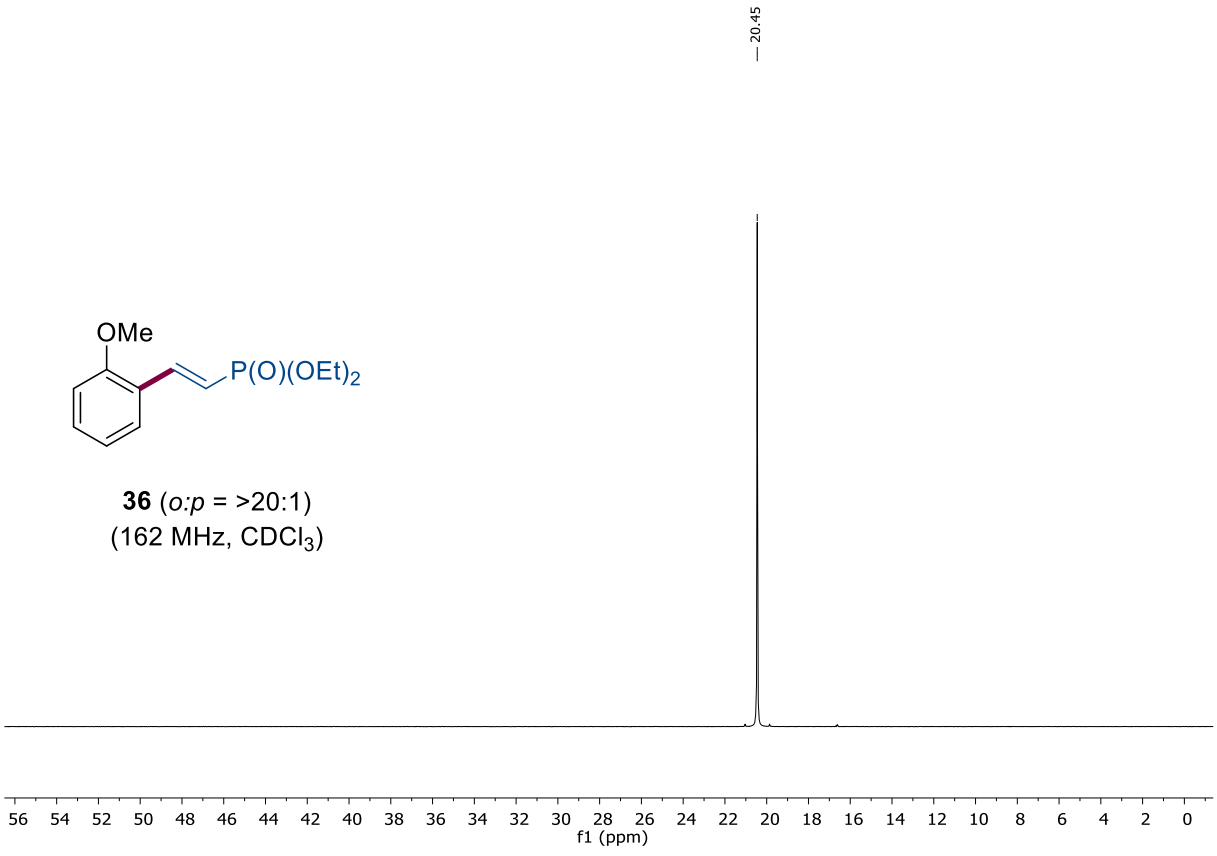

166.81
158.16
138.88
131.07
128.70
123.63
120.64
120.60
111.03
80.16
55.42
28.20
OMe
CO2t-Bu
34 (o:p = >20:1)
(150 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

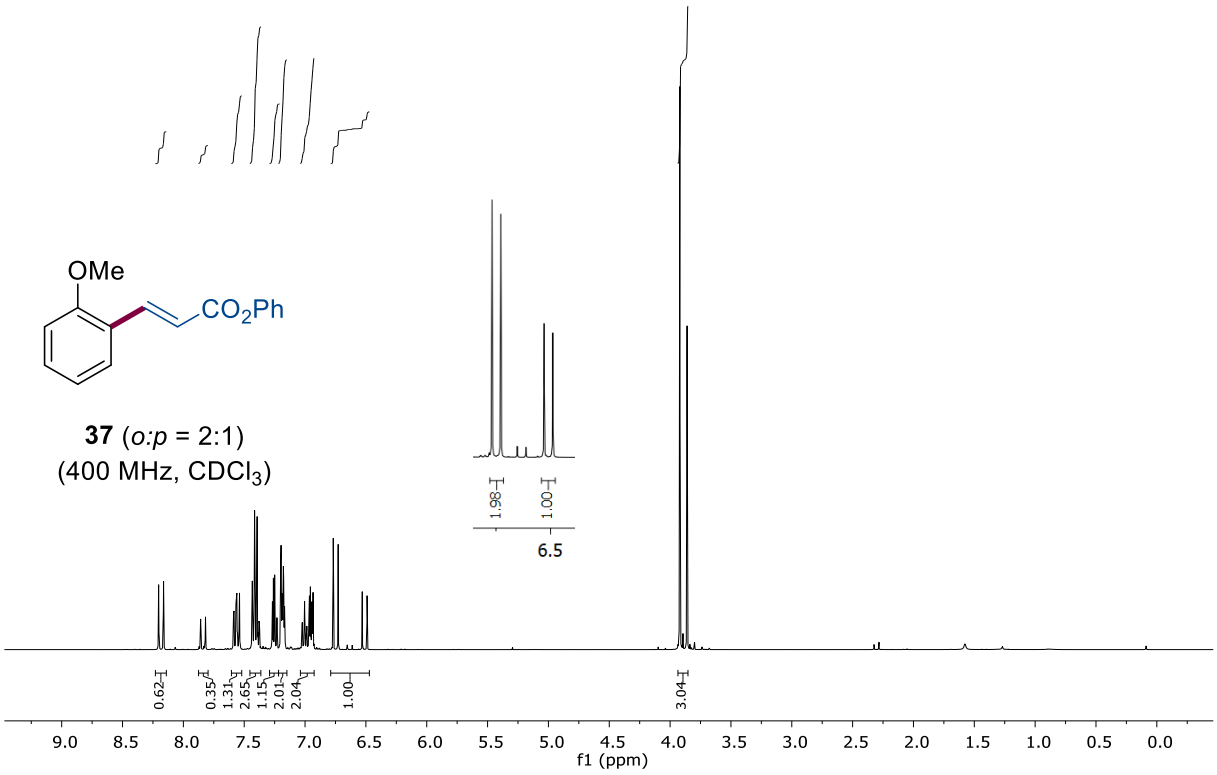

OMe
SO2Ph
35 (o:p = >20:1)
(400 MHz, CDCl3)
1.99
1.08
1.14
2.09
1.04
1.04
0.98
1.06
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

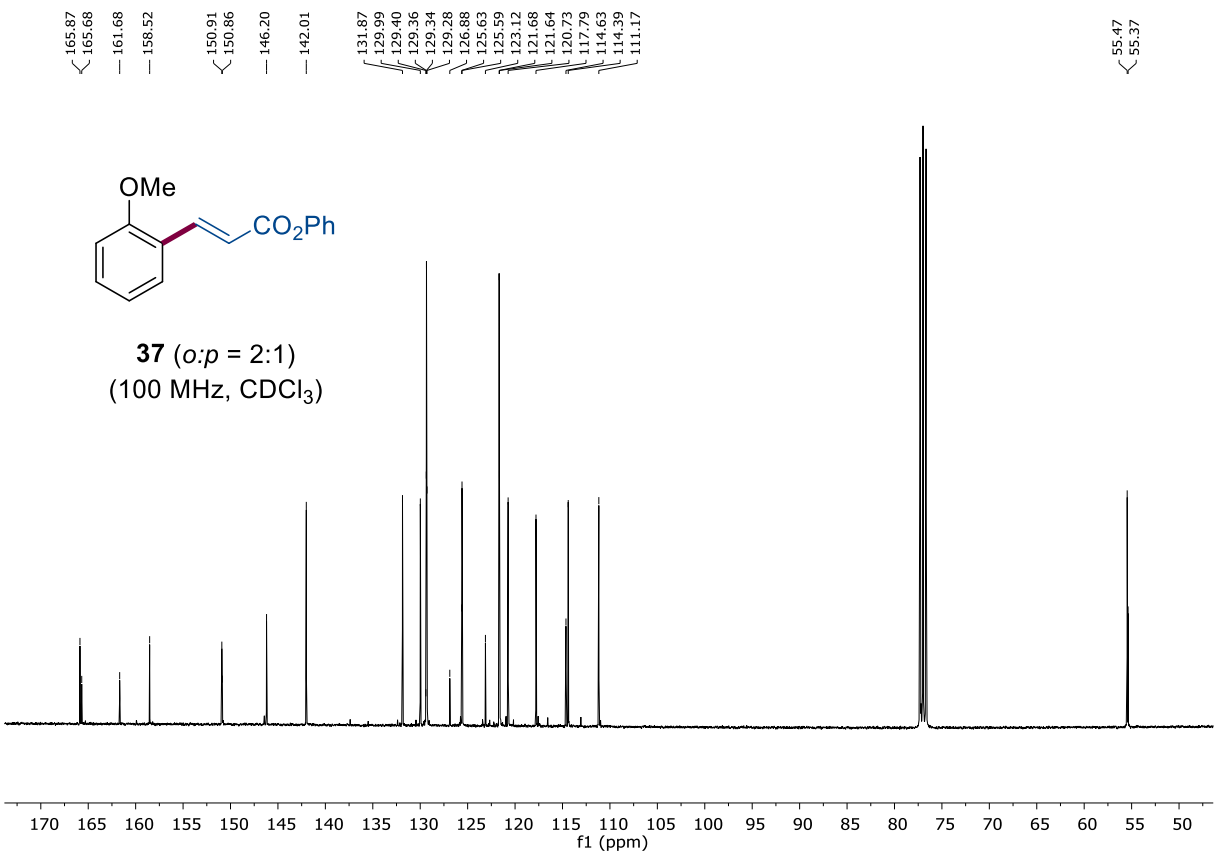

158.82
141.17
138.54
133.06
132.47
130.78
129.19
127.83
127.57
121.17
120.75
111.21
55.47
OMe
SO2Ph
35 (o:p = >20:1)
(100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

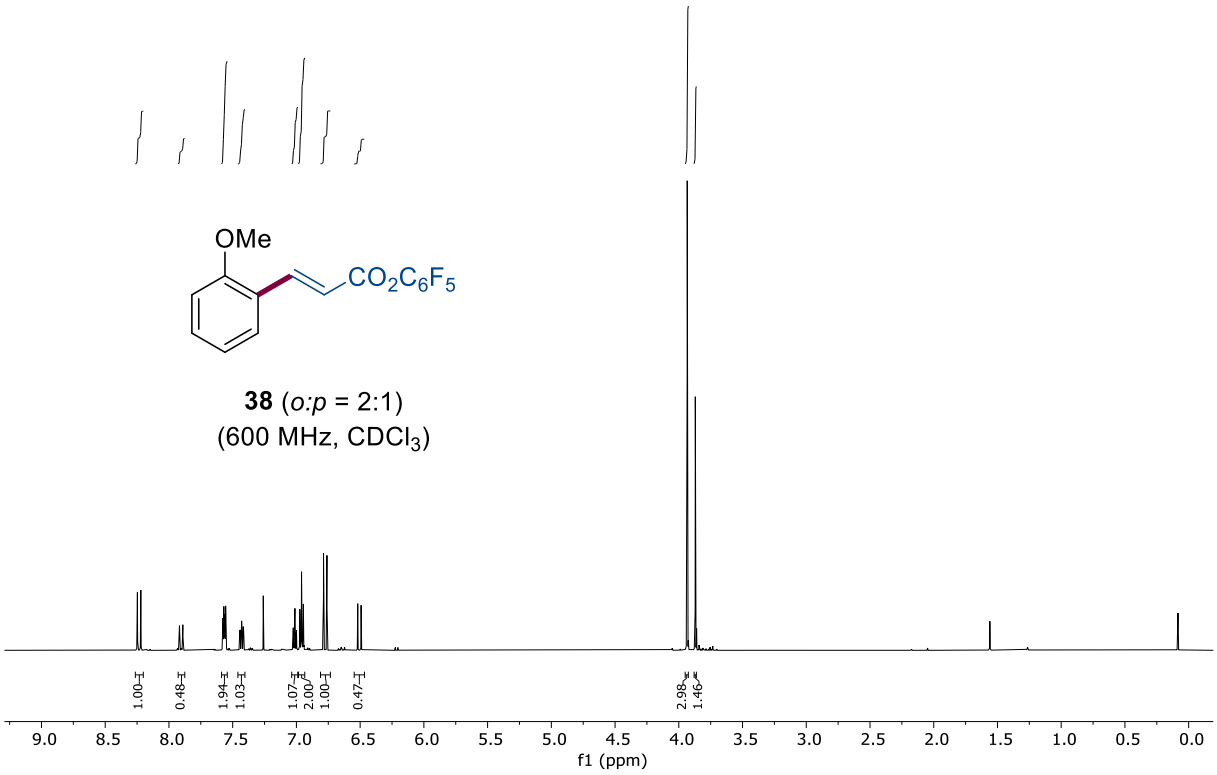

OMe
P(O)(OEt)2
36 (o:p = >20:1)
(400 MHz, CDCl3)
1.00
1.01
1.00
1.02
1.00
0.99
4.06
3.07
6.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.03
144.00
143.92
131.33
128.43
123.83
123.60
120.53
115.16
113.27
111.07
61.68
61.62
55.35
16.37
16.31
OMe
P(O)(OEt)2
36 (o:p = >20:1)
(100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

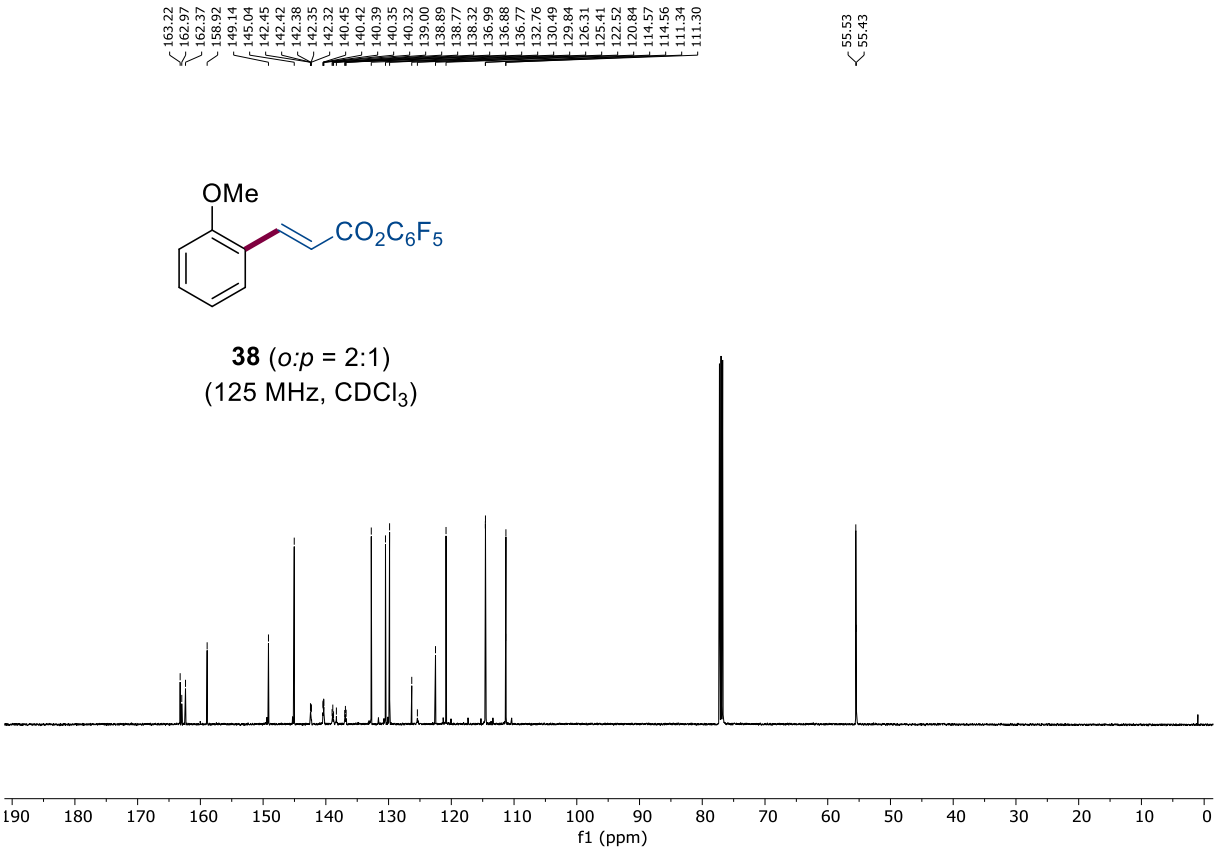

20.45
OMe
P(O)(OEt)2
36 (o:p = >20:1)
(162 MHz, CDCl3)
56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm)


OMe
CO2Ph
37 (o:p = 2:1)
(400 MHz, CDCl3)
1.98
1.00
6.5
0.62
0.35
1.31
2.65
1.15
2.01
2.04
1.00
3.04
f1 (ppm)

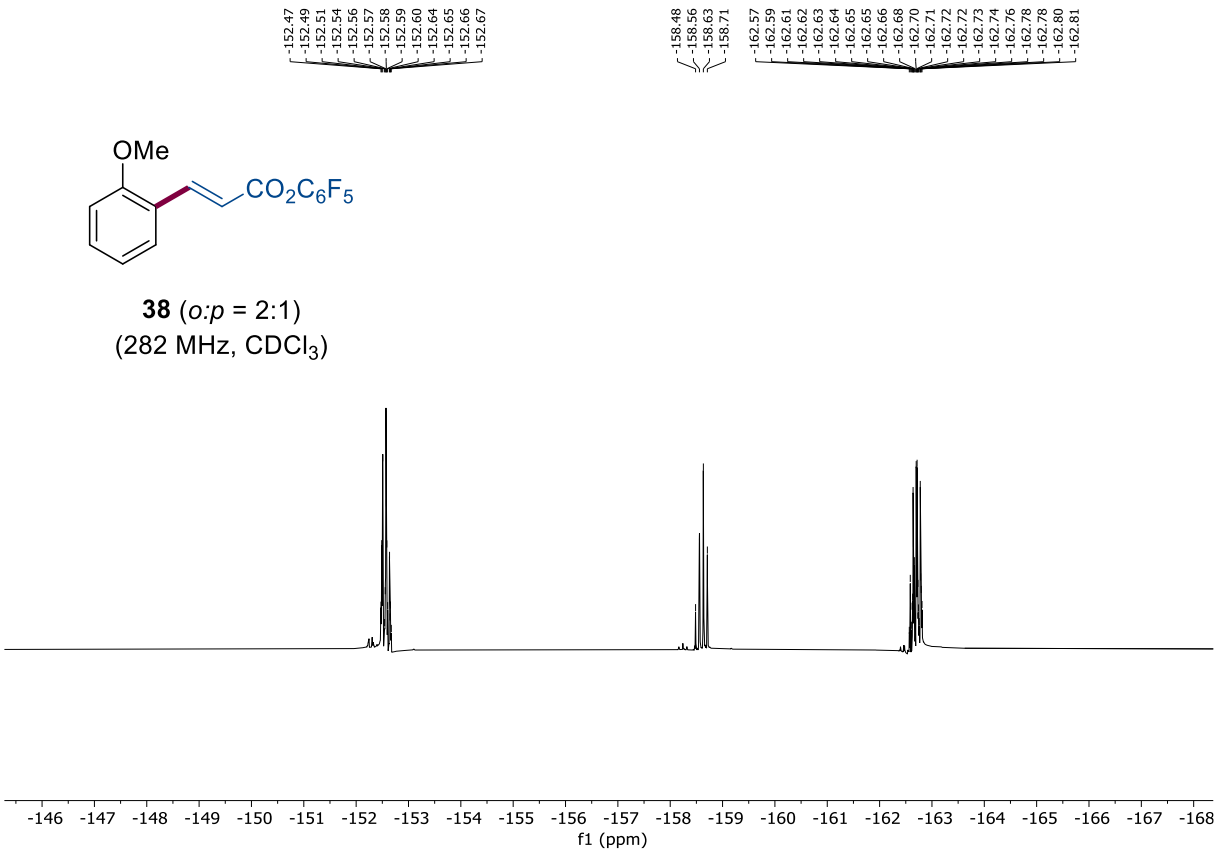

165.87
165.68
161.68
158.52
150.91
150.86
146.20
142.01
131.87
129.99
129.40
129.36
129.34
129.28
126.88
125.63
125.59
123.12
121.68
121.64
120.73
117.79
114.63
114.39
111.17
55.47
55.37
OMe
CO2Ph
37 (o:p = 2:1)
(100 MHz, CDCl3)
f1 (ppm)

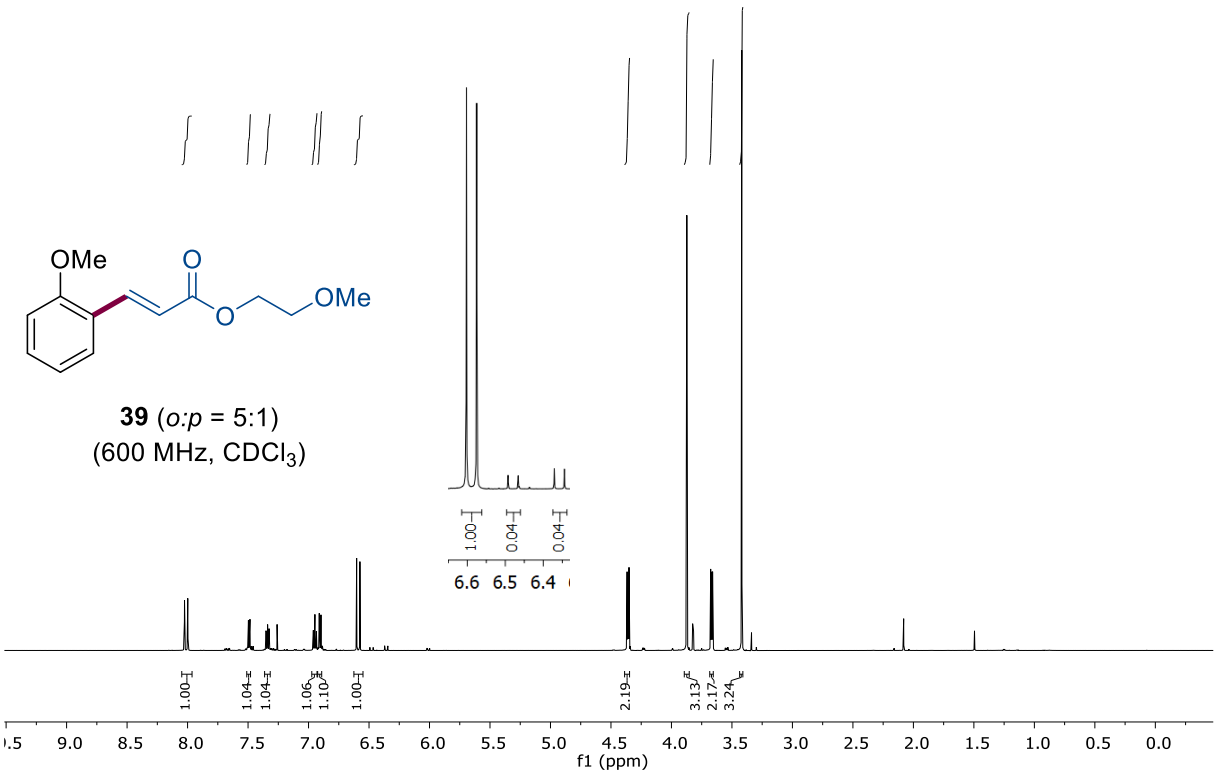


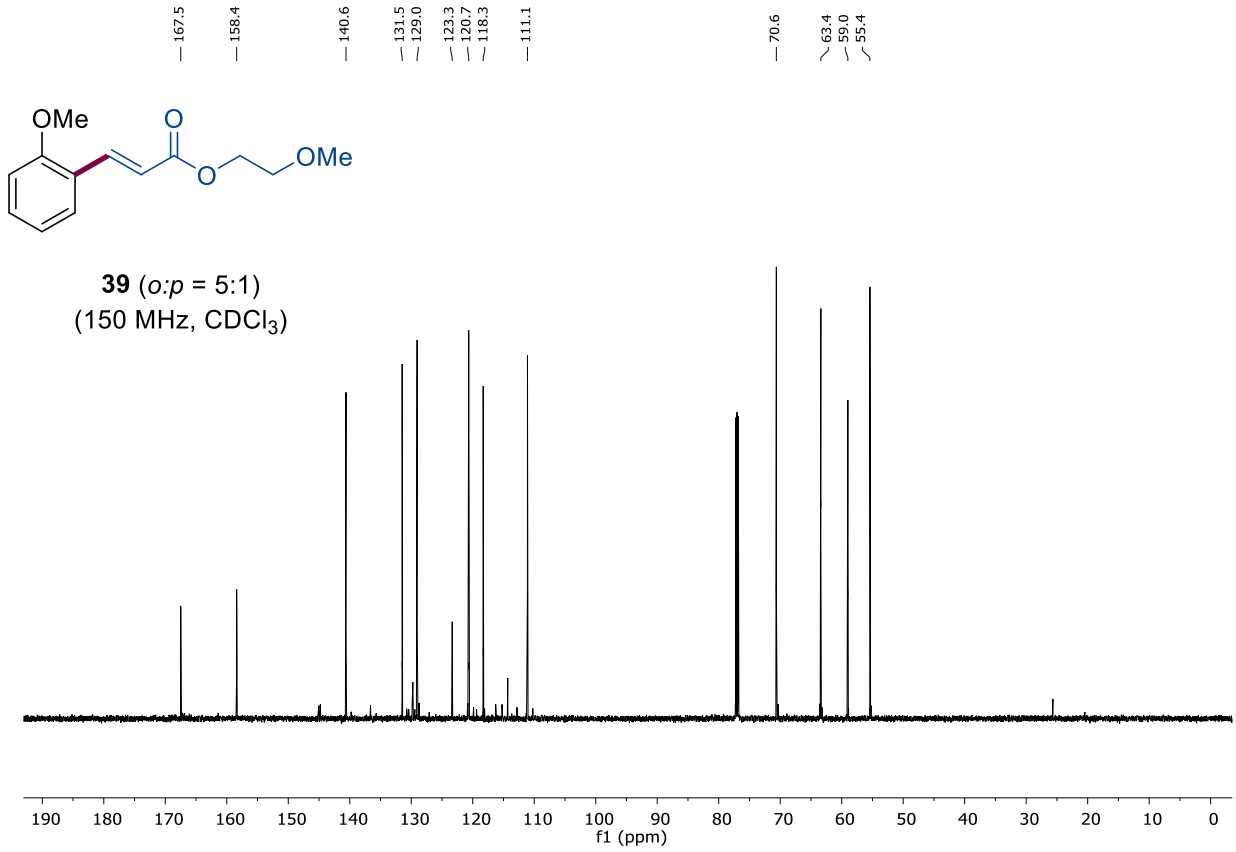
38 (*o*:*p* = 2:1)
(600 MHz, $CDCl_3$)

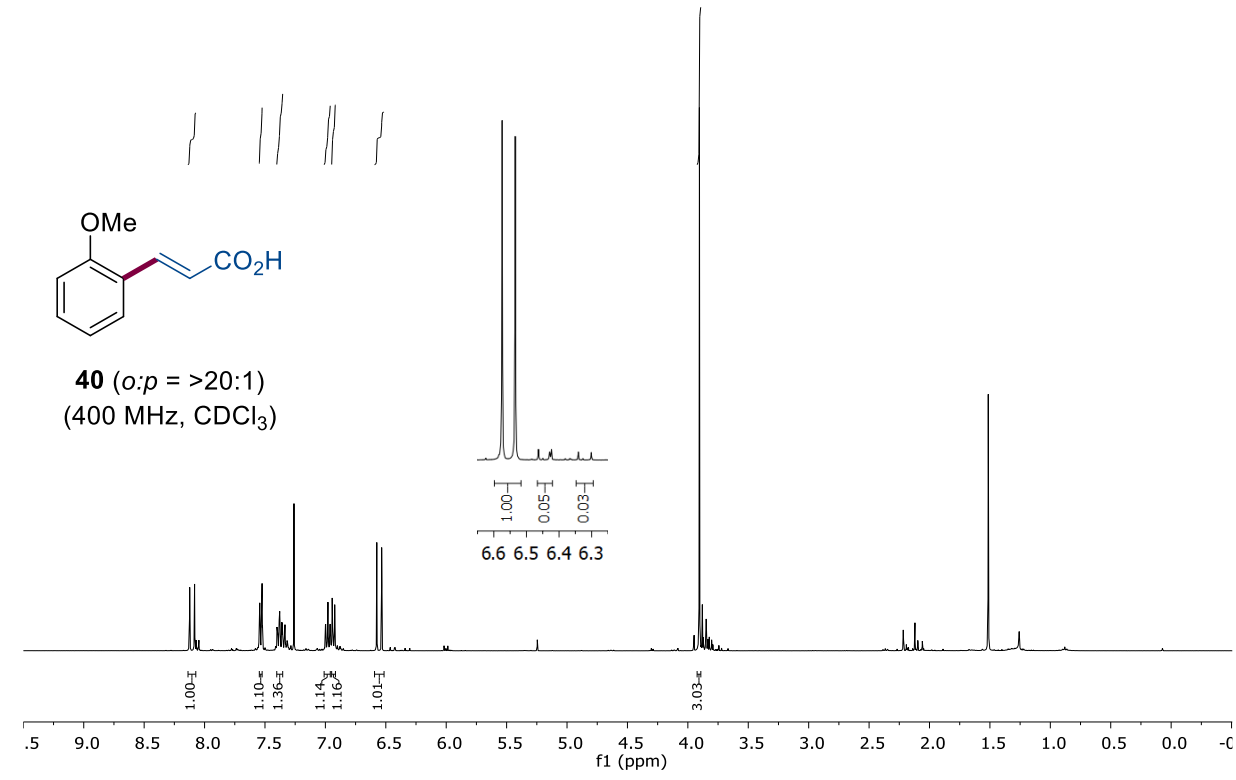


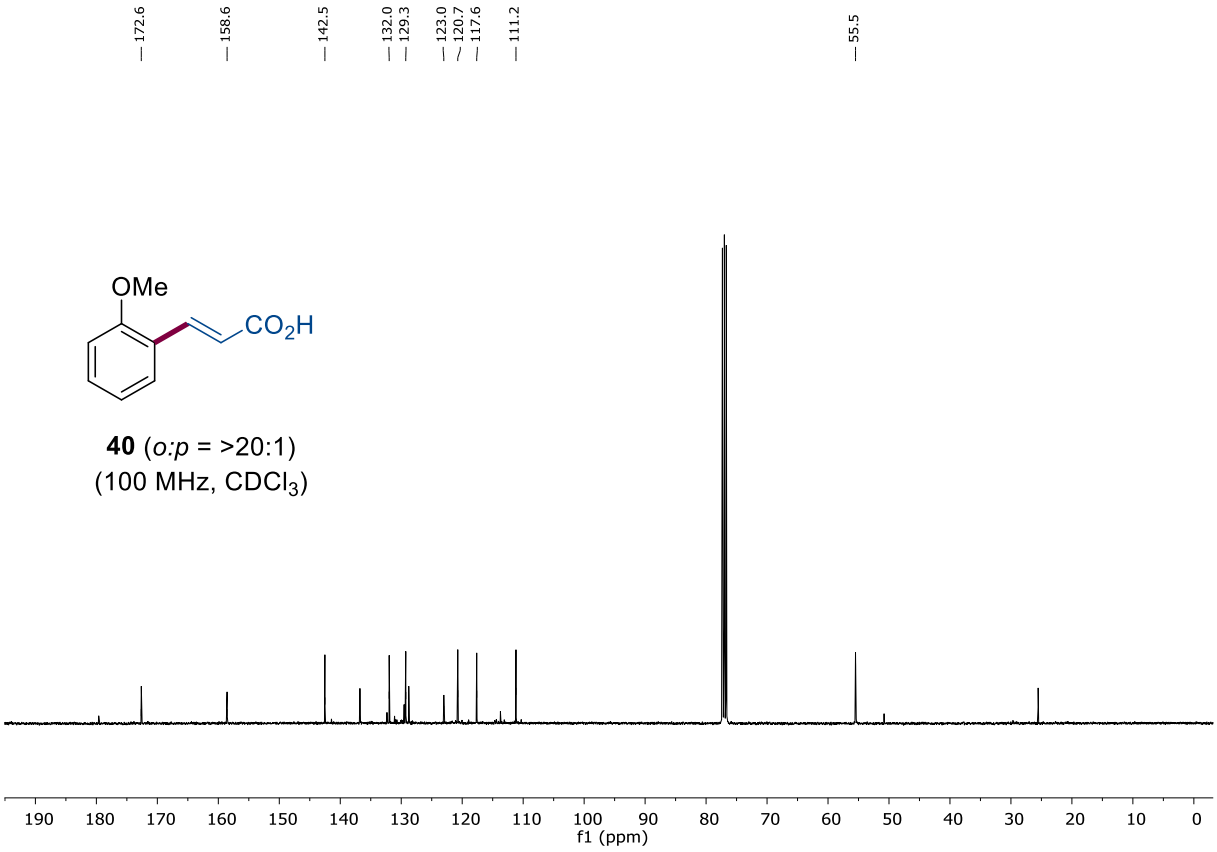
38 (*o*:*p* = 2:1)
(125 MHz, $CDCl_3$)

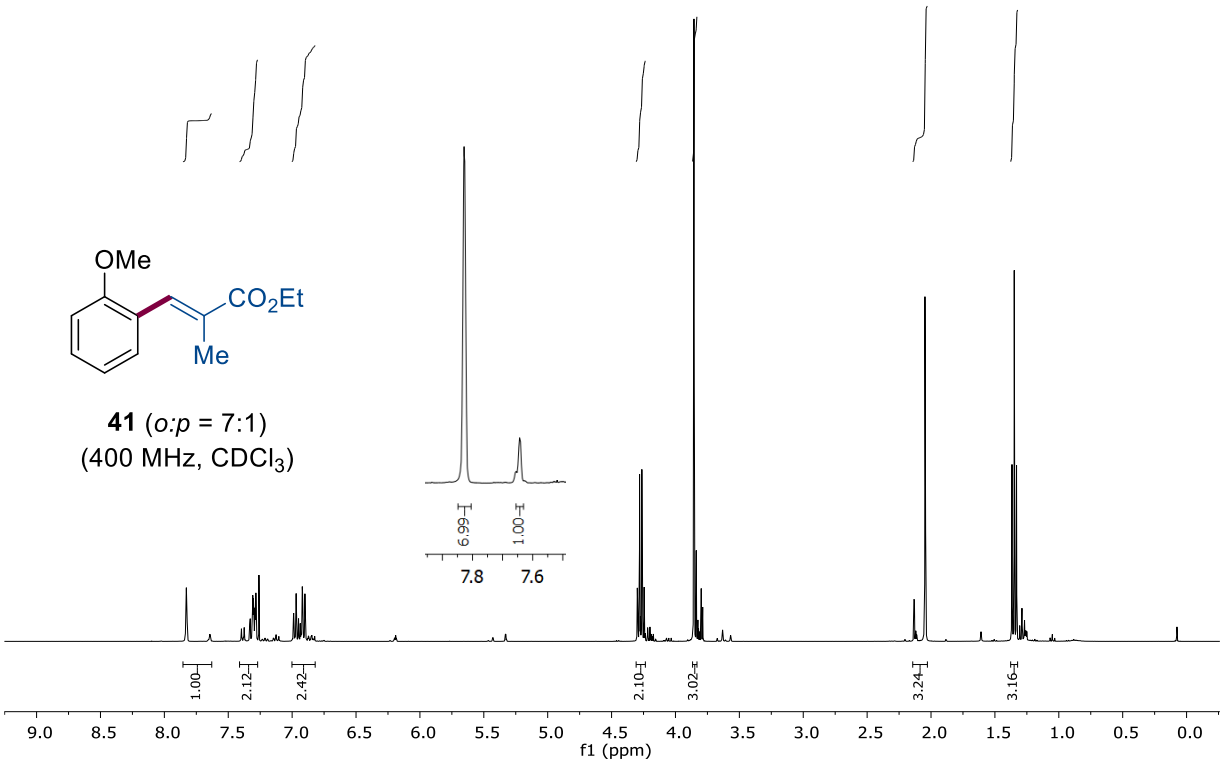

-152.47
-152.49
-152.51
-152.54
-152.56
-152.57
-152.58
-152.59
-152.60
-152.64
-152.65
-152.66
-152.67
-158.48
-158.56
-158.63
-158.71
-162.57
-162.59
-162.61
-162.62
-162.63
-162.64
-162.65
-162.65
-162.66
-162.68
-162.70
-162.71
-162.72
-162.72
-162.73
-162.74
-162.76
-162.78
-162.78
-162.80
-162.81
OMe
CO2C6F5
38 (o:p = 2:1)
(282 MHz, CDCl3)
-146 -147 -148 -149 -150 -151 -152 -153 -154 -155 -156 -157 -158 -159 -160 -161 -162 -163 -164 -165 -166 -167 -168
f1 (ppm)

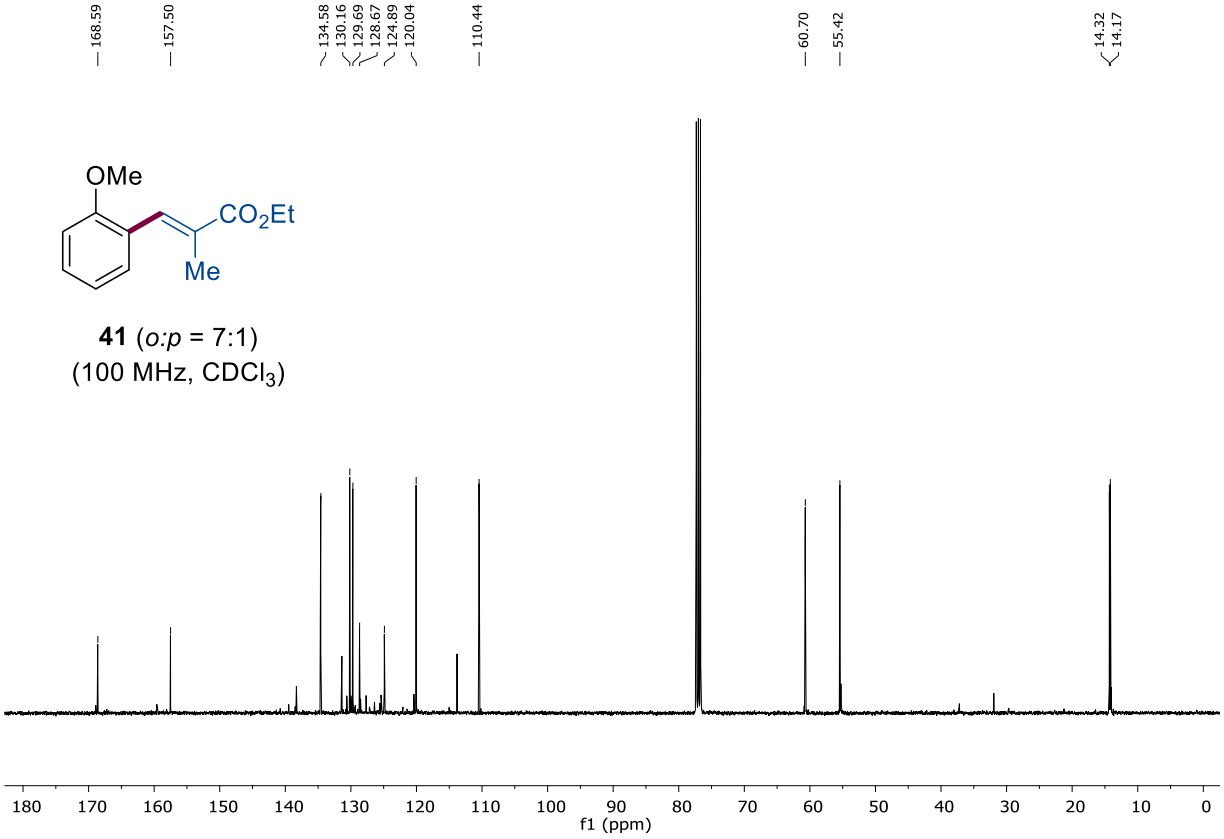

OMe
O
O
OMe
39 (o:p = 5:1)
(600 MHz, CDCl3)
1.00
0.04
0.04
6.6 6.5 6.4
1.00
1.04
1.04
1.06
1.10
1.00
2.19
3.13
2.17
3.24
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

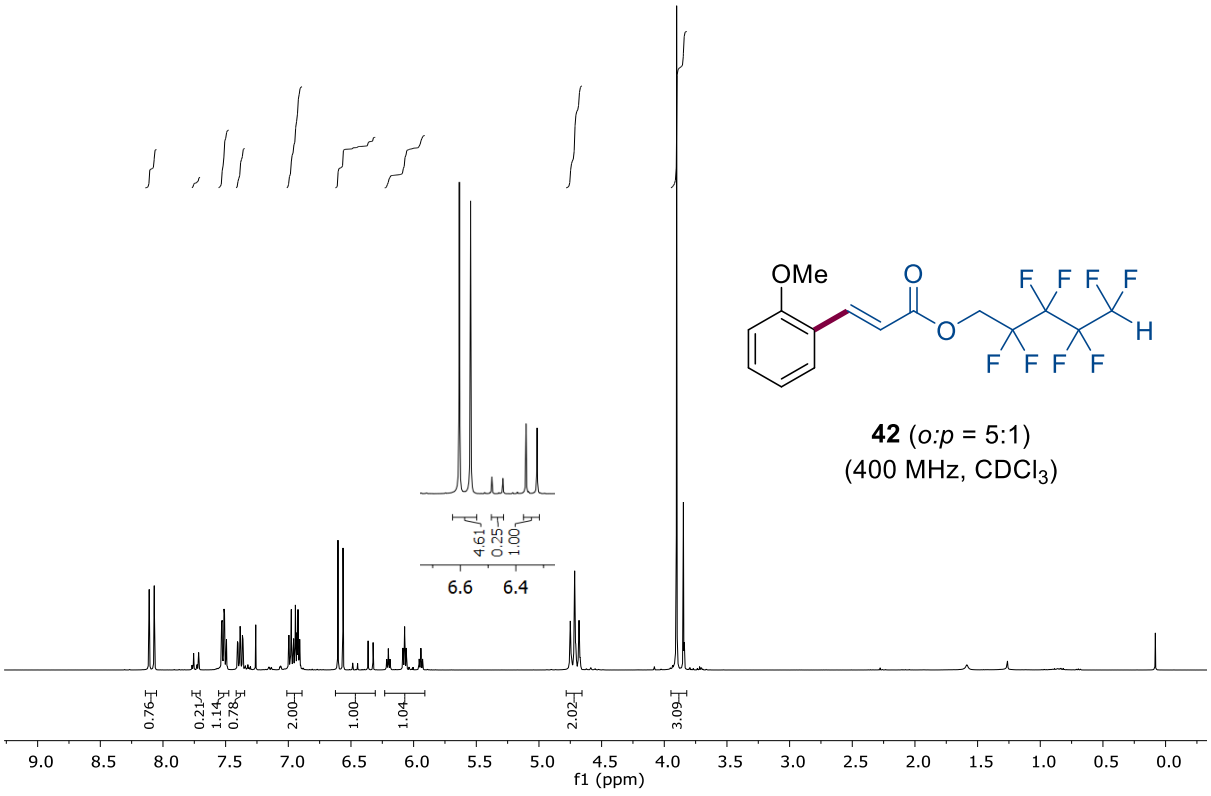

167.5
158.4
140.6
131.5
129.0
123.3
120.7
118.3
111.1
70.6
63.4
59.0
55.4
OMe
O
O
OMe
39 (o:p = 5:1)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

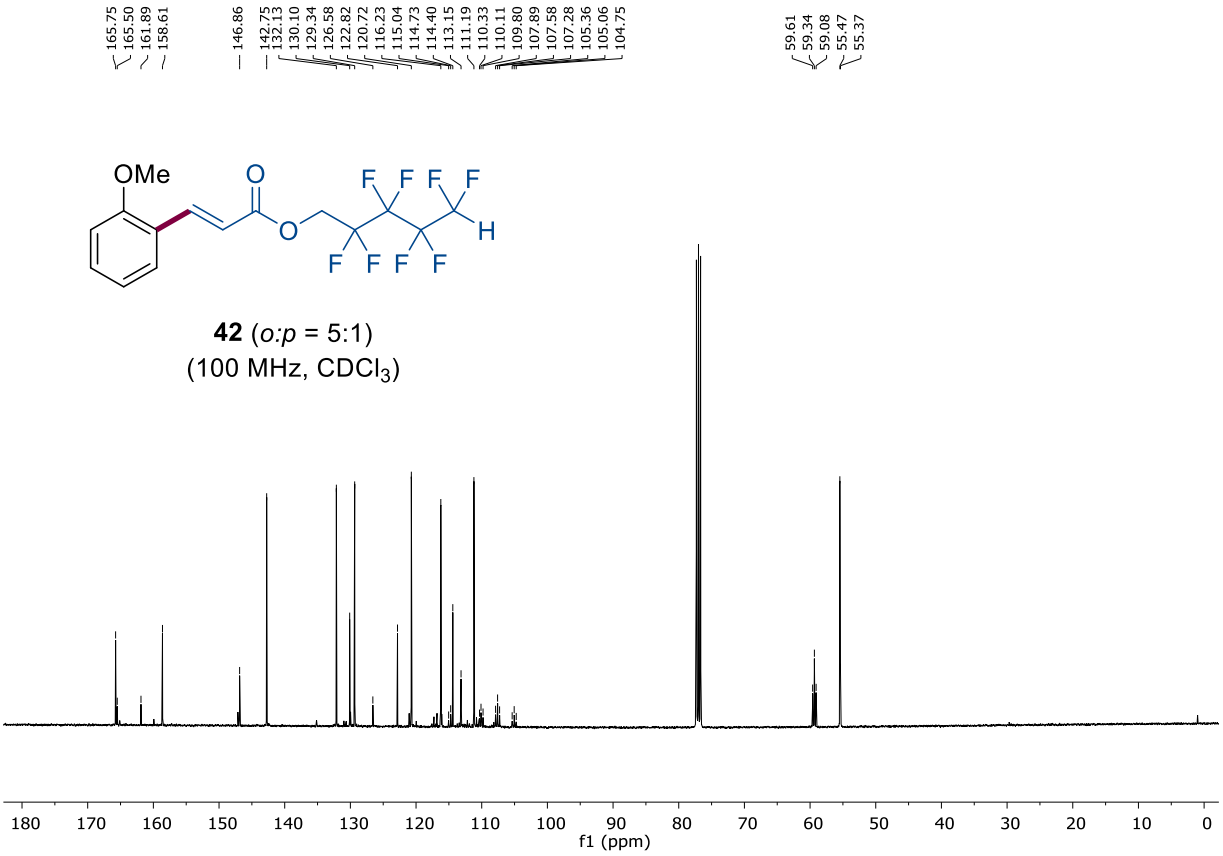

OMe
CO2H
40 (o:p = >20:1)
(400 MHz, CDCl3)
1.00
0.05
0.03
6.6 6.5 6.4 6.3
1.00
1.10
1.36
1.14
1.16
1.01
3.03
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.6
158.6
142.5
132.0
129.3
123.0
120.7
117.6
111.2
55.5
OMe
CO2H
40 (o:p = >20:1)
(100 MHz, CDCl3)
f1 (ppm)

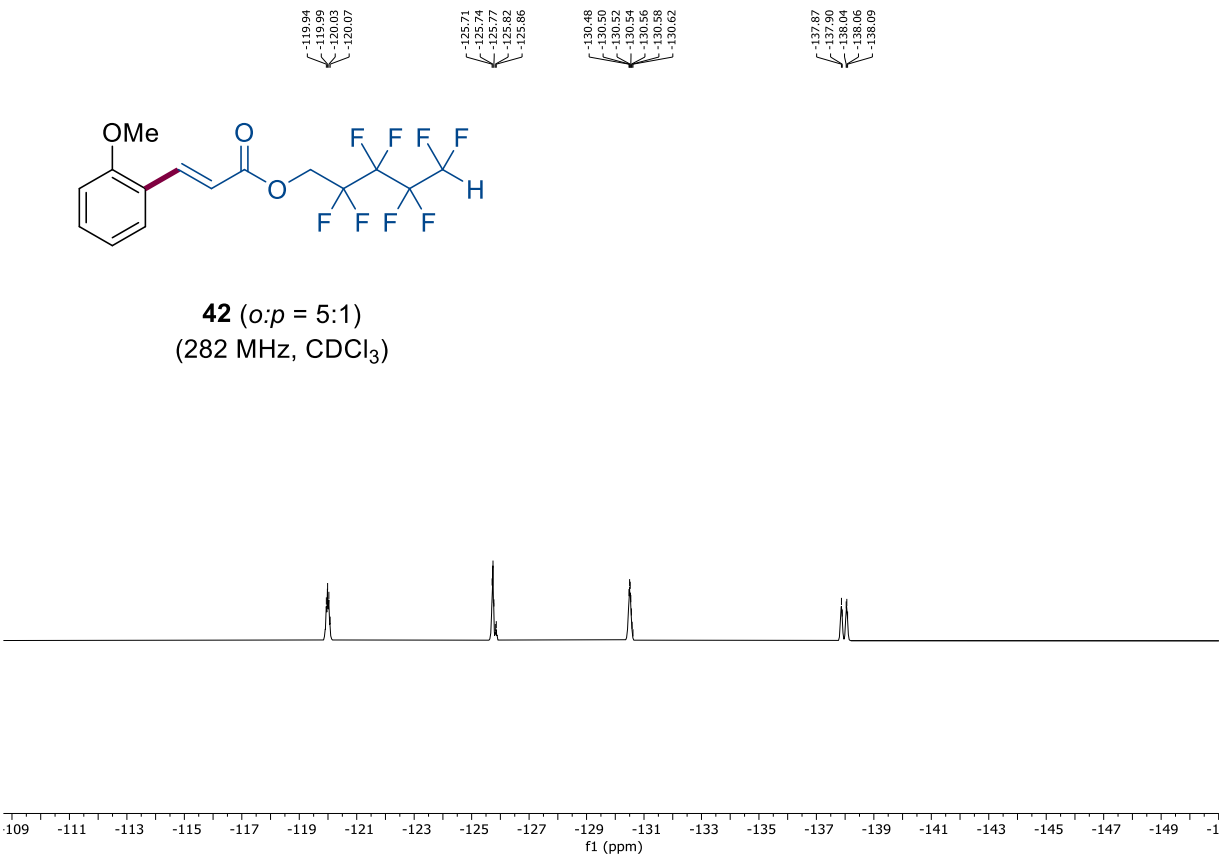

OMe
CO2Et
Me
41 (o:p = 7:1)
(400 MHz, CDCl3)
6.99
1.00
7.8
7.6
1.00
2.12
2.42
2.10
3.02
3.24
3.16
f1 (ppm)


168.59
157.50
134.58
130.16
129.69
128.67
124.89
120.04
110.44
60.70
55.42
14.32
14.17
OMe
CO2Et
Me
41 (o:p = 7:1)
(100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

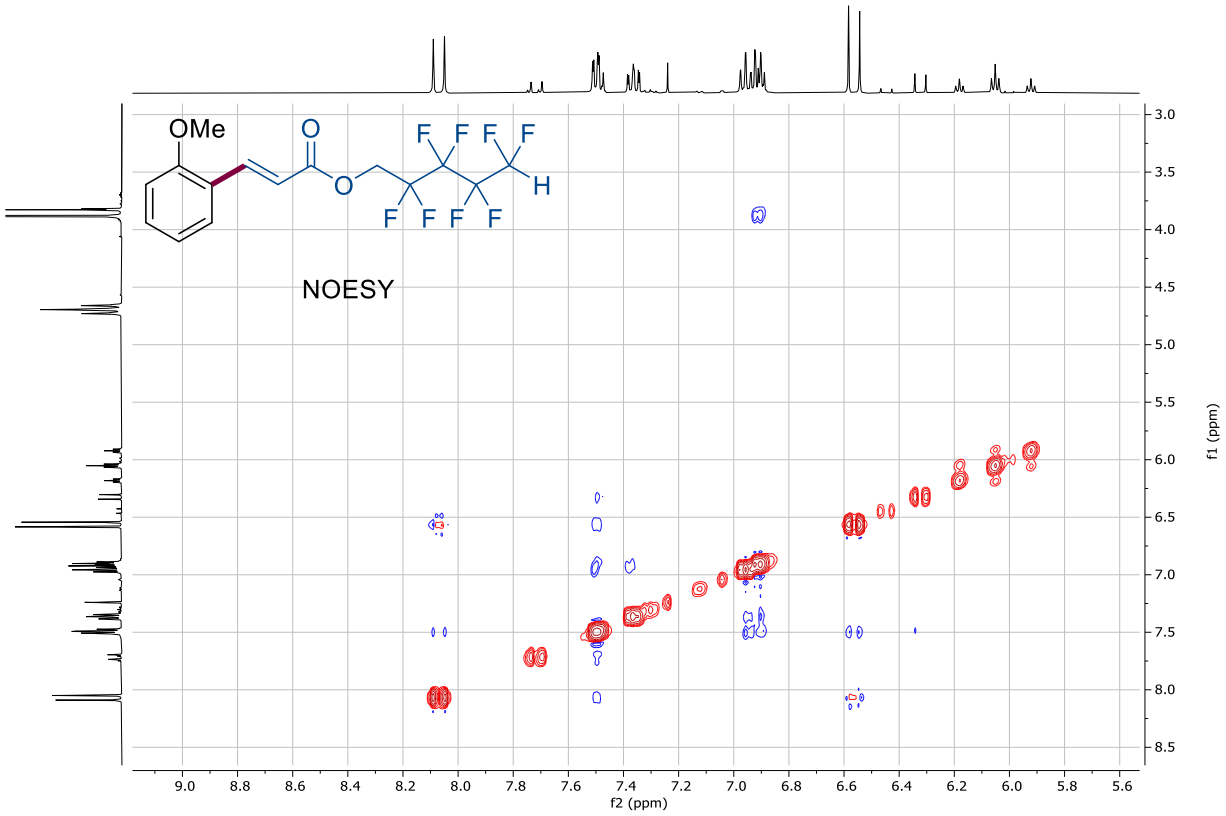

OMe
O
O
F F F F
F F F F
H
42 (o:p = 5:1)
(400 MHz, CDCl3)
4.61
0.25
1.00
6.6
6.4
0.76
0.21
1.14
0.78
2.00
1.00
1.04
2.02
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

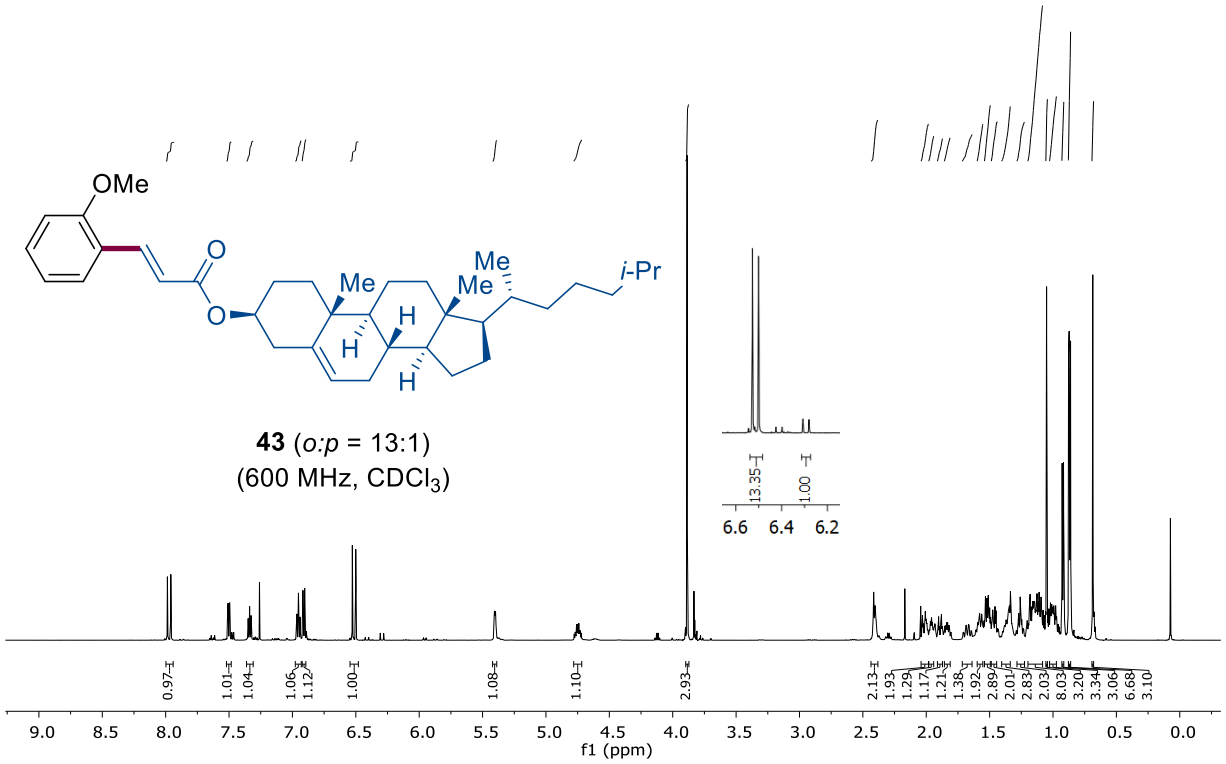


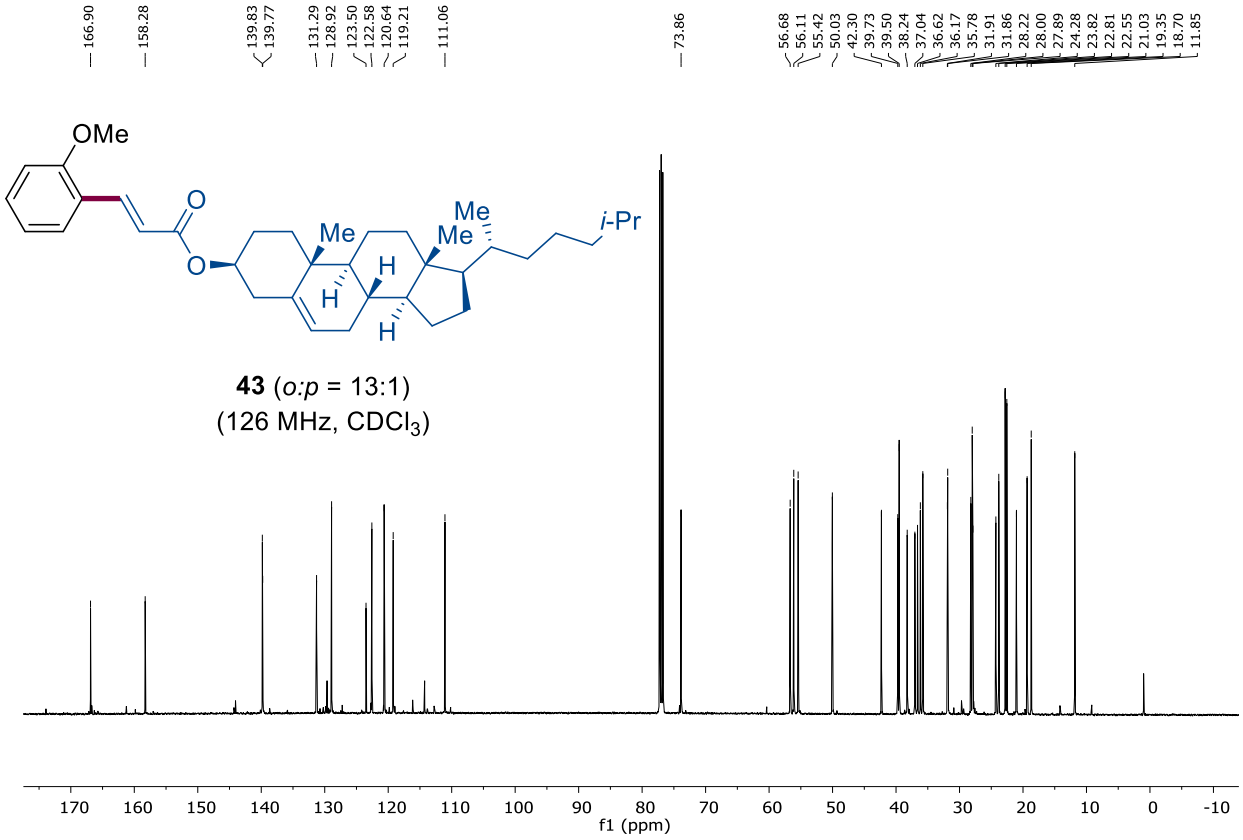
42 (*o:p* = 5:1)
(100 MHz, $CDCl_3$)

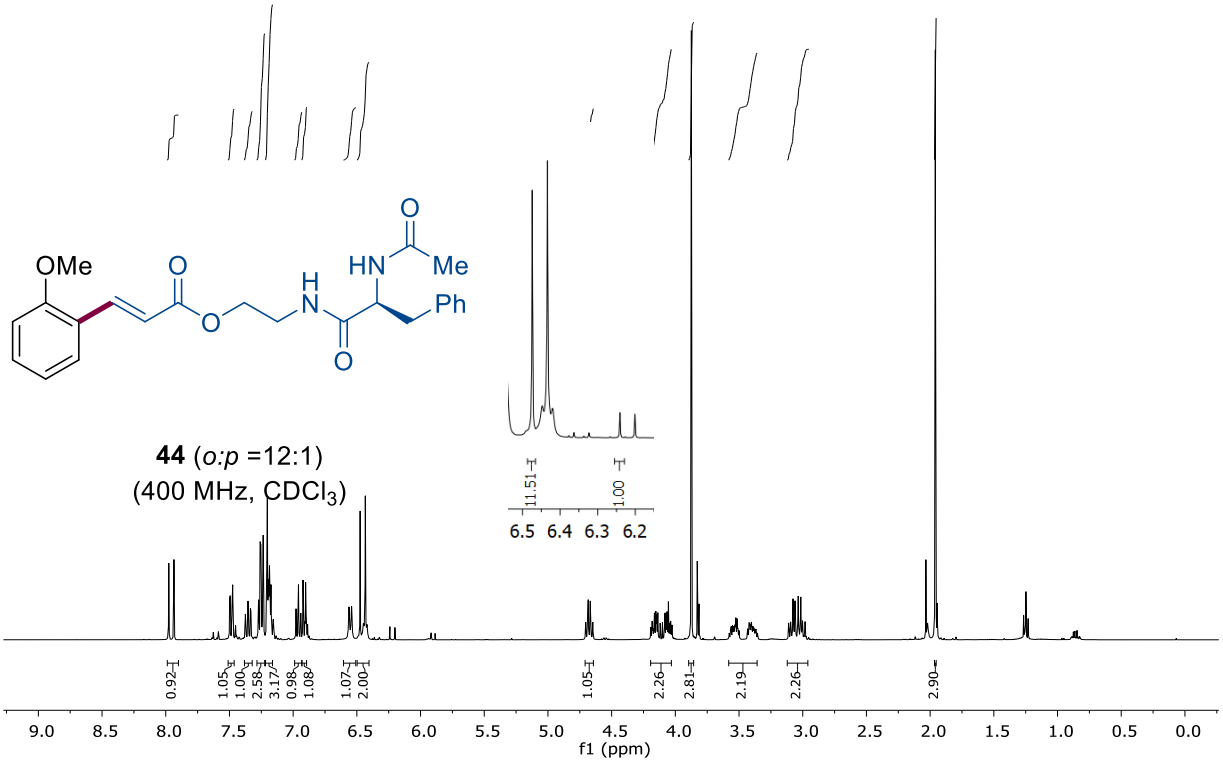


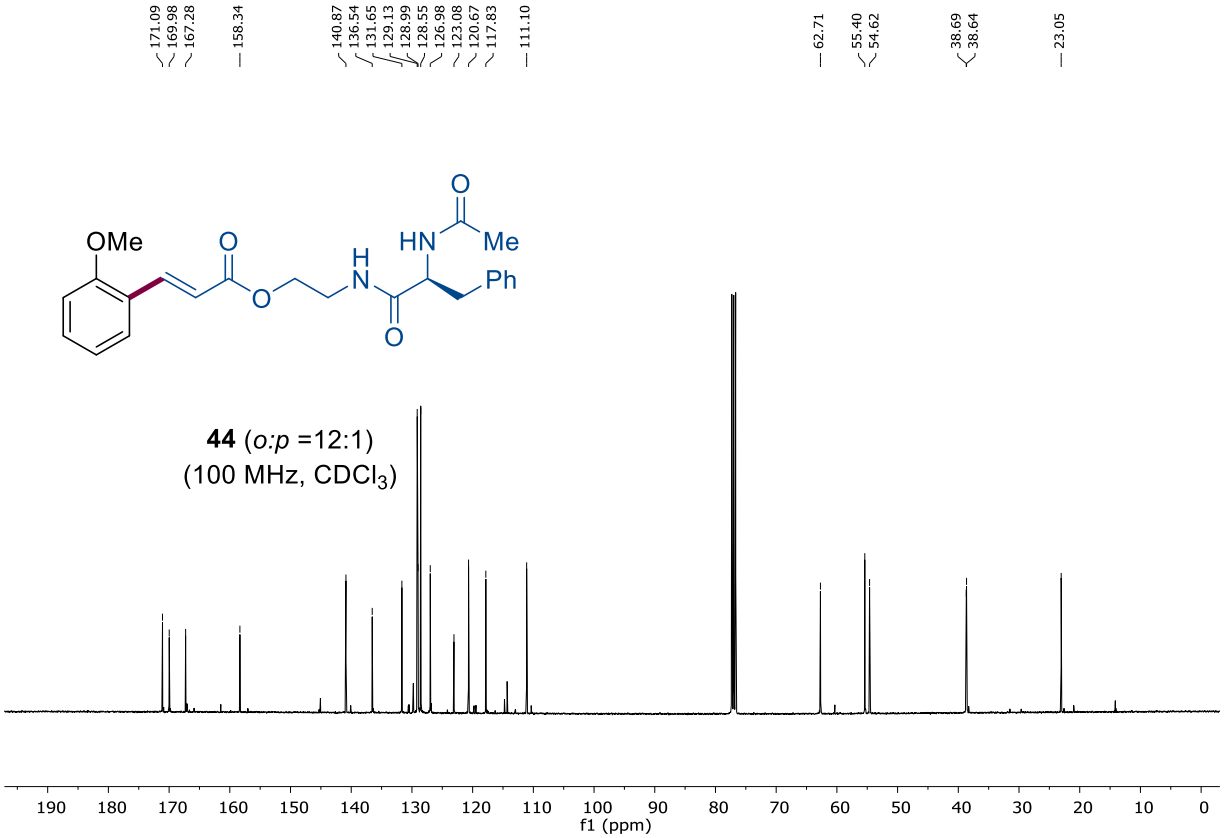
42 (*o:p* = 5:1)
(282 MHz, $CDCl_3$)

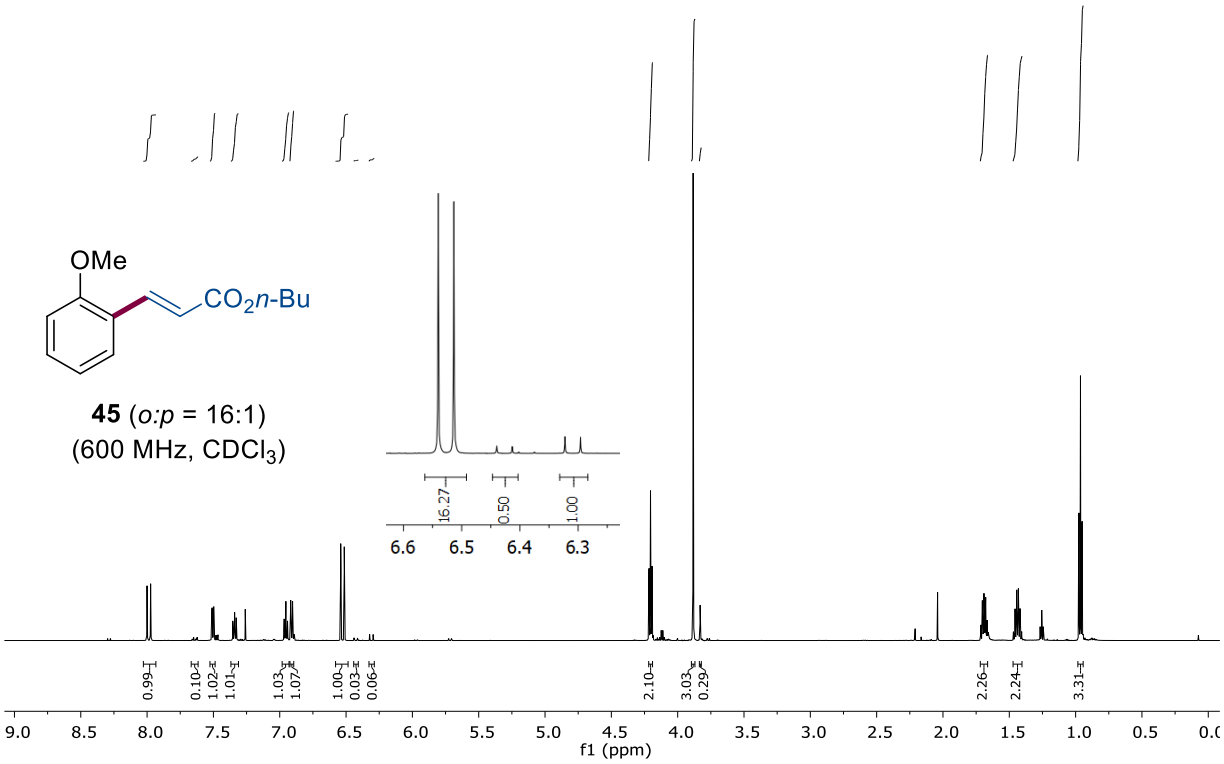

OMe
O
O
F F F F
F F F F
H
NOESY
f2 (ppm)
f1 (ppm)

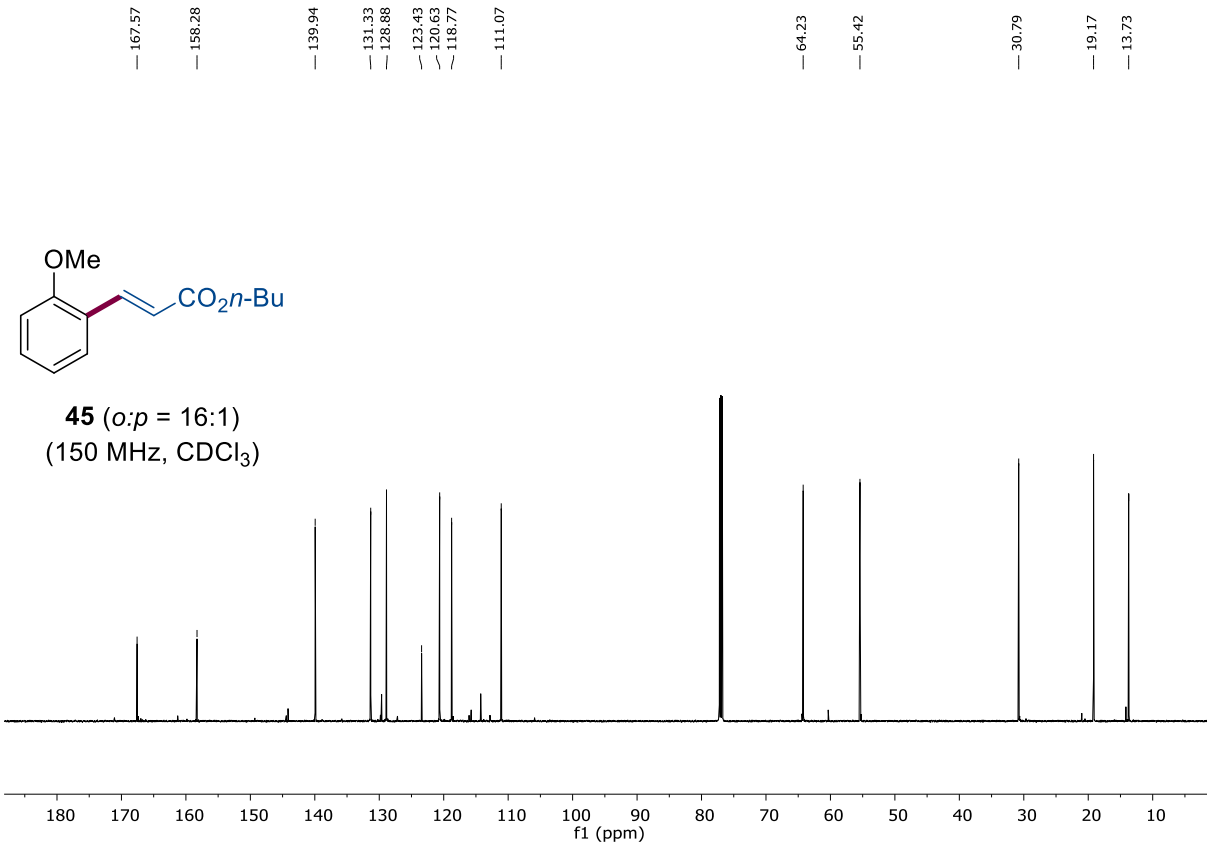

OMe
O
O
Me
Me
Me
H
H
H
i-Pr
43 (o:p = 13:1)
(600 MHz, CDCl3)
f1 (ppm)

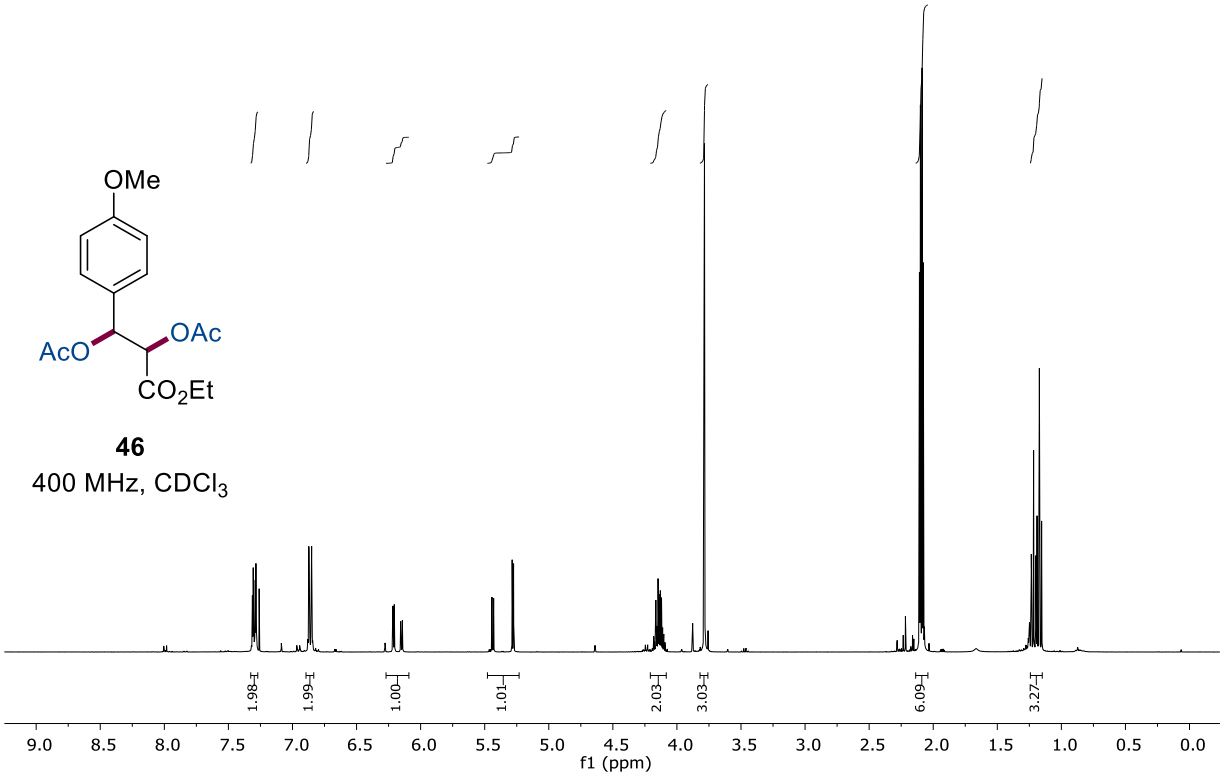

166.90
158.28
139.83
139.77
131.29
128.92
123.50
122.58
120.64
119.21
111.06
73.86
56.68
56.11
55.42
50.03
42.30
39.73
39.50
38.24
37.04
36.62
36.17
35.78
31.91
31.86
28.22
28.00
27.89
24.28
23.82
22.81
22.55
21.03
19.35
18.70
11.85
OMe
O
O
Me
Me
Me
H
H
H
i-Pr
43 (o:p = 13:1)
(126 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

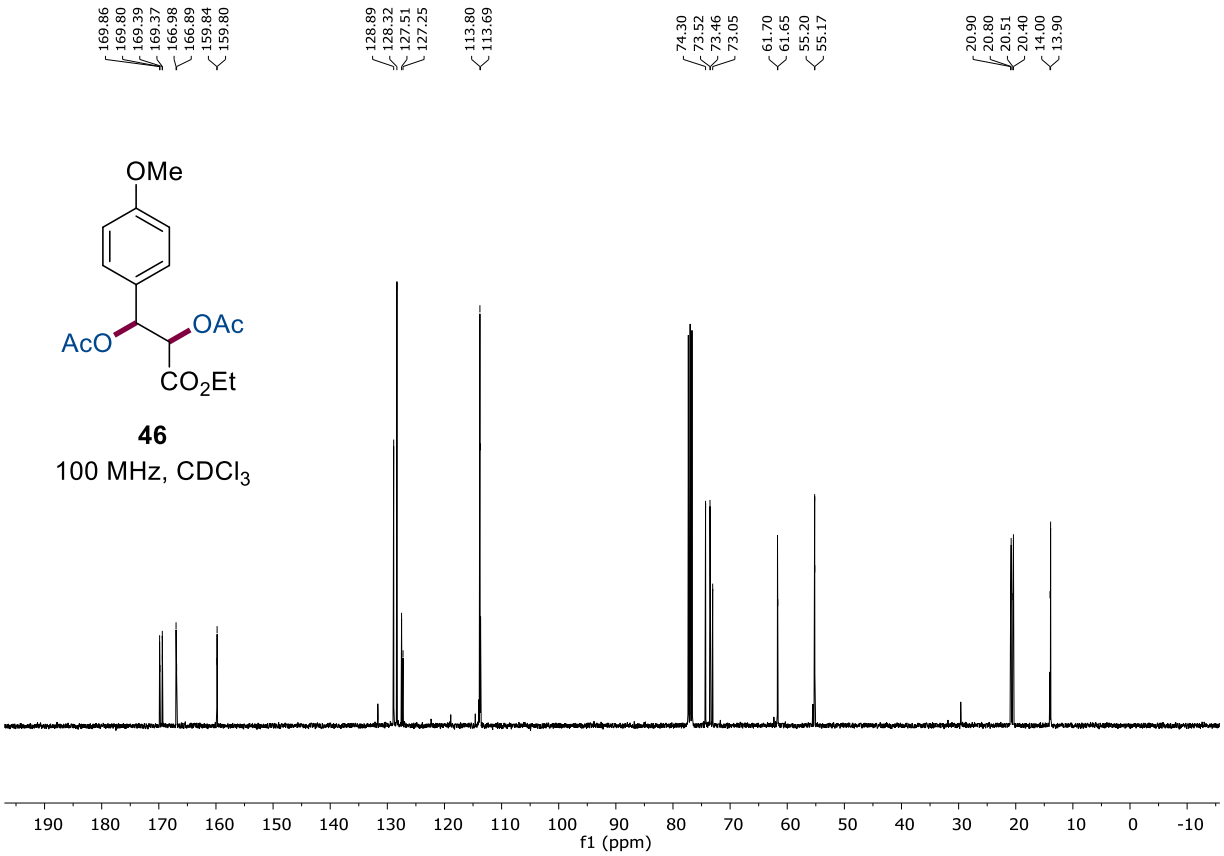

OMe
O
O
H
N
HN
O
Me
Ph
O
44 (o:p =12:1)
(400 MHz, CDCl3)
11.51
1.00
6.5 6.4 6.3 6.2
0.92
1.05
1.00
2.58
3.17
0.98
1.08
1.07
2.00
1.05
2.26
2.81
2.19
2.26
2.90
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

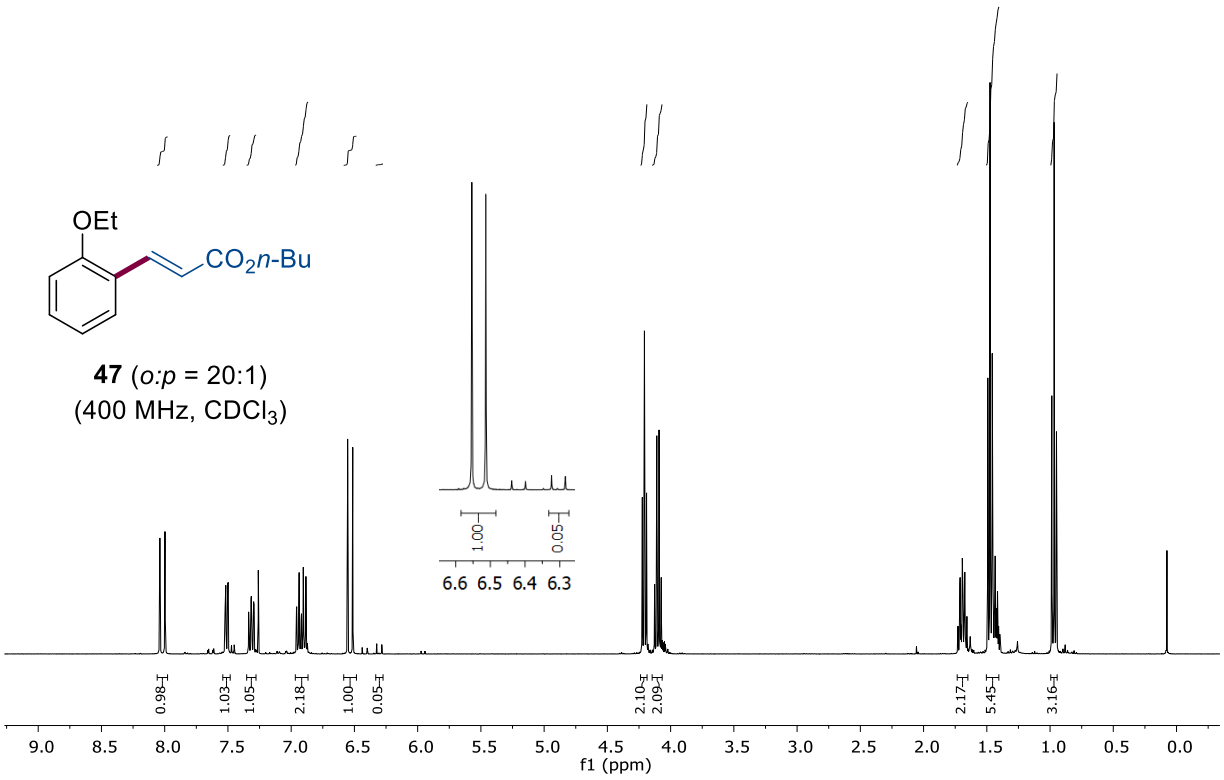

171.09
169.98
167.28
158.34
140.87
136.54
131.65
129.13
128.99
128.55
126.98
123.08
120.67
117.83
111.10
62.71
55.40
54.62
38.69
38.64
23.05
OMe
O
O
H
N
HN
Me
Ph
O
O
44 (o:p =12:1)
(100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

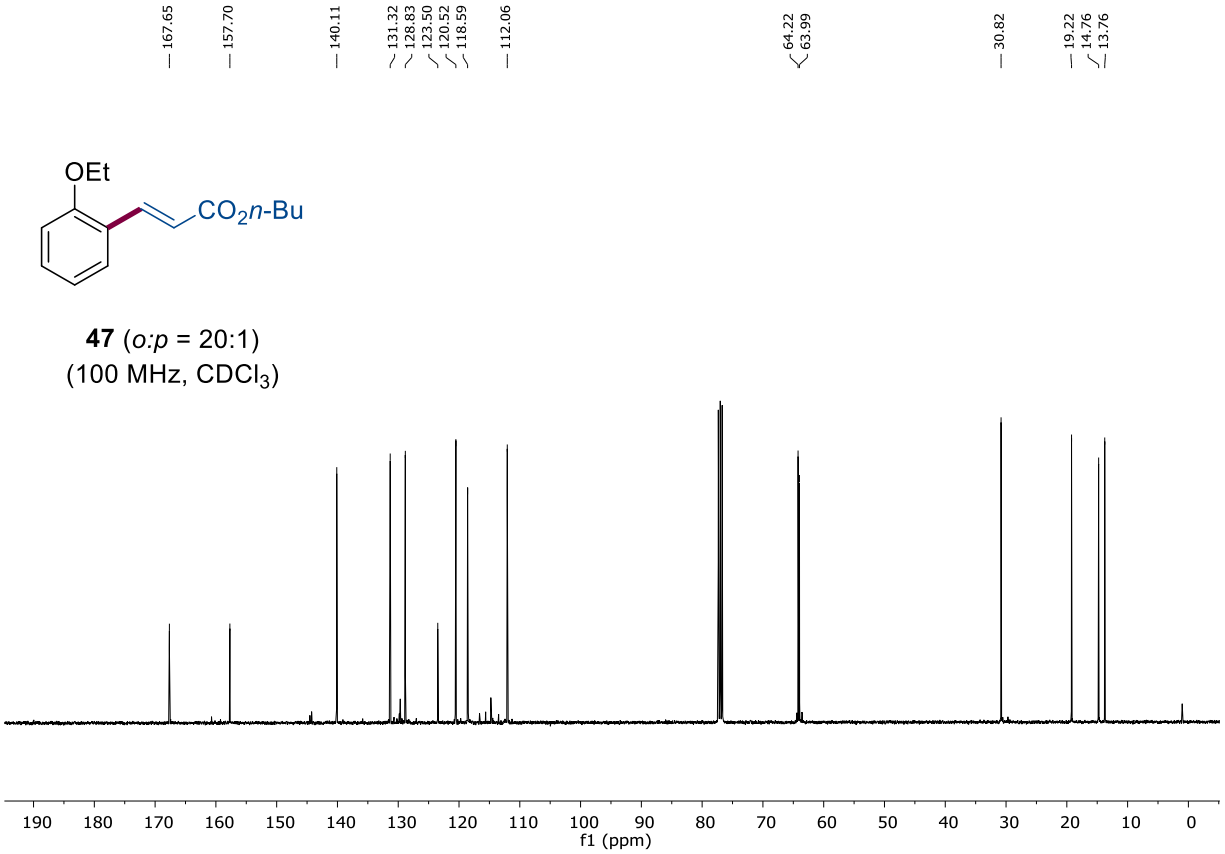

OMe
CO2n-Bu
45 (o:p = 16:1)
(600 MHz, CDCl3)
16.27
0.50
1.00
6.6 6.5 6.4 6.3
0.99
0.10
1.02
1.01
1.03
1.07
1.00
0.03
0.06
2.10
3.03
0.29
2.26
2.24
3.31
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.57
158.28
139.94
131.33
128.88
123.43
120.63
118.77
111.07
64.23
55.42
30.79
19.17
13.73
OMe
CO2n-Bu
45 (o:p = 16:1)
(150 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

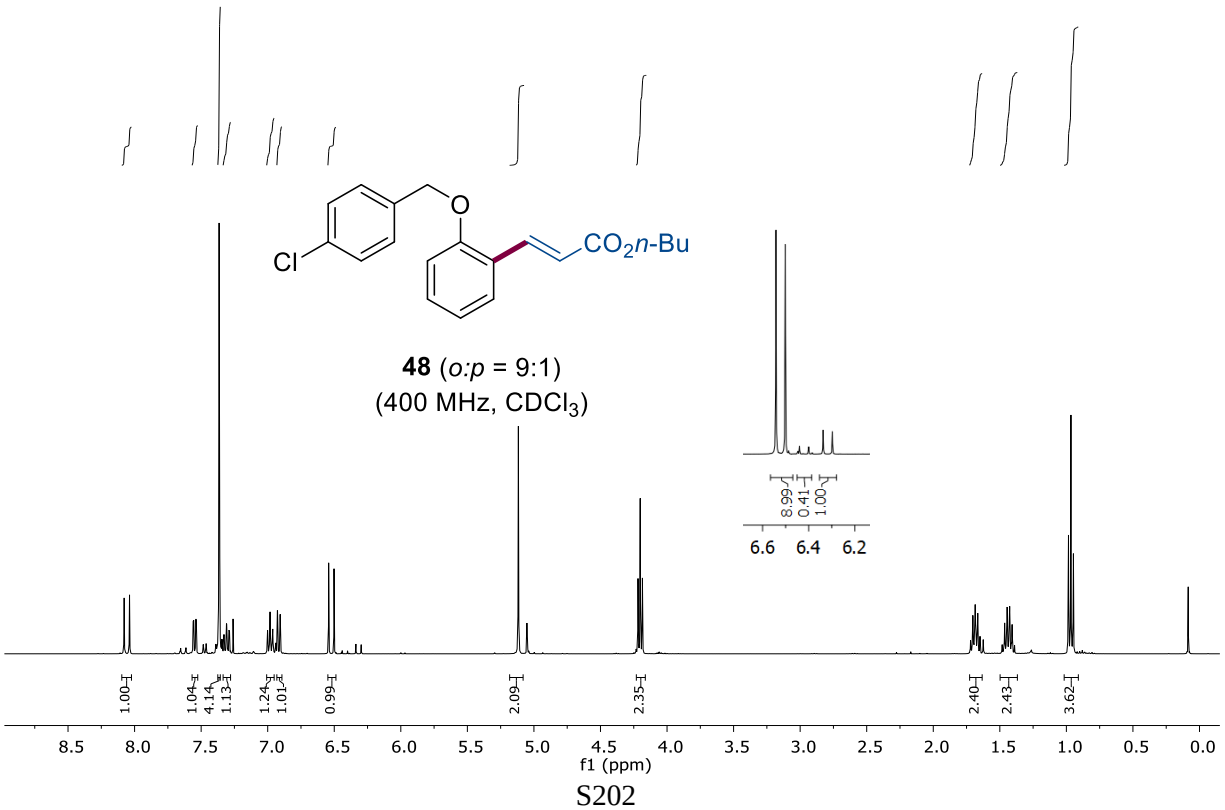

OMe
AcO
OAc
CO2Et
46
400 MHz, CDCl3
1.98
1.99
1.00
1.01
2.03
3.03
6.09
3.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.86
169.80
169.39
169.37
166.98
166.89
159.84
159.80
128.89
128.32
127.51
127.25
113.80
113.69
74.30
73.52
73.46
73.05
61.70
61.65
55.20
55.17
20.90
20.80
20.51
20.40
14.00
13.90
OMe
AcO
OAc
CO2Et
46
100 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

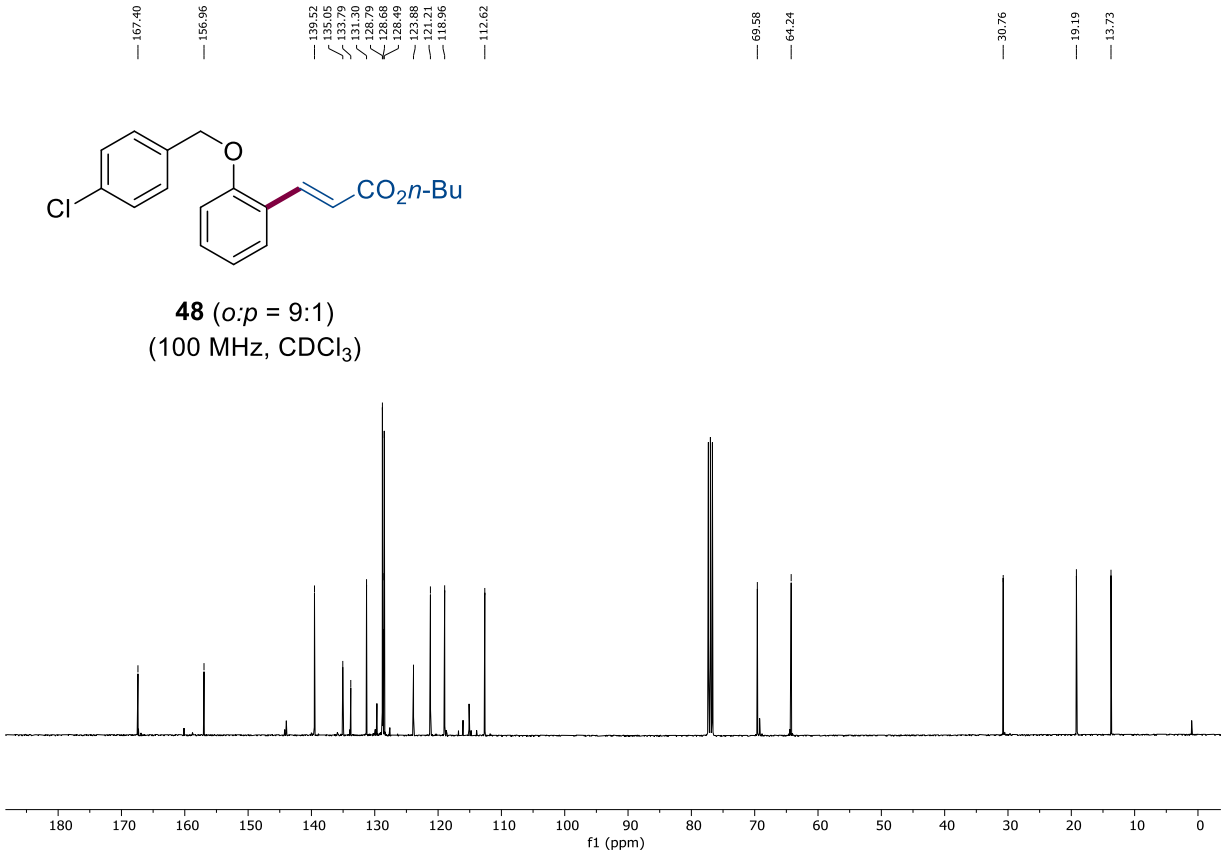

OEt
CO2n-Bu
47 (o:p = 20:1)
(400 MHz, CDCl3)
1.00
0.05
6.6 6.5 6.4 6.3
0.98
1.03
1.05
2.18
1.00
0.05
2.10
2.09
2.17
5.45
3.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



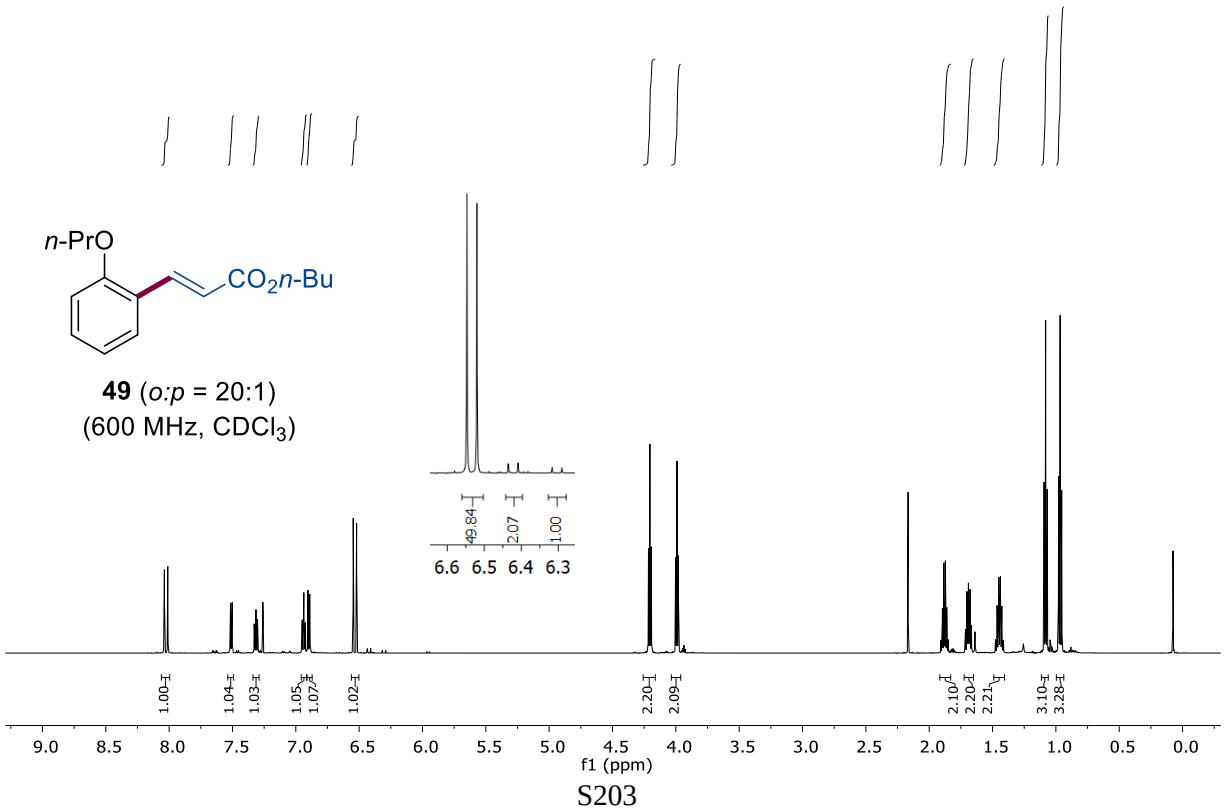
47 (*o*:*p* = 20:1)
(100 MHz, $CDCl_3$)



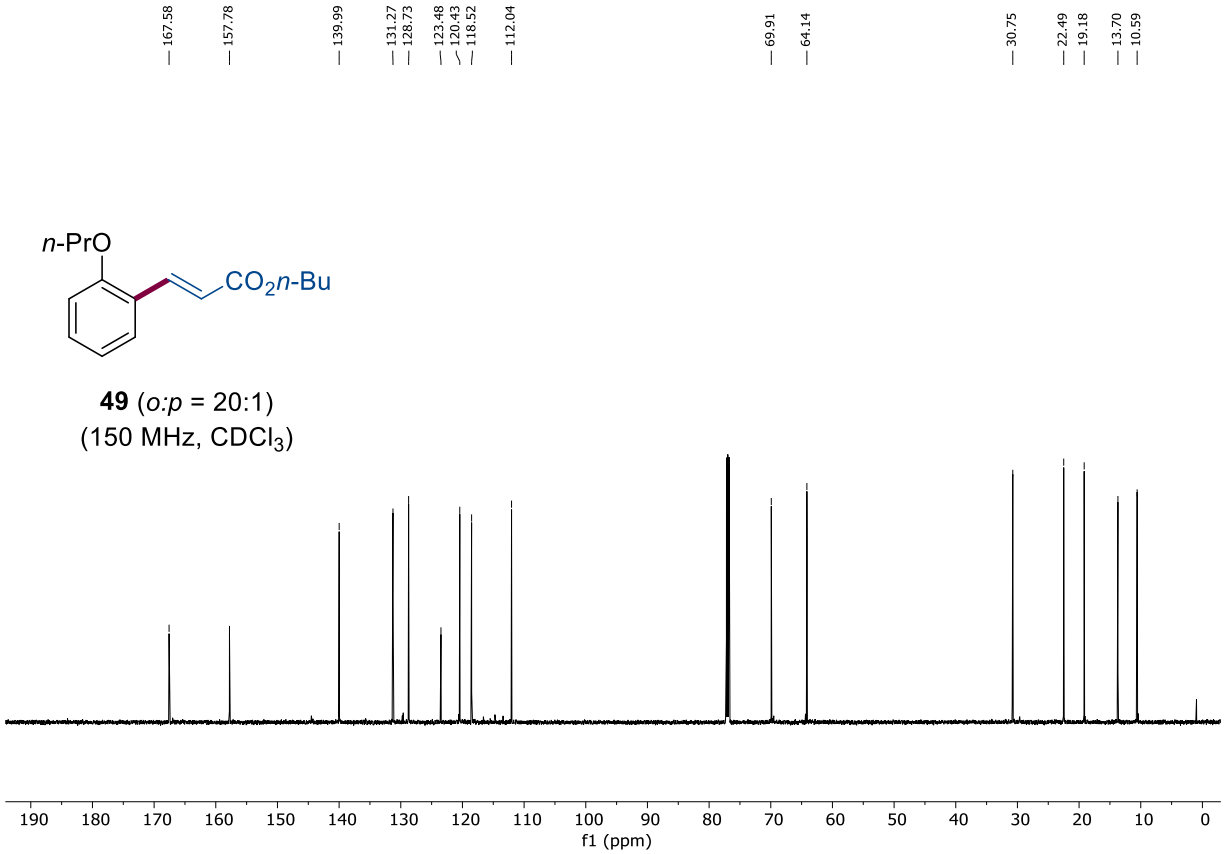
48 (*o*:*p* = 9:1)
(400 MHz, $CDCl_3$)

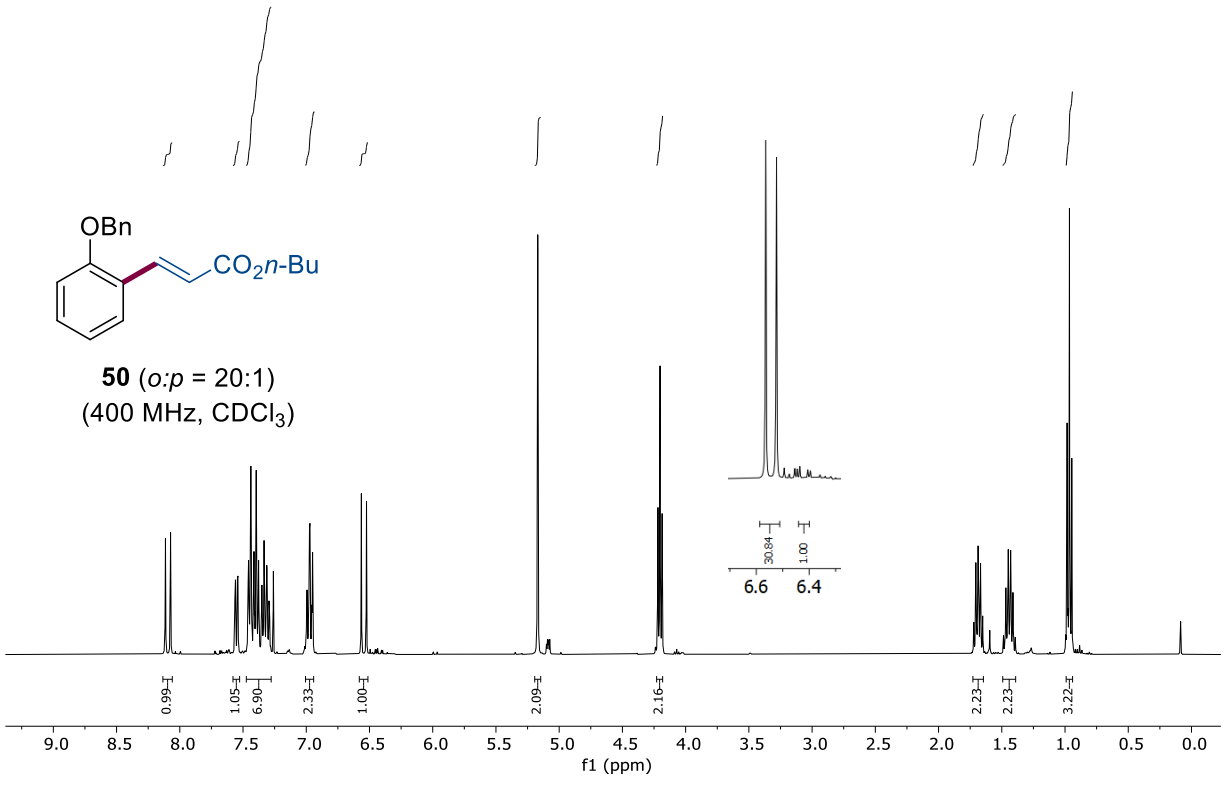


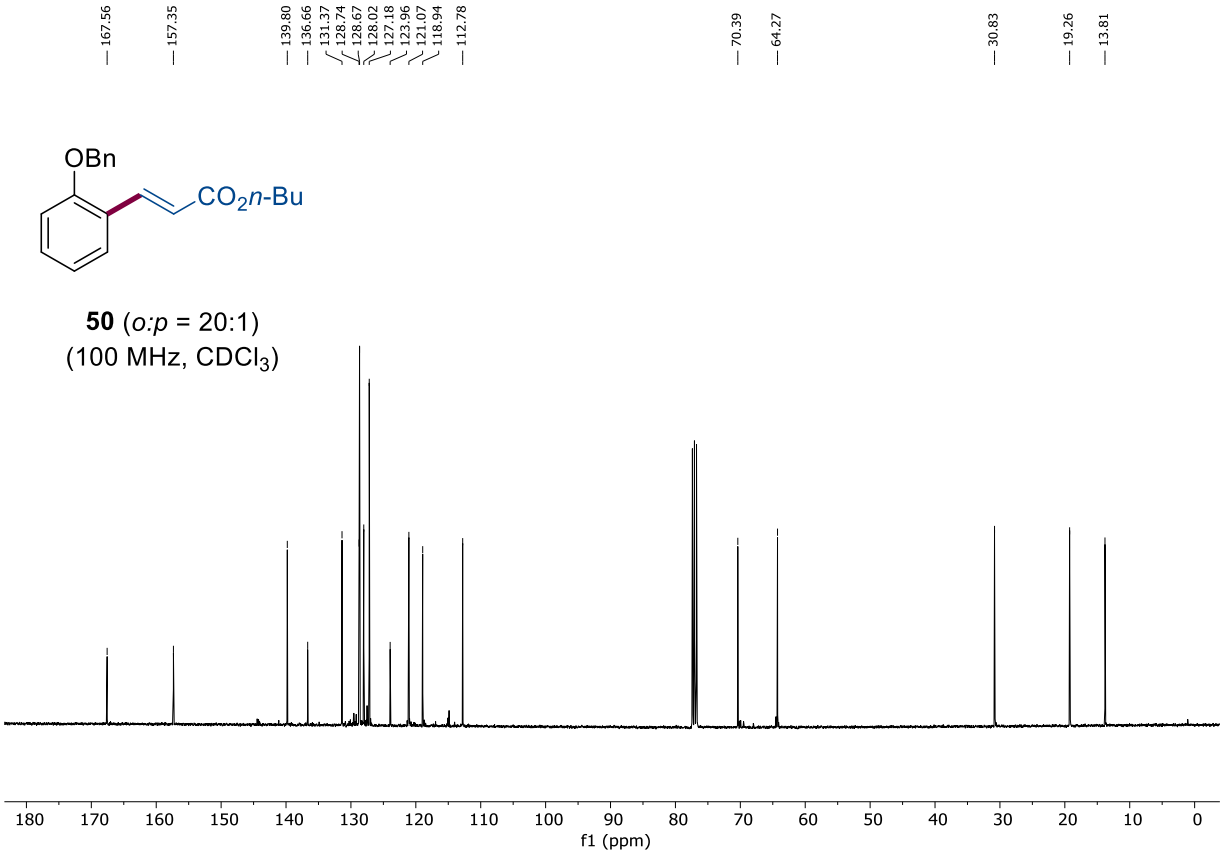
48 (*o*:*p* = 9:1)
(100 MHz, $CDCl_3$)

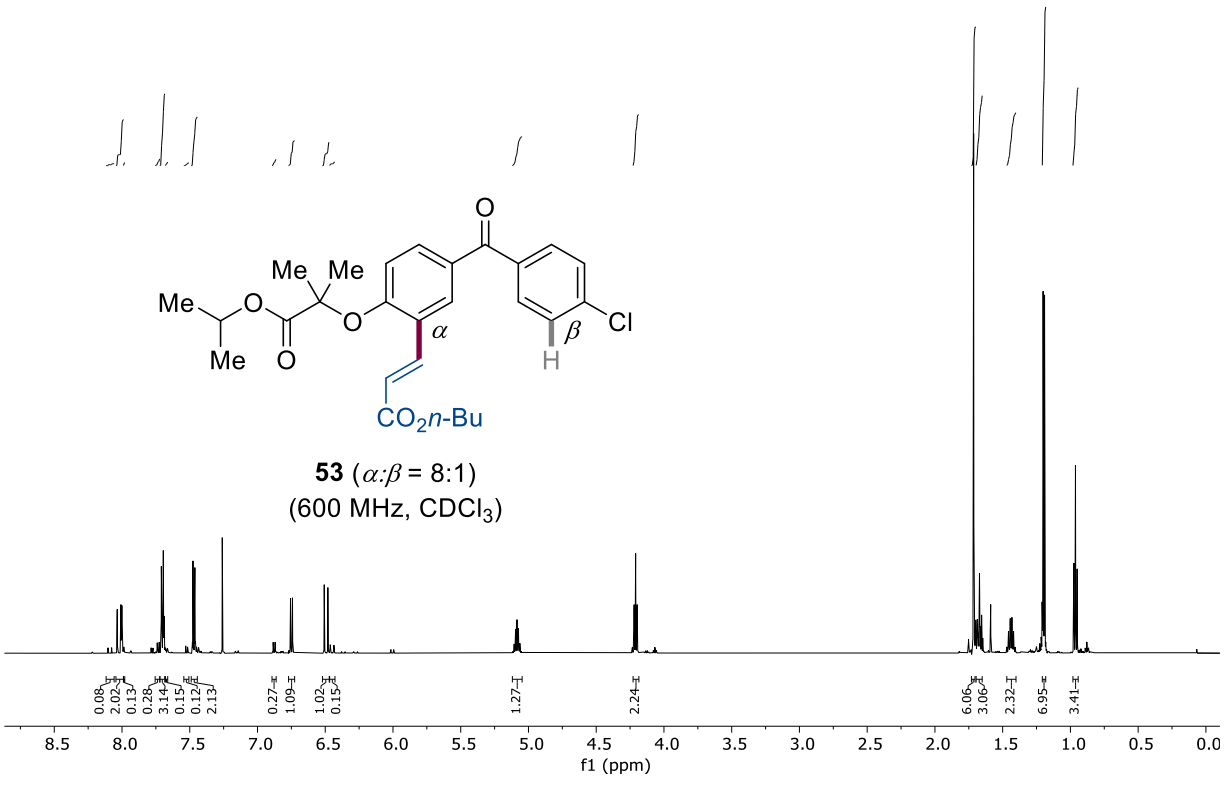


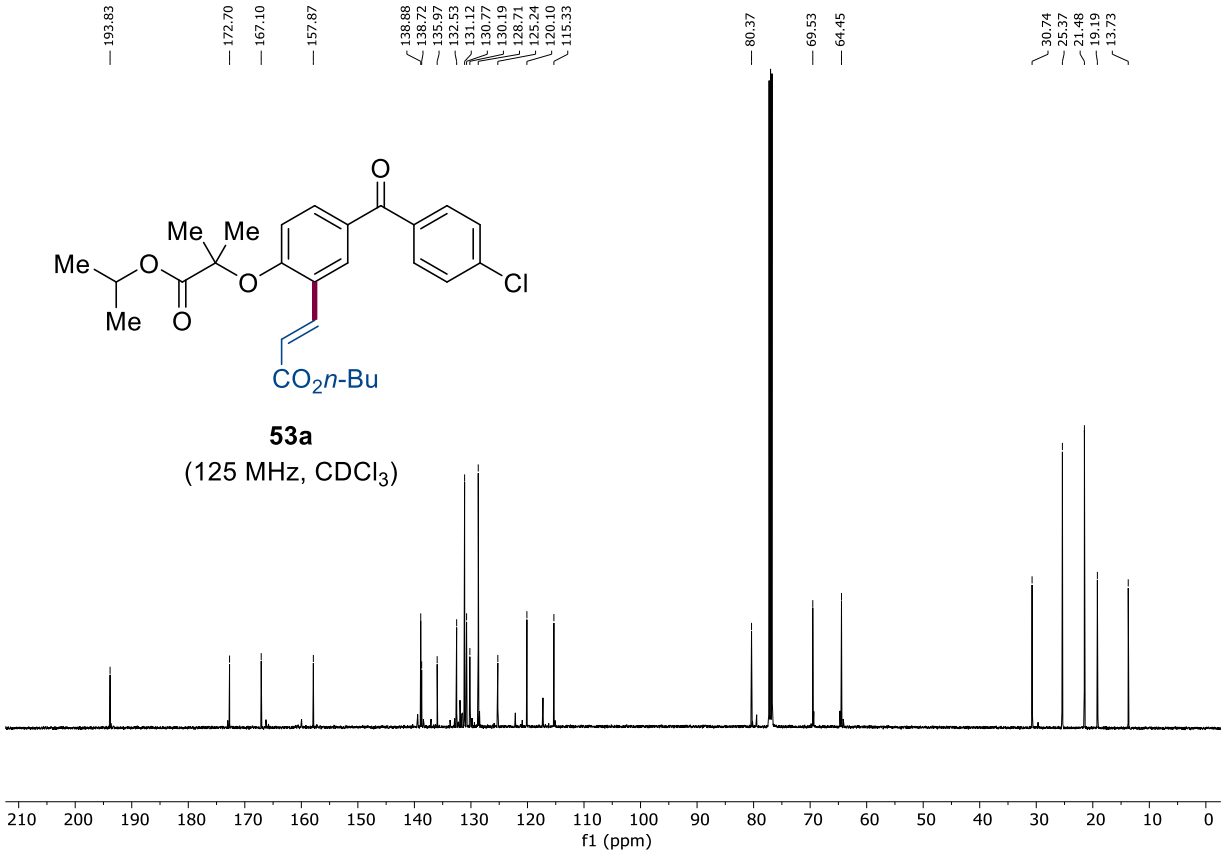
49 (*o*:*p* = 20:1)
(600 MHz, $CDCl_3$)

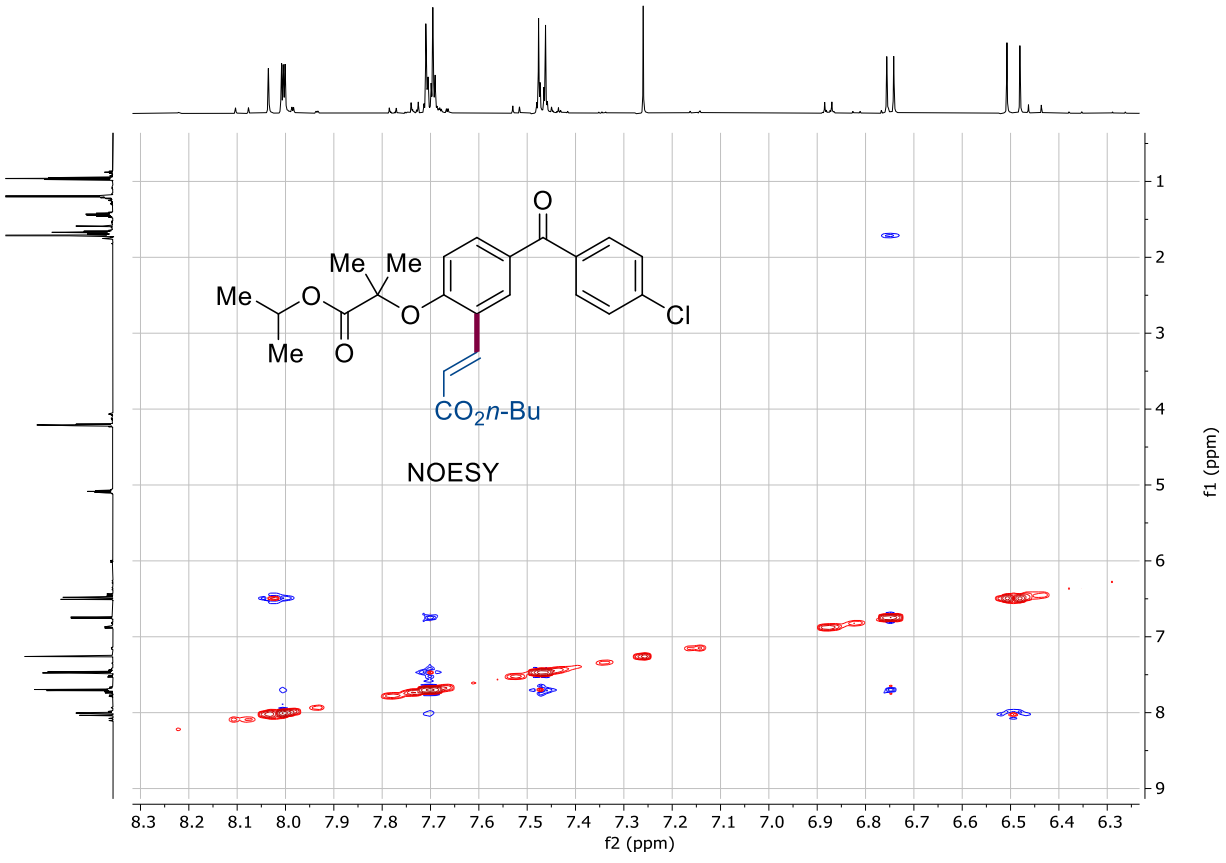

167.58
157.78
139.99
131.27
128.73
123.48
120.43
118.52
112.04
69.91
64.14
30.75
22.49
19.18
13.70
10.59
n-PrO
CO2n-Bu
49 (o:p = 20:1)
(150 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

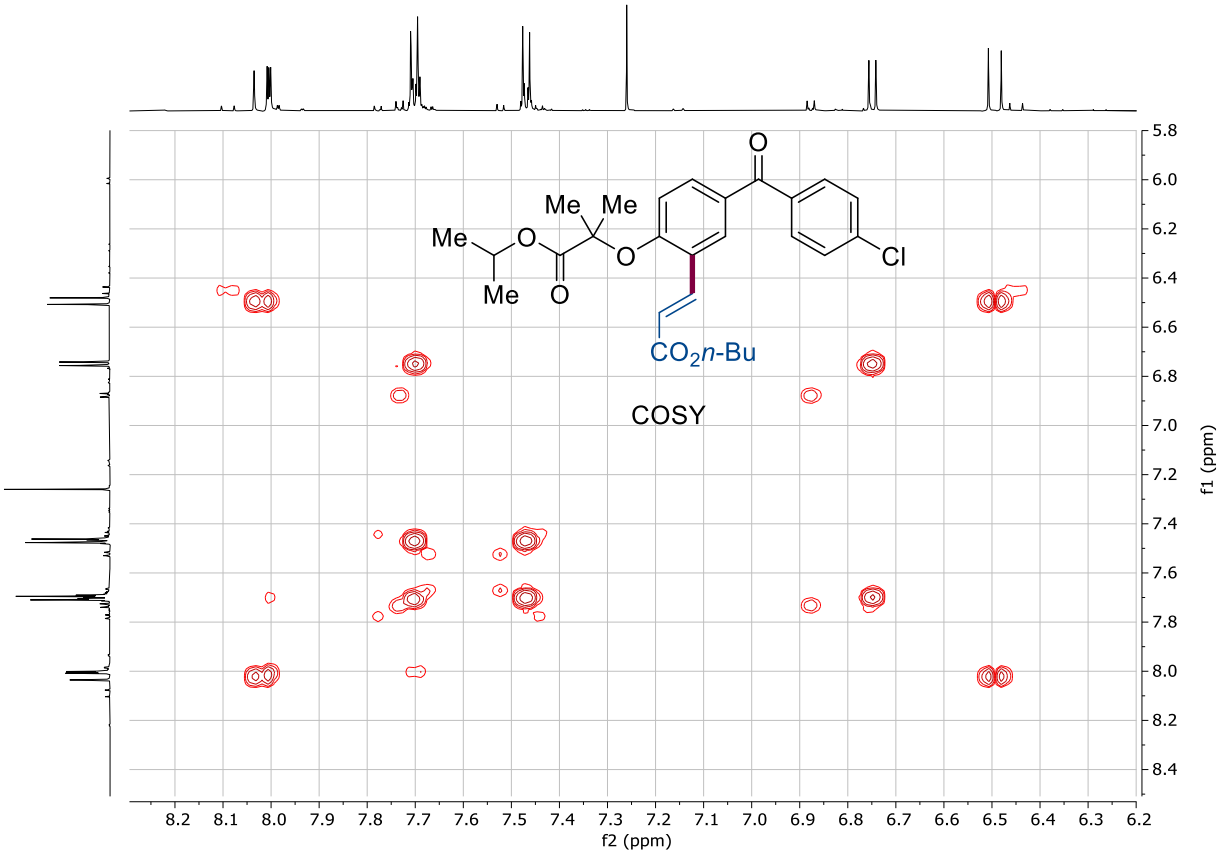

OBn
CO2n-Bu
50 (o:p = 20:1)
(400 MHz, CDCl3)
30.84
1.00
6.6
6.4
0.99
1.05
6.90
2.33
1.00
2.09
2.16
2.23
2.23
3.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

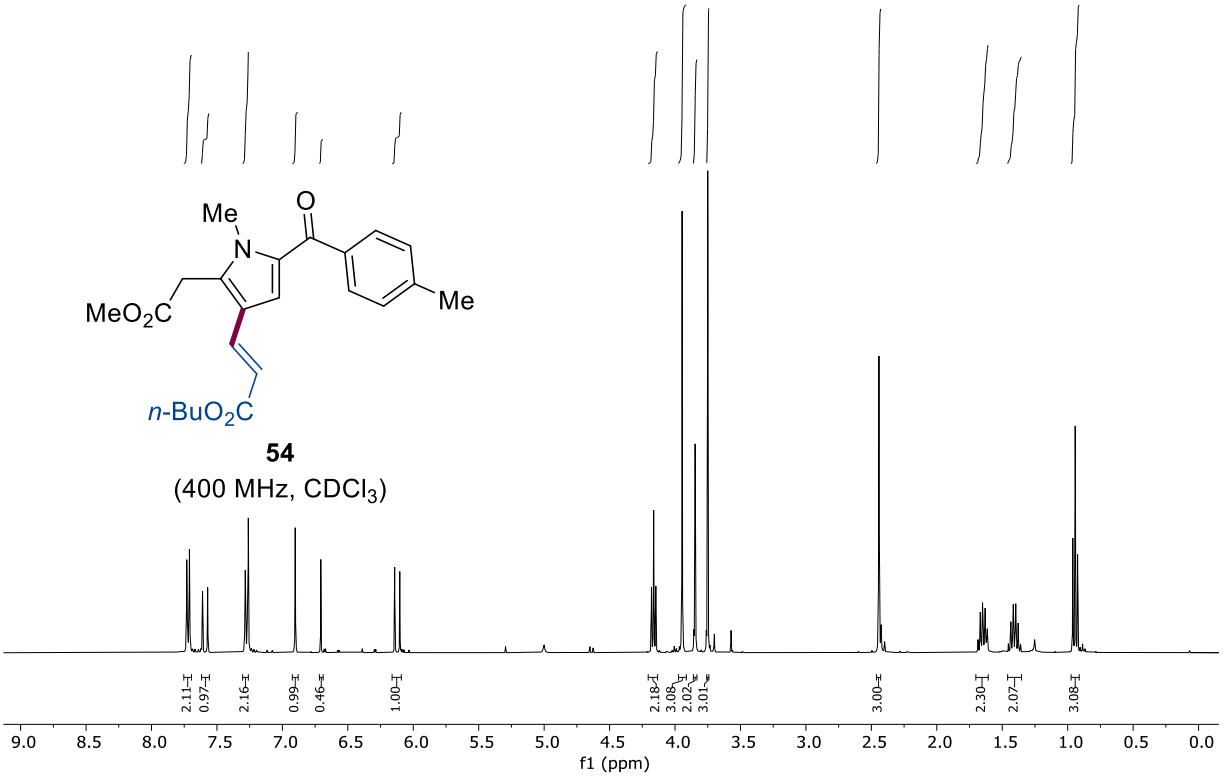

167.56
157.35
139.80
136.66
131.37
128.74
128.67
128.02
127.18
123.96
121.07
118.94
112.78
70.39
64.27
30.83
19.26
13.81
OBn
CO2n-Bu
50 (o:p = 20:1)
(100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

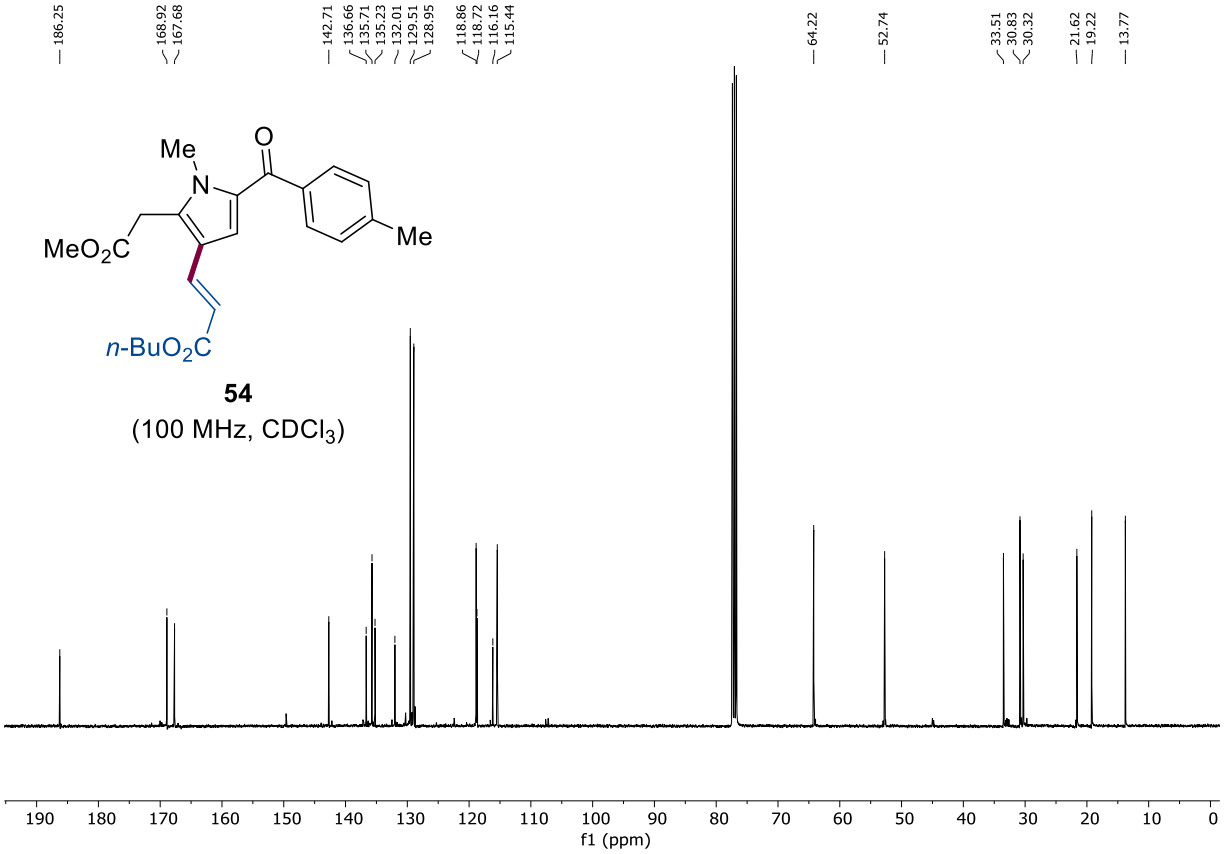

O
Me Me
Me
O
O
Me
O
α
β
Cl
H
CO2n-Bu
53 (α:β = 8:1)
(600 MHz, CDCl3)
0.08
2.02
0.13
0.28
3.14
0.15
0.12
2.13
0.27
1.09
1.02
0.15
1.27
2.24
6.06
3.06
2.32
6.95
3.41
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

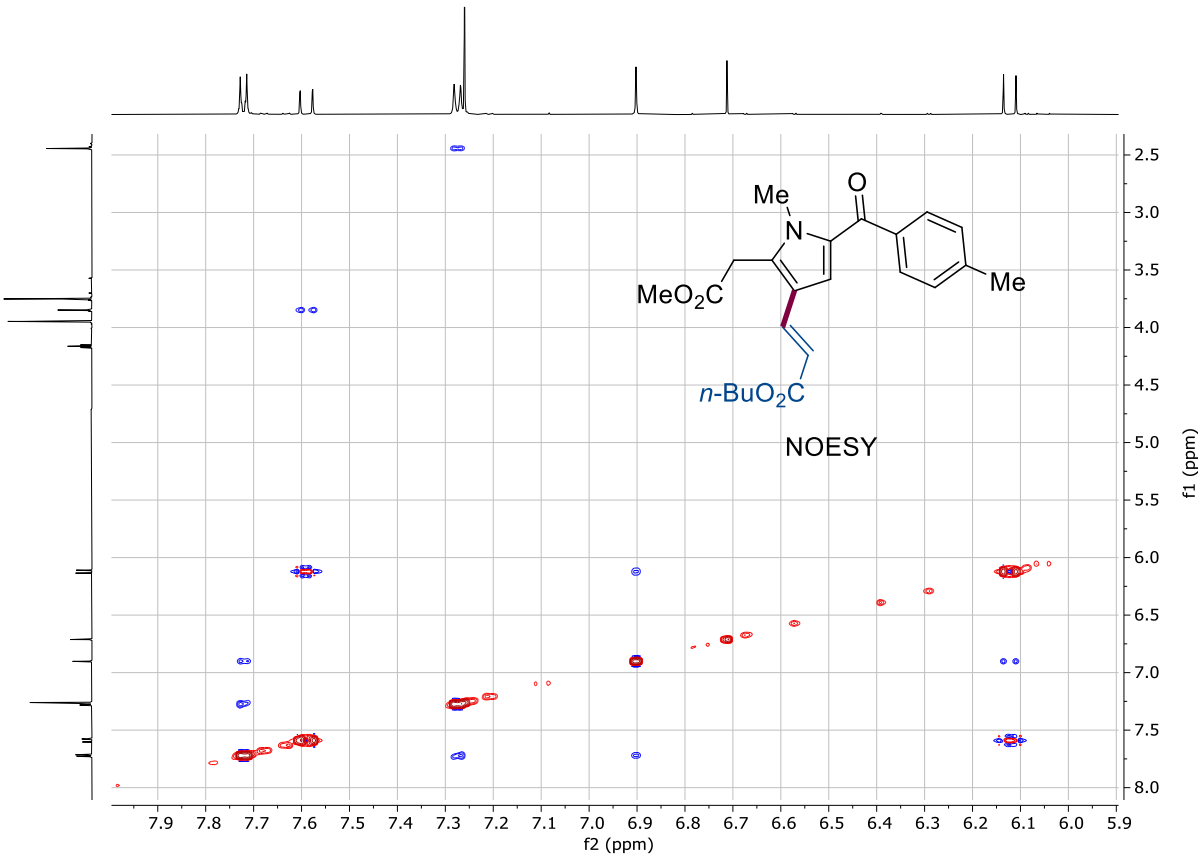

193.83
172.70
167.10
157.87
138.88
138.72
135.97
132.53
131.12
130.77
130.19
128.71
125.24
120.10
115.33
80.37
69.53
64.45
30.74
25.37
21.48
19.19
13.73
Me
Me
Me
Me
O
O
O
O
Cl
CO2n-Bu
53a
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

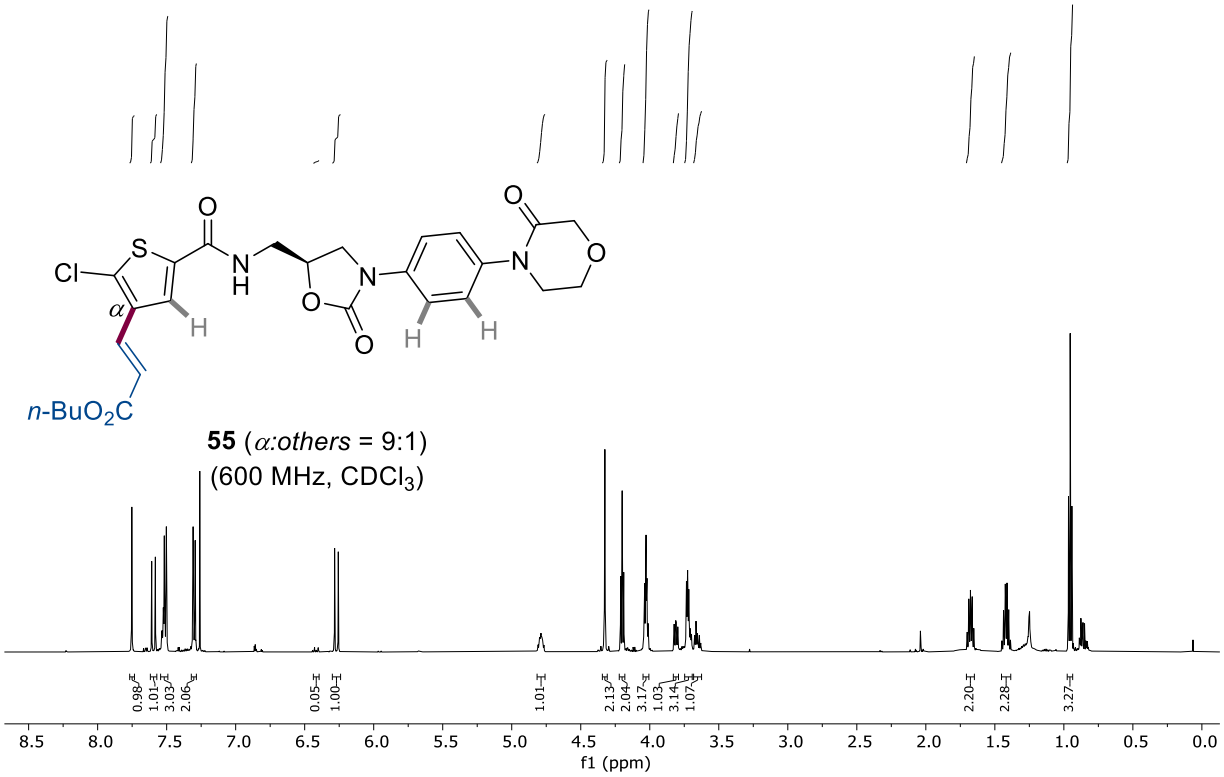

Me
Me
Me
Me
O
O
O
O
Cl
CO2n-Bu
NOESY
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
f2 (ppm)
1 2 3 4 5 6 7 8 9
f1 (ppm)

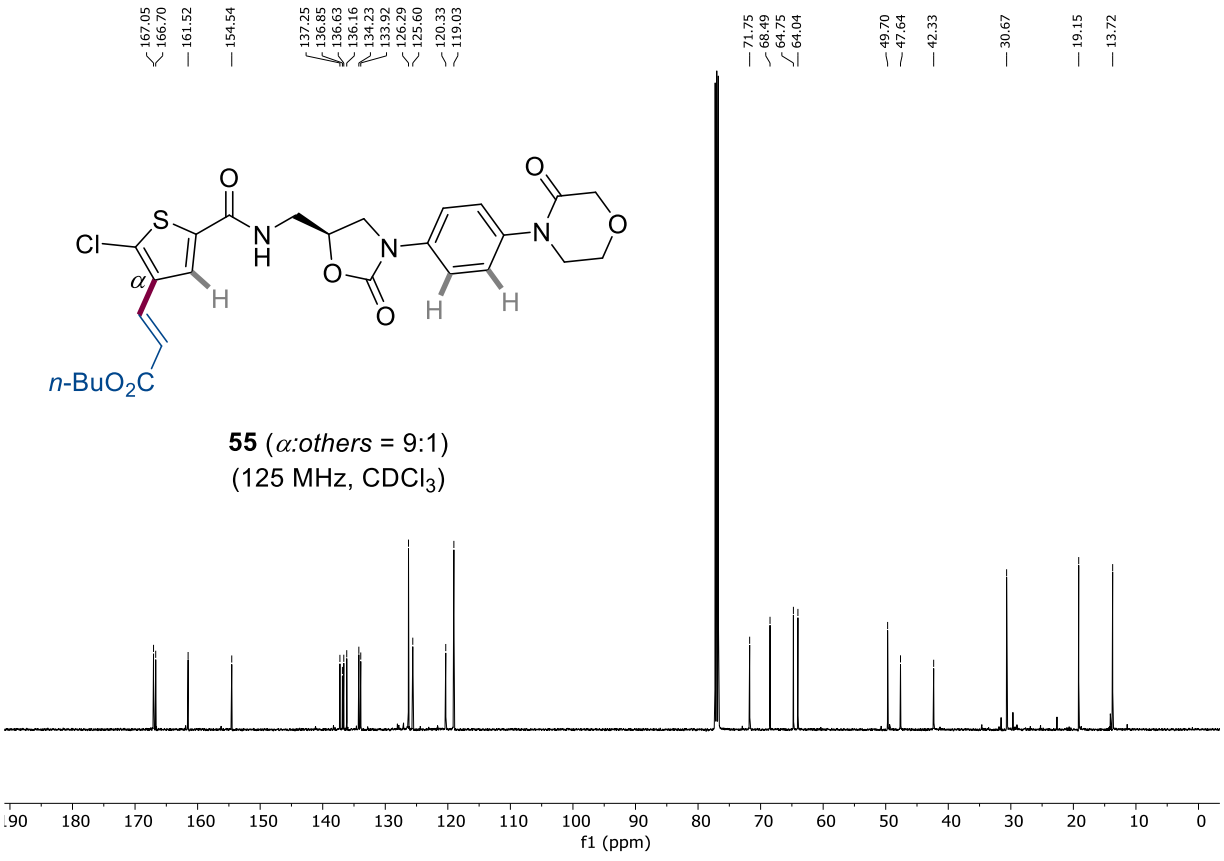

Me
Me
Me
O
O
O
O
Cl
CO2n-Bu
COSY
f2 (ppm)
f1 (ppm)

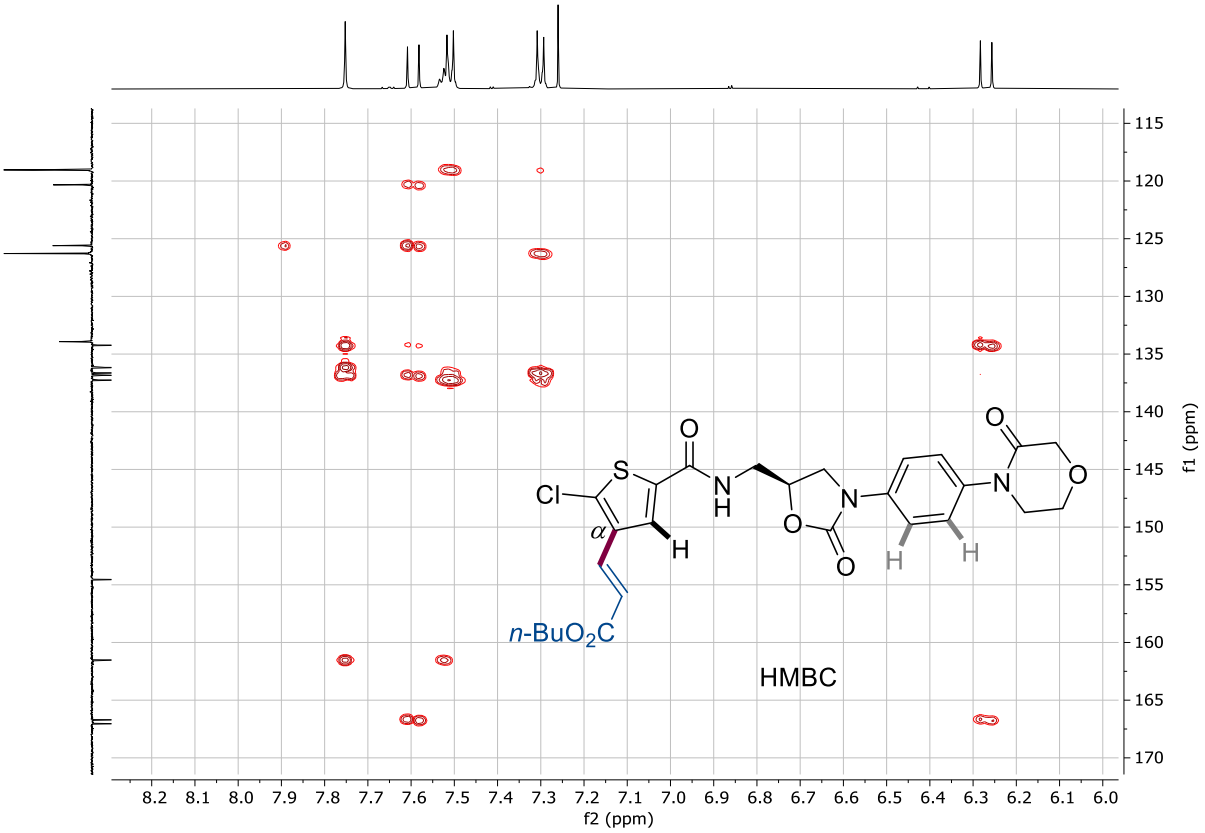

Me
N
O
MeO2C
Me
n-BuO2C
54
(400 MHz, CDCl3)
f1 (ppm)

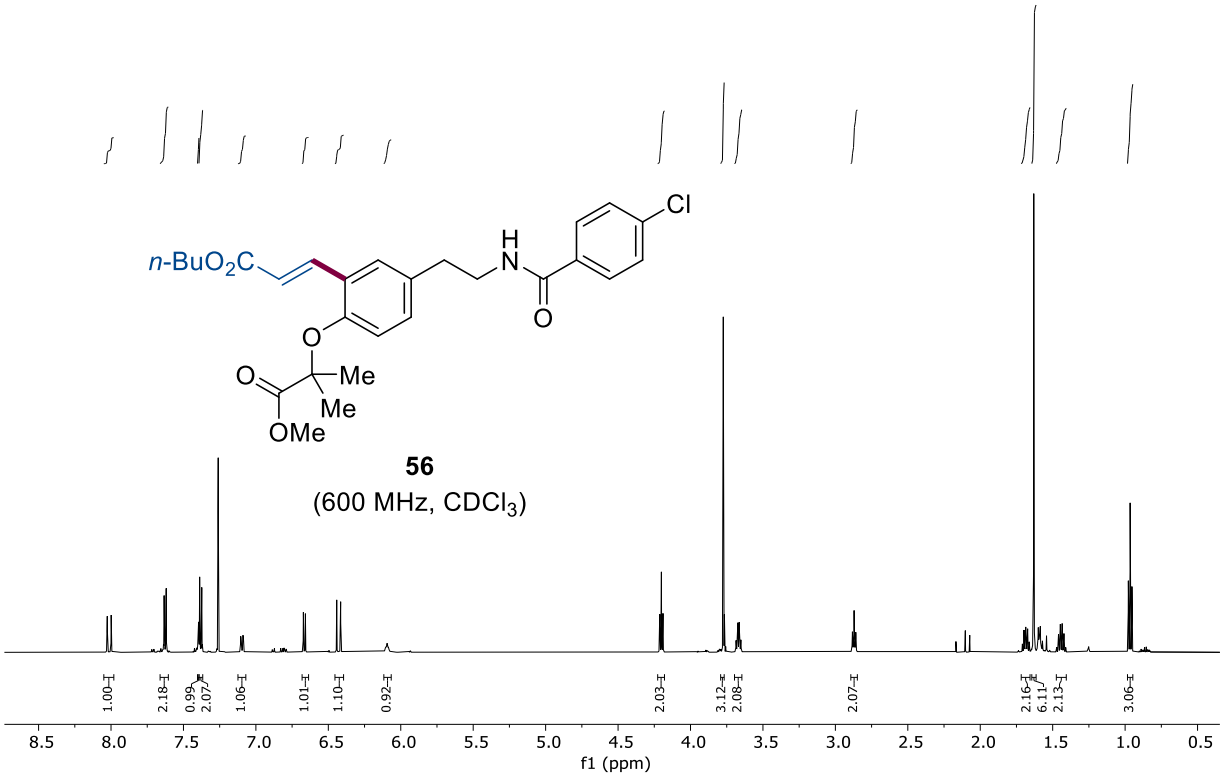

186.25
168.92
167.68
142.71
136.66
135.71
135.23
132.01
129.51
128.95
118.86
118.72
116.16
115.44
64.22
52.74
33.51
30.83
30.32
21.62
19.22
13.77
Me
N
O
MeO2C
Me
n-BuO2C
54
(100 MHz, CDCl3)
f1 (ppm)

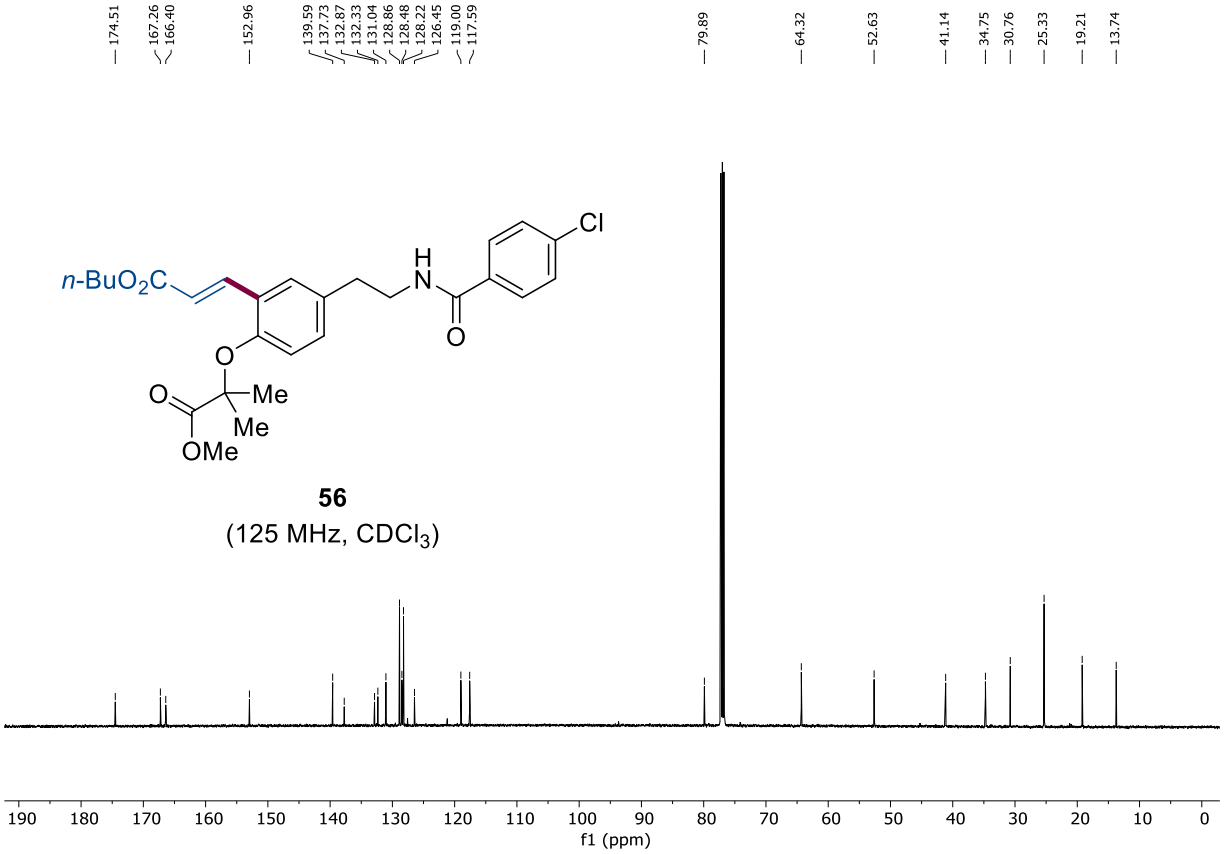

Me
N
O
MeO2C
Me
n-BuO2C
NOESY
f2 (ppm)
f1 (ppm)

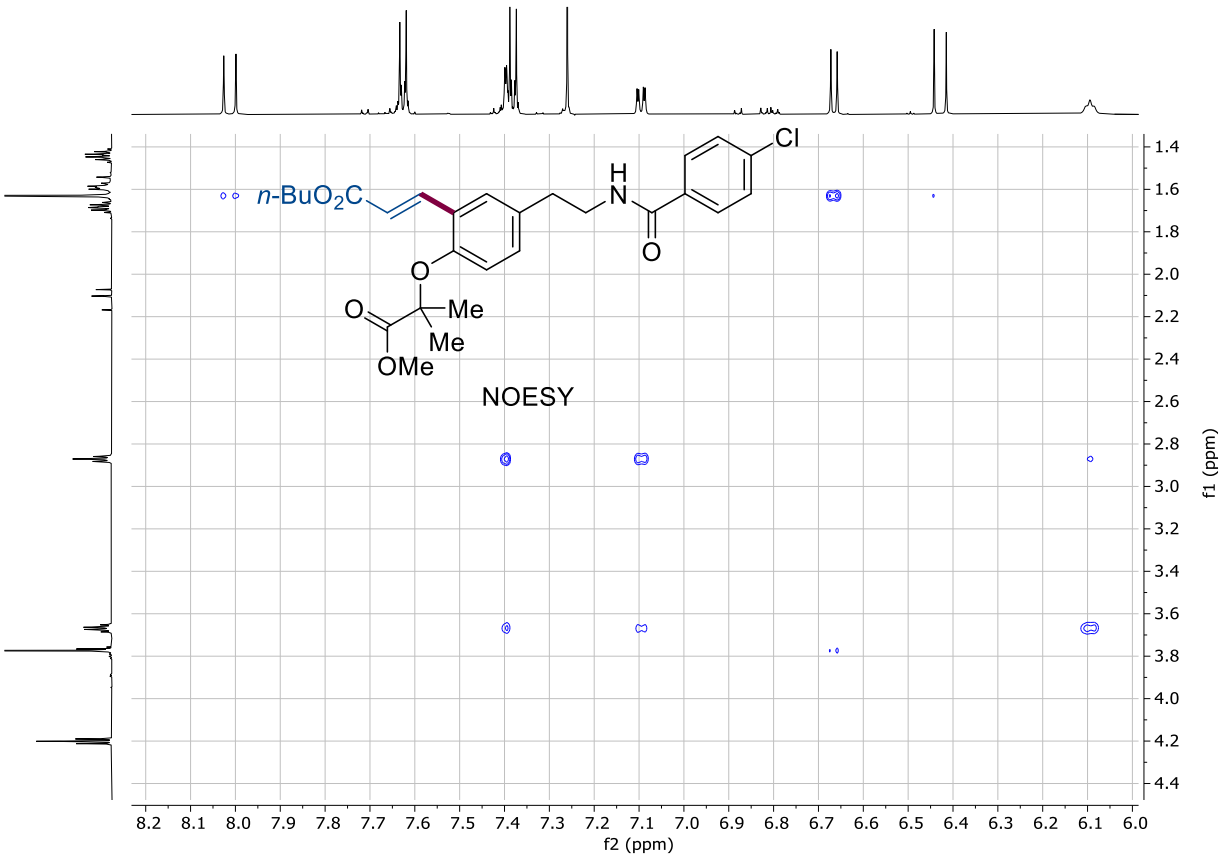

n-BuO2C
55 (α:others = 9:1)
(600 MHz, CDCl3)
f1 (ppm)

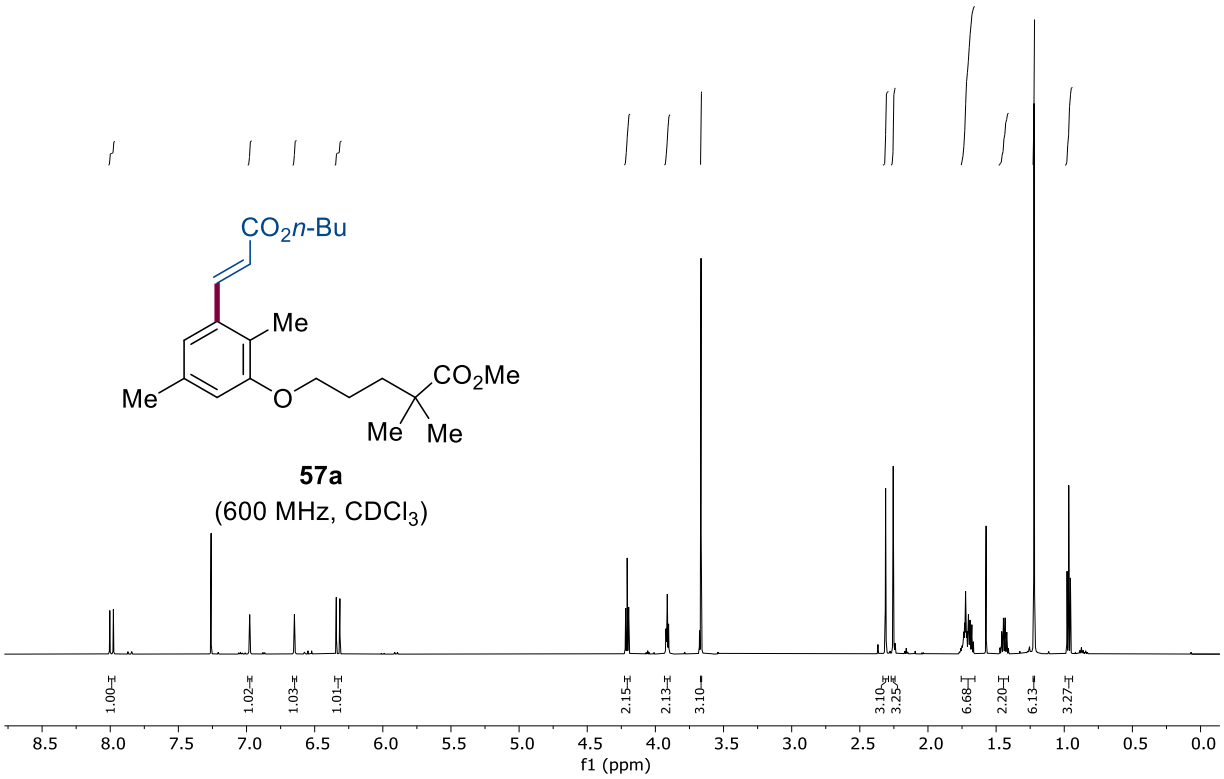

n-BuO2C
55 (α:others = 9:1)
(125 MHz, CDCl3)
f1 (ppm)

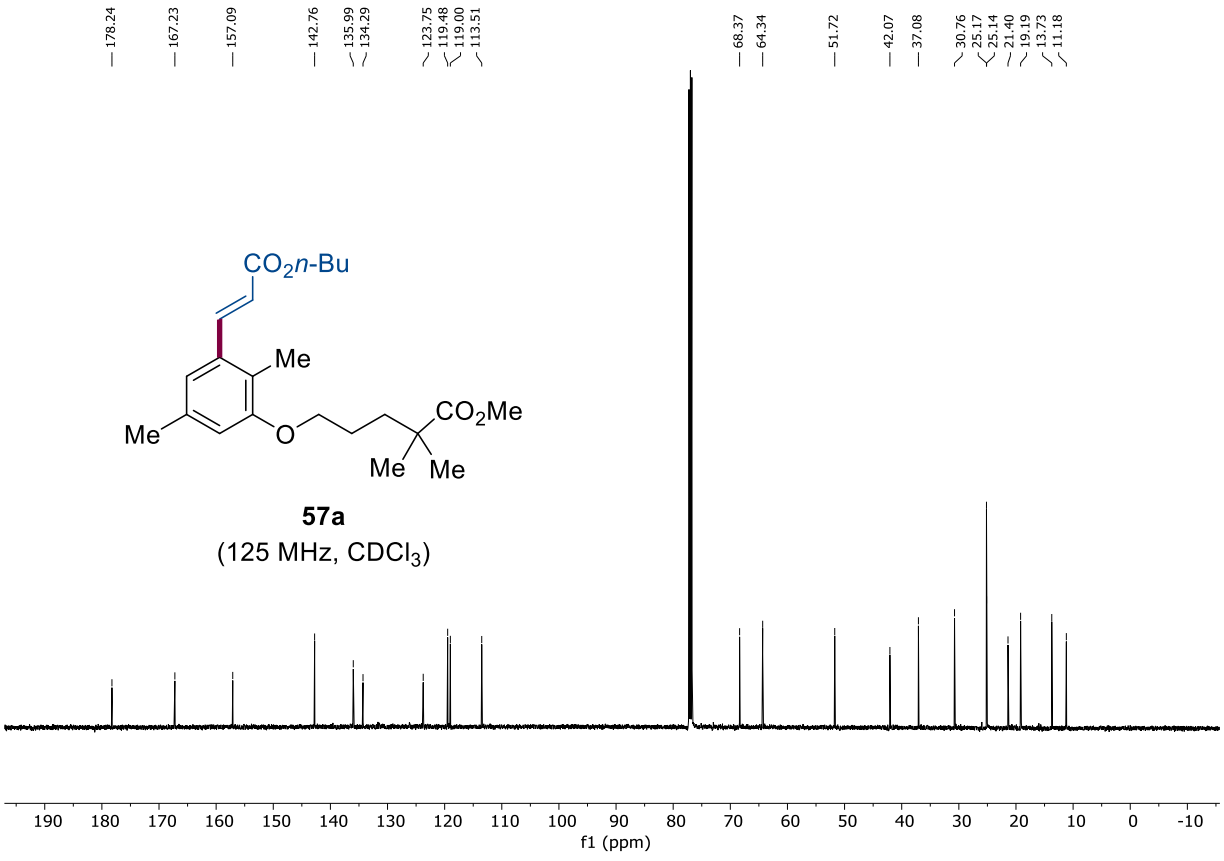

HMBC
f2 (ppm)
f1 (ppm)

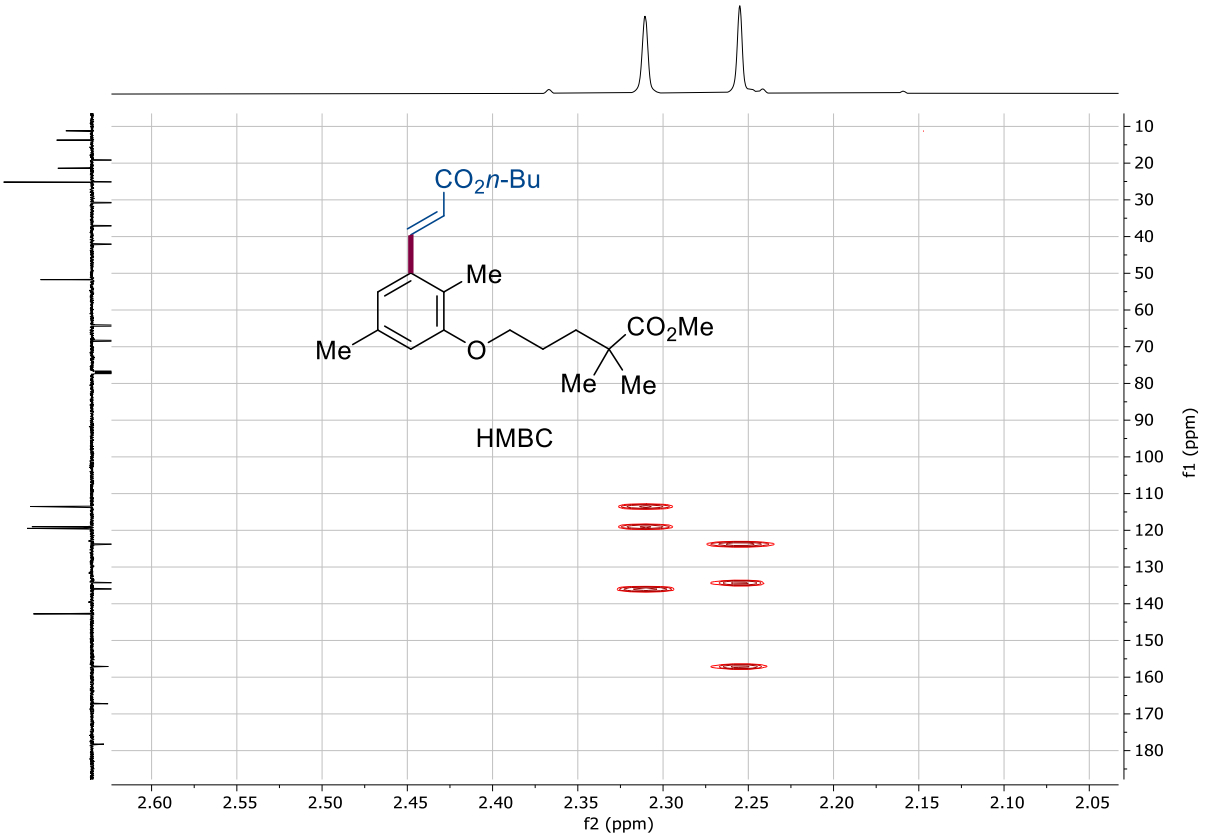

56
(600 MHz, CDCl3)
f1 (ppm)

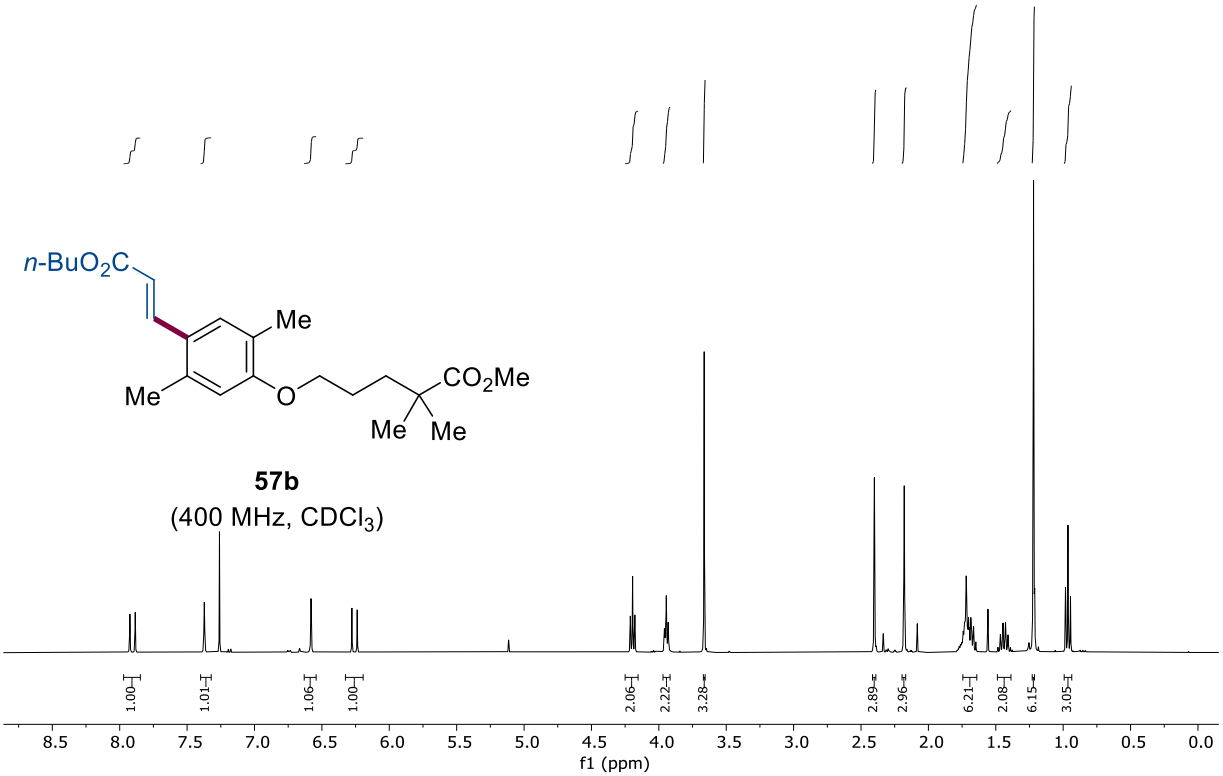

174.51
167.26
166.40
152.96
139.59
137.73
132.87
132.33
131.04
128.86
128.48
128.22
126.45
119.00
117.59
79.89
64.32
52.63
41.14
34.75
30.76
25.33
19.21
13.74
n-BuO2C
Cl
H
N
O
O
O
Me
Me
OMe
56
(125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

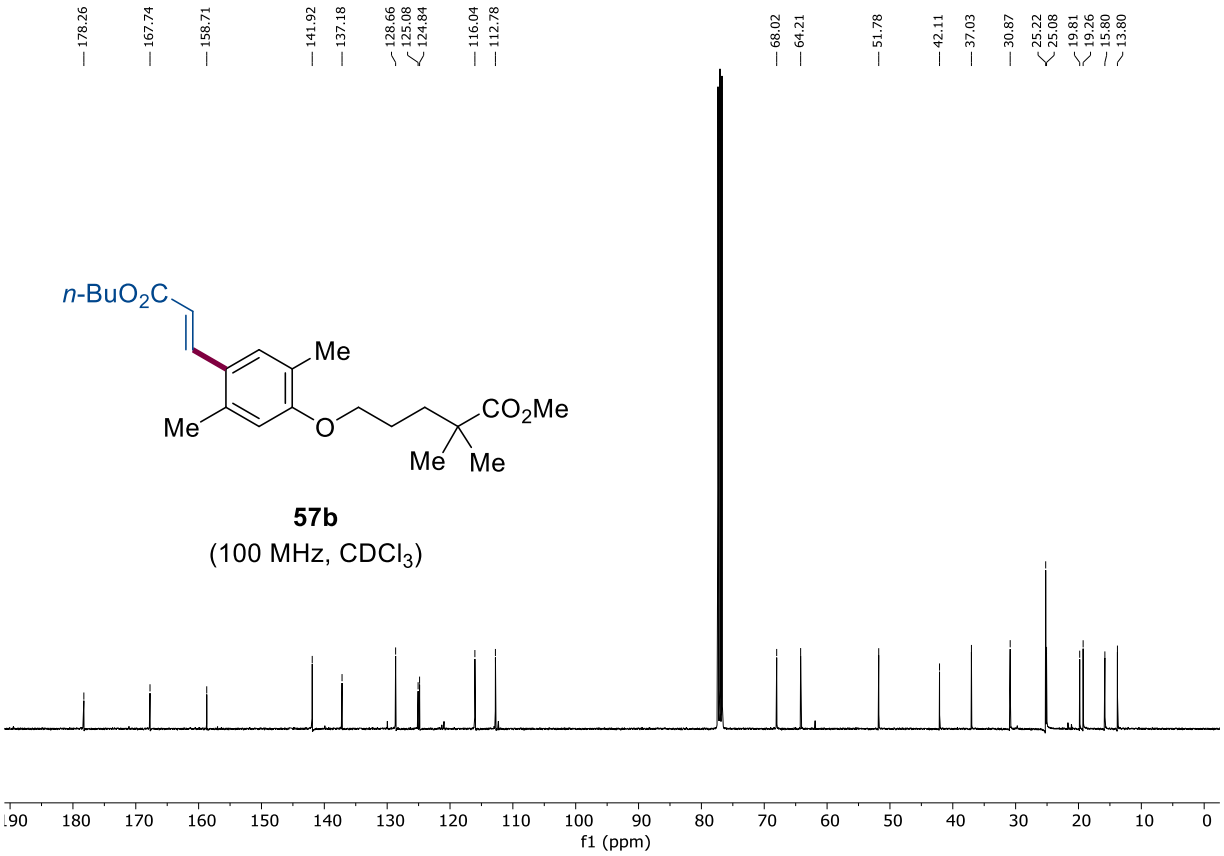

n-BuO2C
Cl
H
N
O
O
O
Me
Me
OMe
NOESY
1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4
f1 (ppm)
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0
f2 (ppm)


CO2n-Bu
Me
Me
O
CO2Me
Me
Me
57a
(600 MHz, CDCl3)
1.00
1.02
1.03
1.01
2.15
2.13
3.10
3.10
3.25
6.68
2.20
6.13
3.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.24
167.23
157.09
142.76
135.99
134.29
123.75
119.48
119.00
113.51
68.37
64.34
51.72
42.07
37.08
30.76
25.17
25.14
21.40
19.19
13.73
11.18
CO2n-Bu
Me
Me
O
CO2Me
Me
Me
57a
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

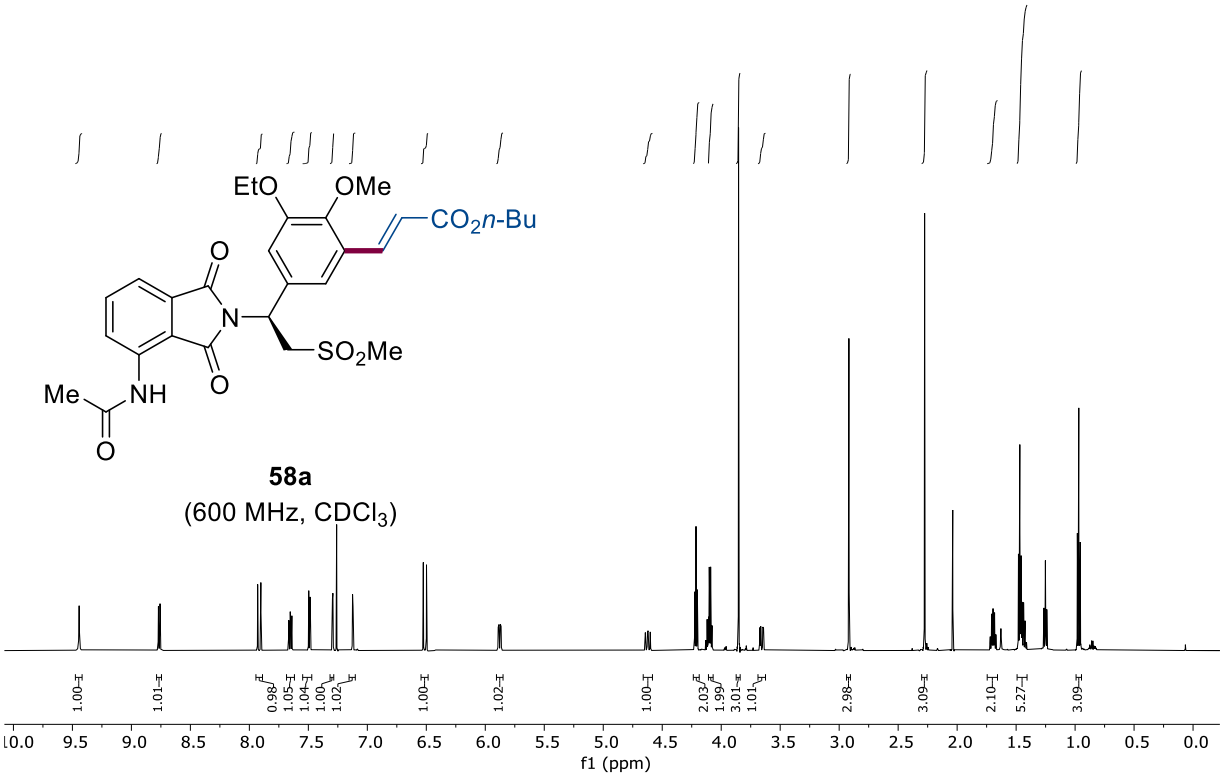

CO2n-Bu
Me
Me
O
CO2Me
Me
Me
HMBC
f2 (ppm)
f1 (ppm)


n-BuO2C
Me
Me
O
CO2Me
Me
Me
57b
(400 MHz, CDCl3)
f1 (ppm)



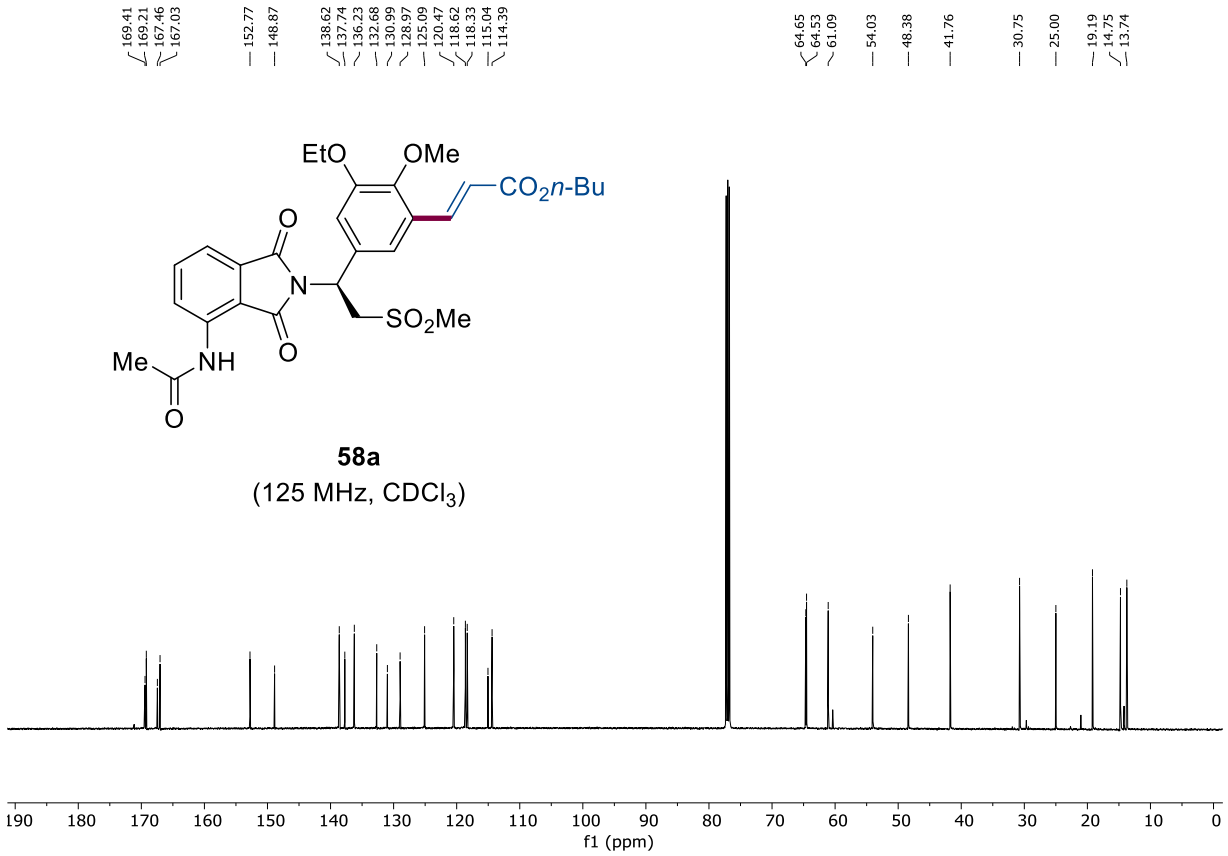
57b

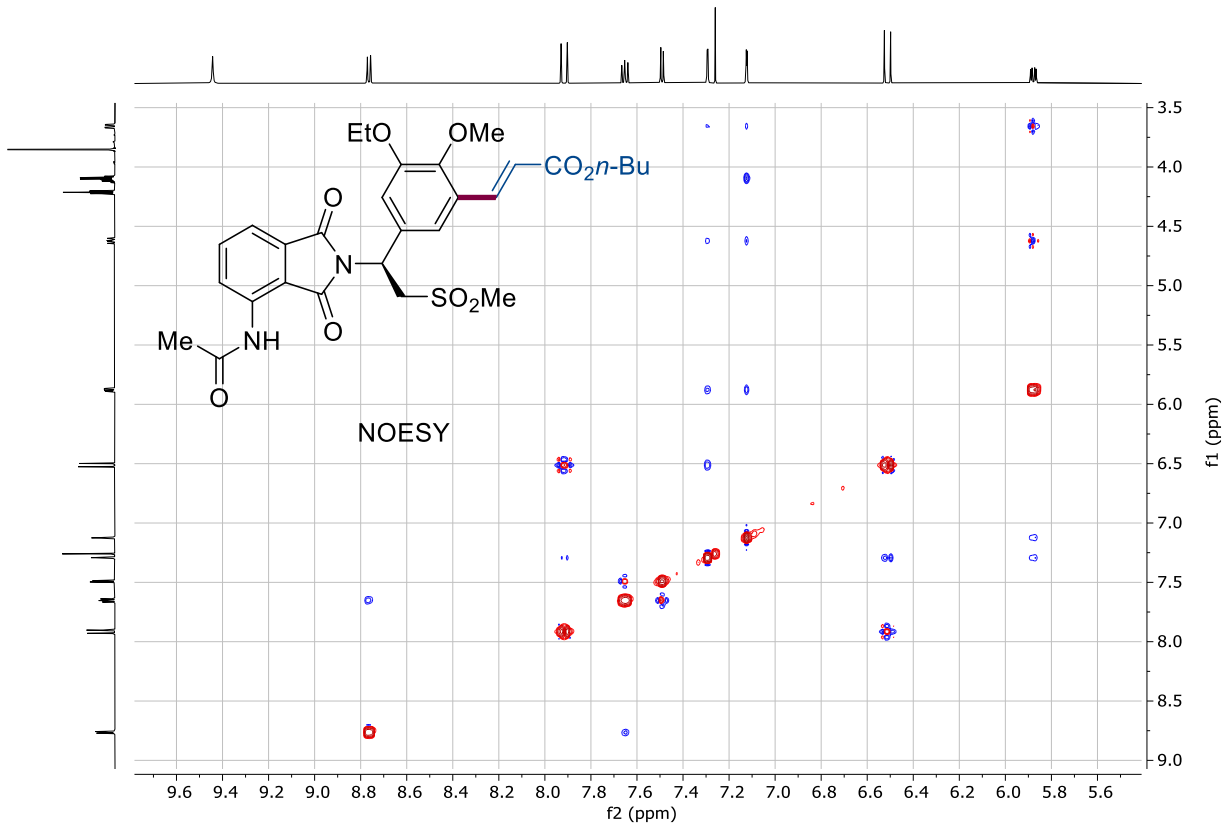
(100 MHz, $CDCl_3$)

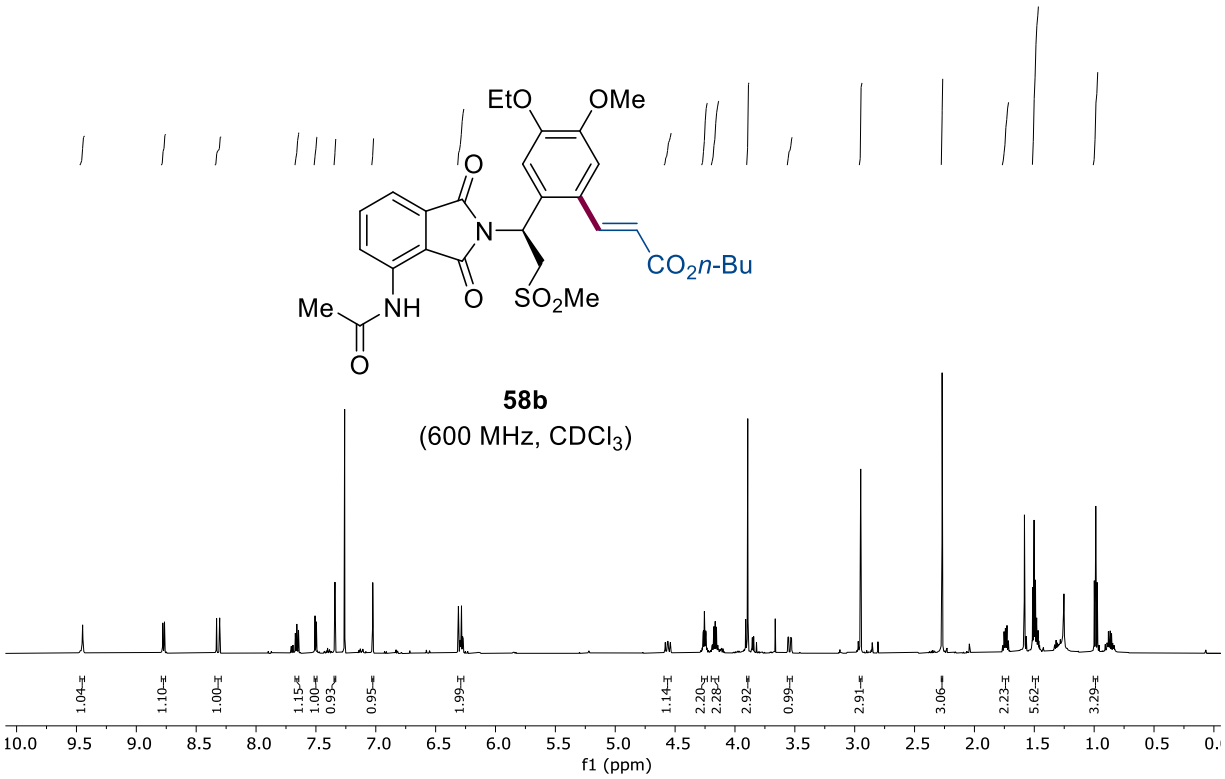


58a

(600 MHz, $CDCl_3$)

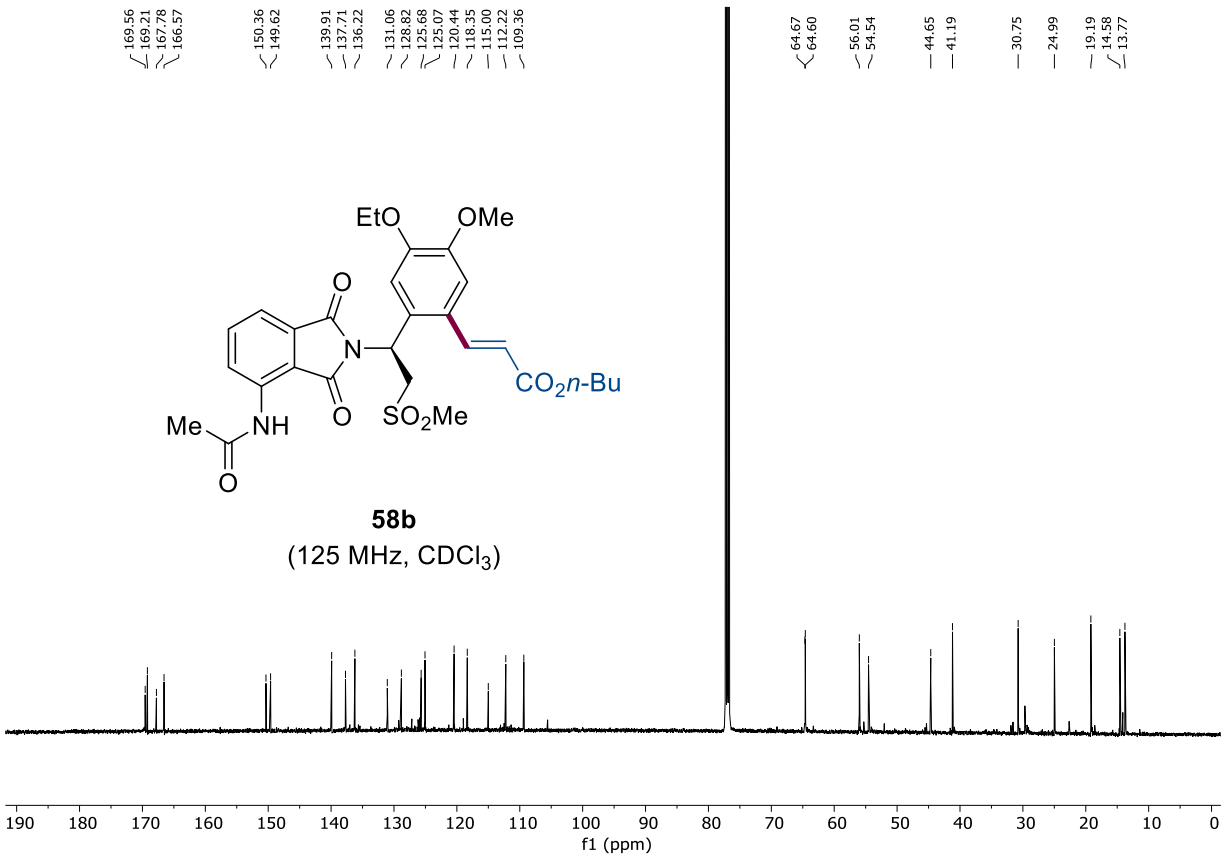

169.41
169.21
167.46
167.03
152.77
148.87
138.62
137.74
136.23
132.68
130.99
128.97
125.09
120.47
118.62
118.33
115.04
114.39
64.65
64.53
61.09
54.03
48.38
41.76
30.75
25.00
19.19
14.75
13.74
EtO
OMe
CO2n-Bu
SO2Me
Me
NH
58a
(125 MHz, CDCl3)
f1 (ppm)


EtO
OMe
CO2n-Bu
SO2Me
Me
NH
NOESY
f1 (ppm)
f2 (ppm)



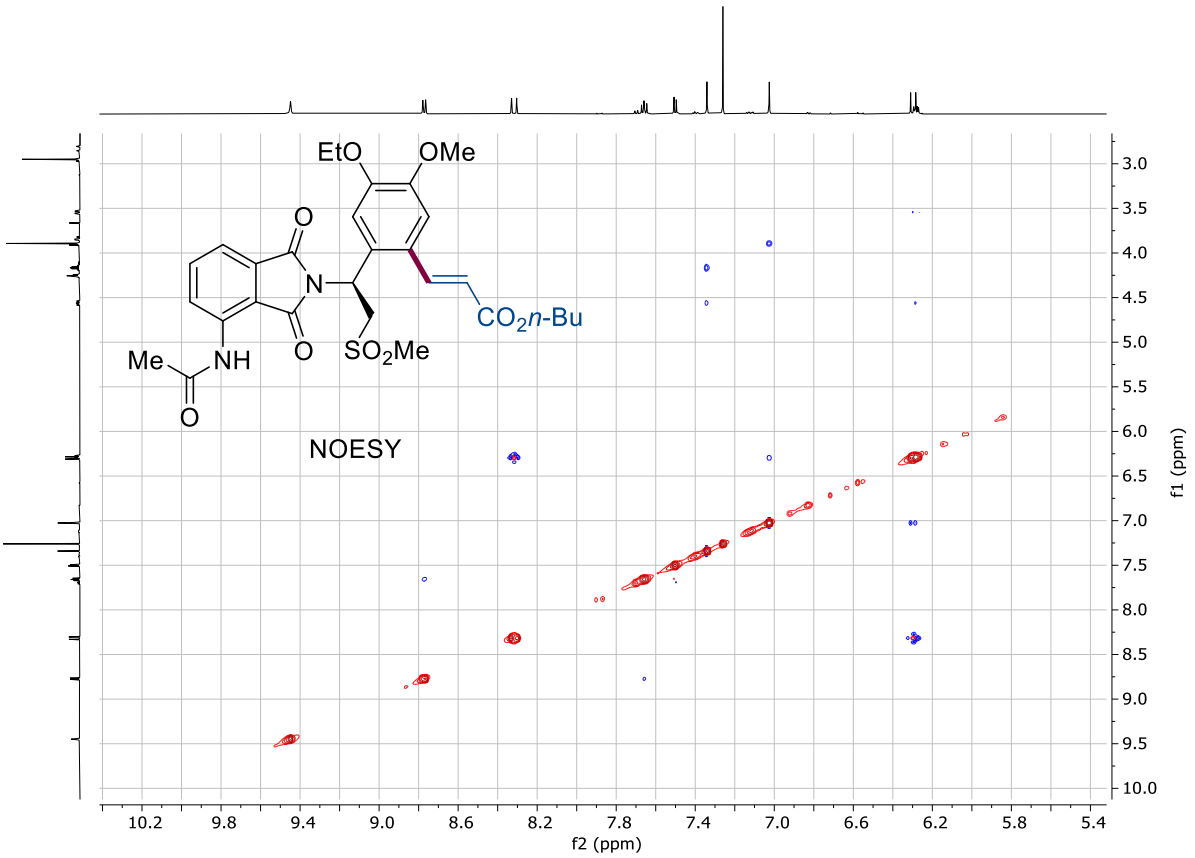
58b

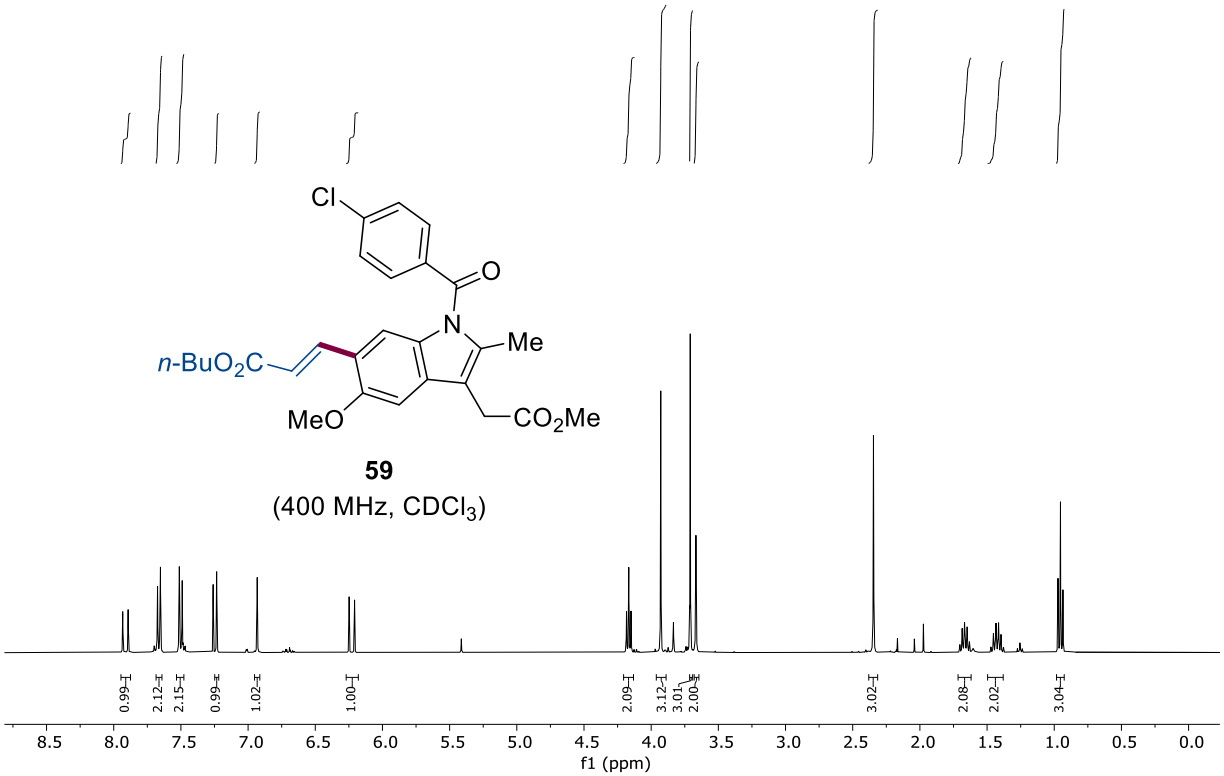
(600 MHz, $CDCl_3$)

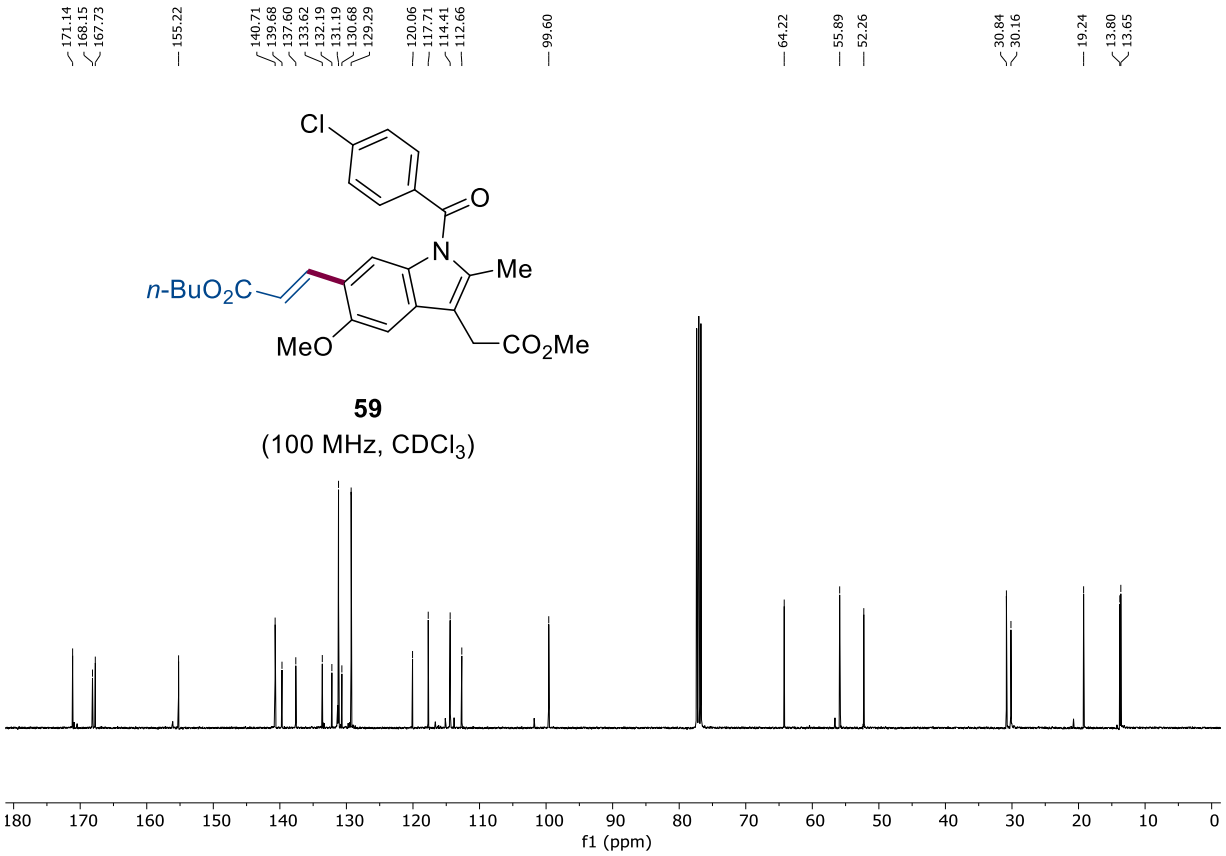


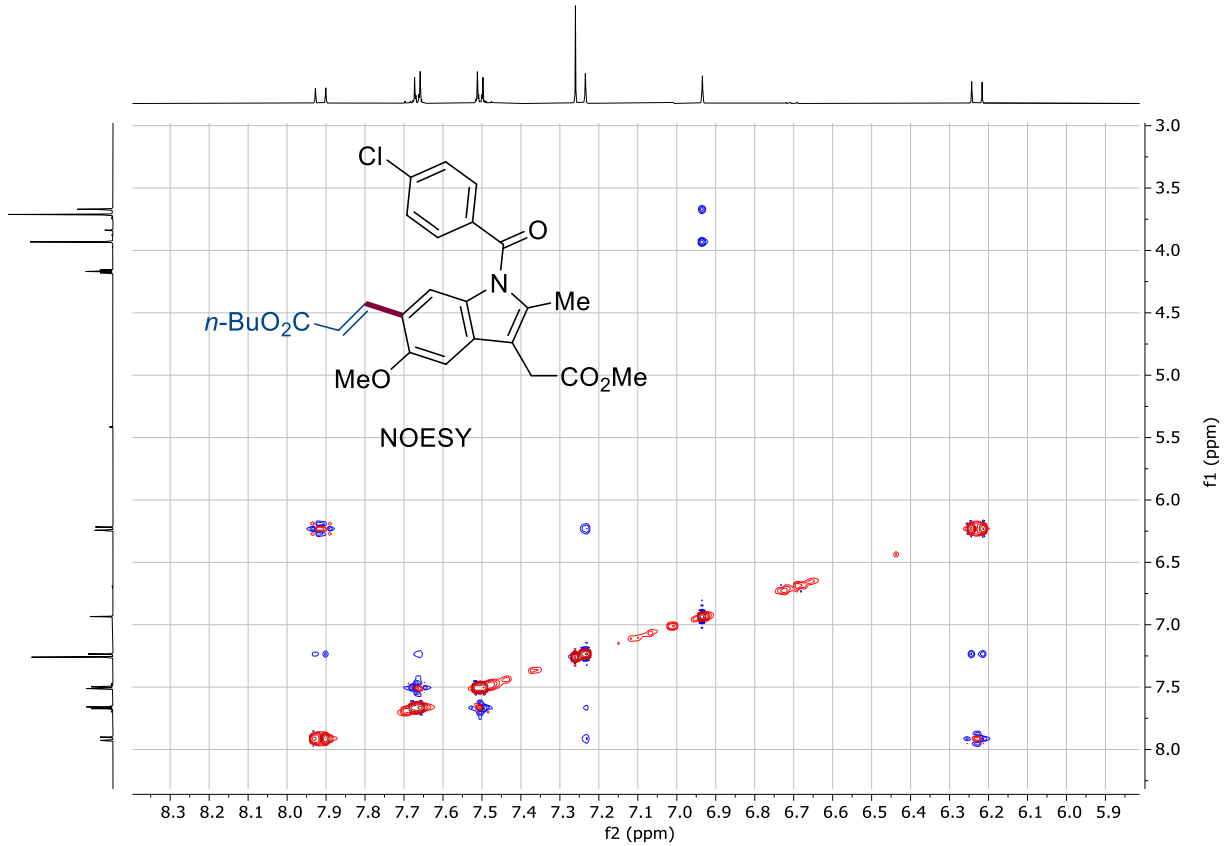
58b

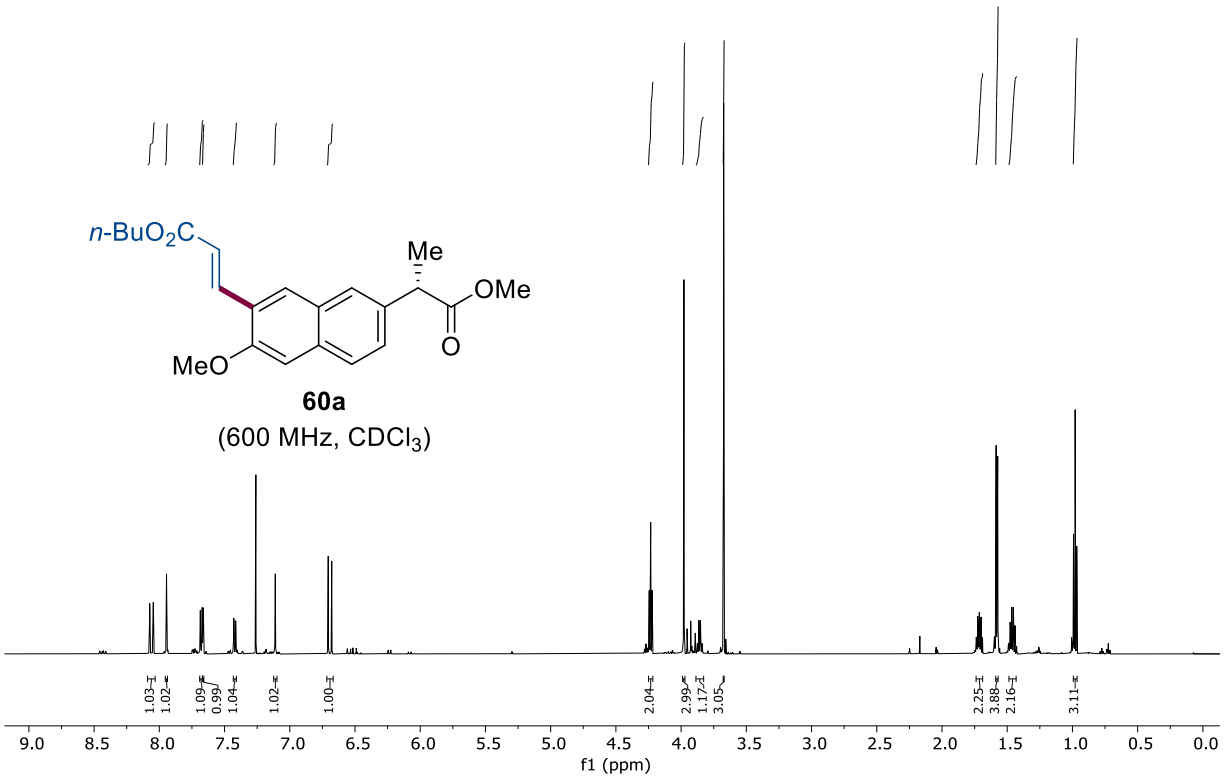
(125 MHz, $CDCl_3$)

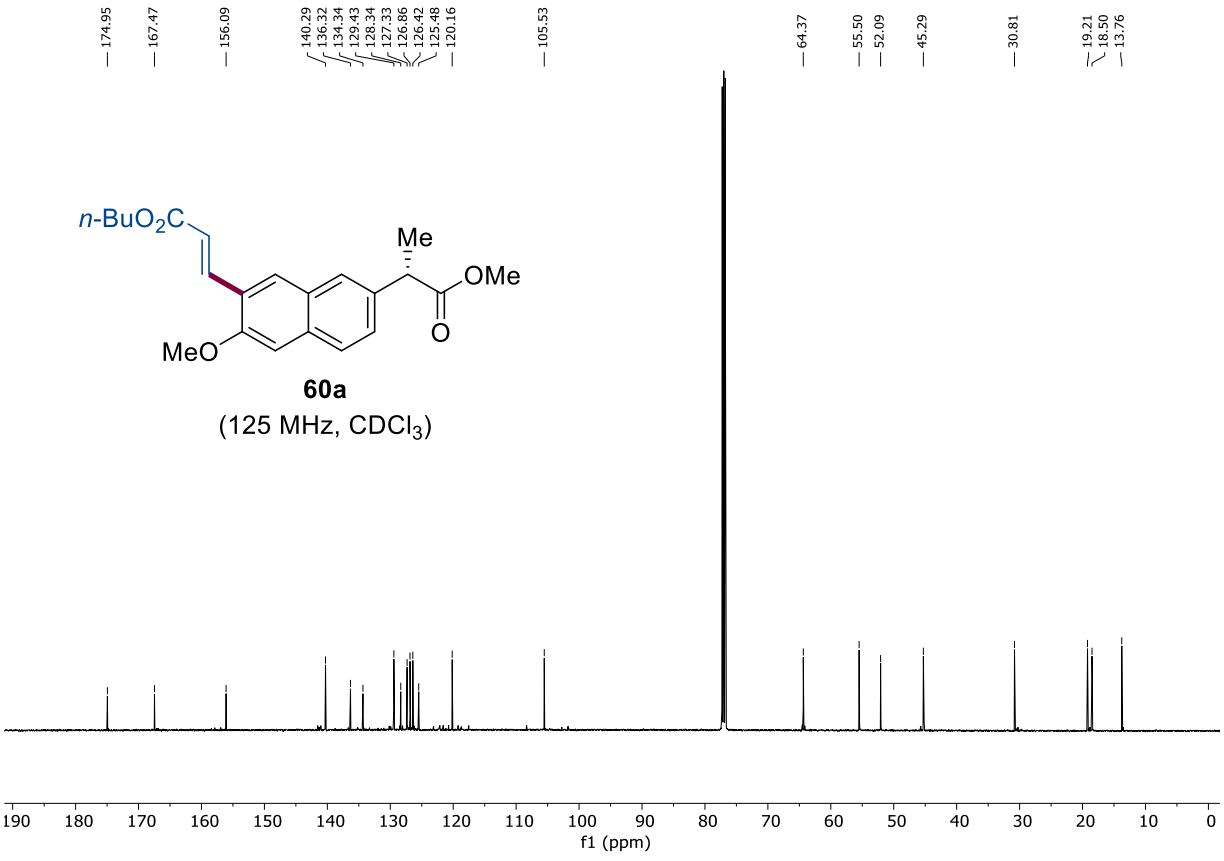

EtO
OMe
O
N
O
CO2n-Bu
Me
NH
O
SO2Me
NOESY
f2 (ppm)
f1 (ppm)

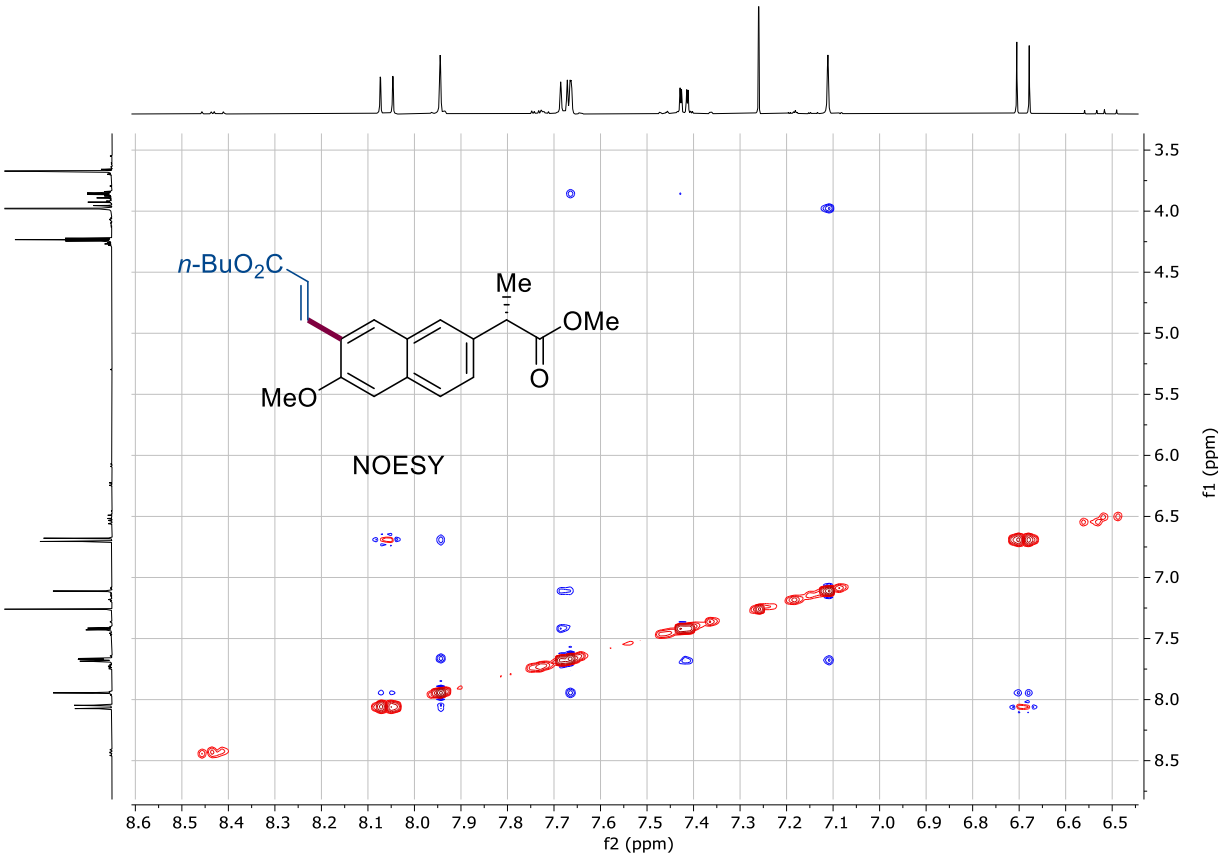

Cl
O
N
Me
n-BuO2C
MeO
CO2Me
59
(400 MHz, CDCl3)
f1 (ppm)

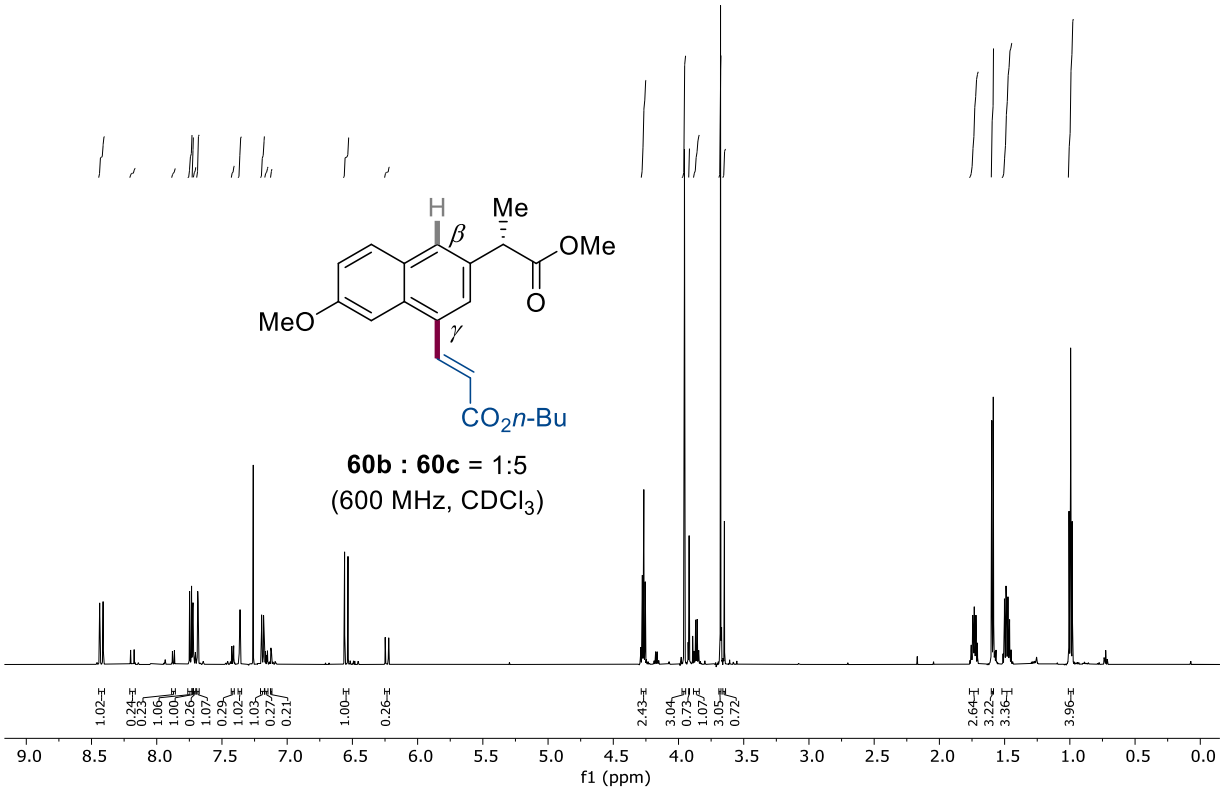

171.14
168.15
167.73
155.22
140.71
139.68
137.60
133.62
132.19
131.19
130.68
129.29
120.06
117.71
114.41
112.66
99.60
64.22
55.89
52.26
30.84
30.16
19.24
13.80
13.65
Cl
O
N
Me
n-BuO2C
MeO
CO2Me
59
(100 MHz, CDCl3)
f1 (ppm)

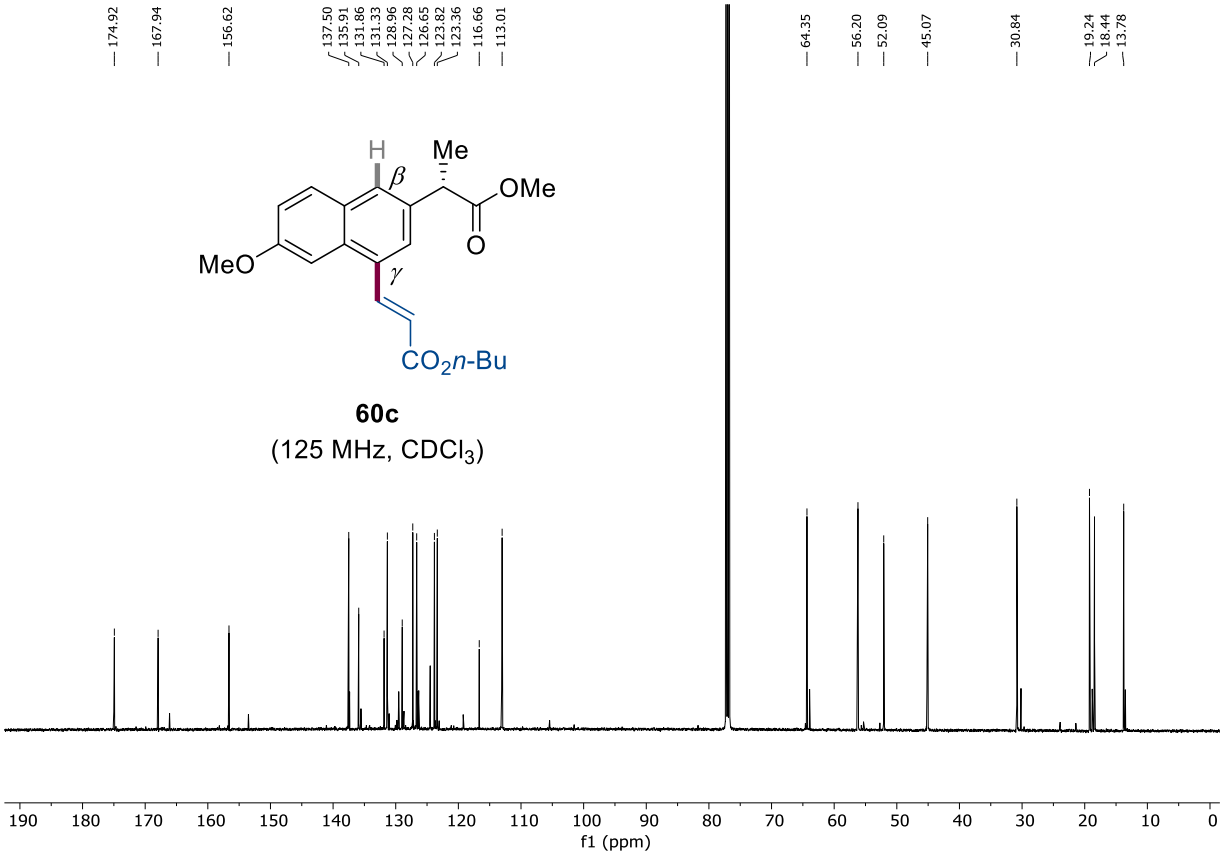

Cl
O
N
Me
n-BuO2C
MeO
CO2Me
NOESY
f1 (ppm)
f2 (ppm)

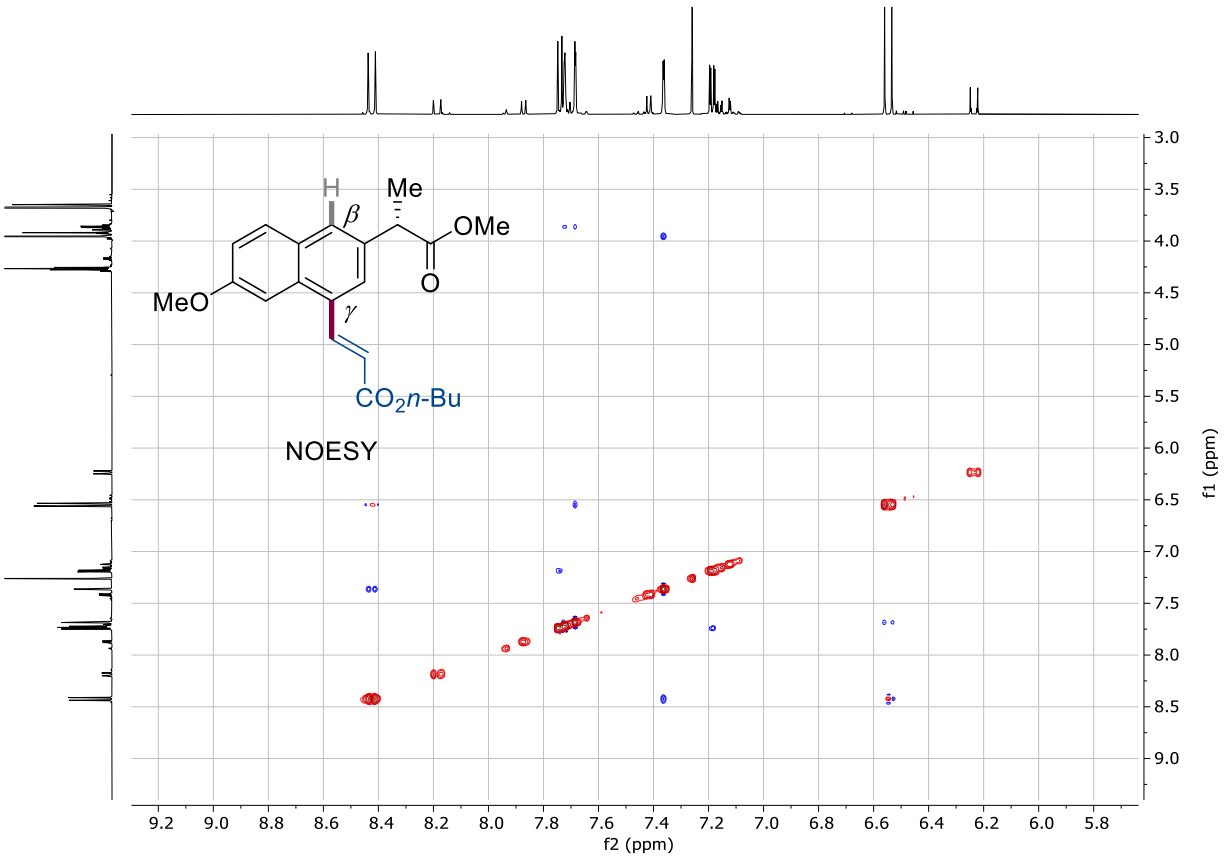

n-BuO2C
Me
OMe
O
MeO
60a
(600 MHz, CDCl3)
1.03
1.02
1.09
0.99
1.04
1.02
1.00
2.04
2.99
1.17
3.05
2.25
3.88
2.16
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

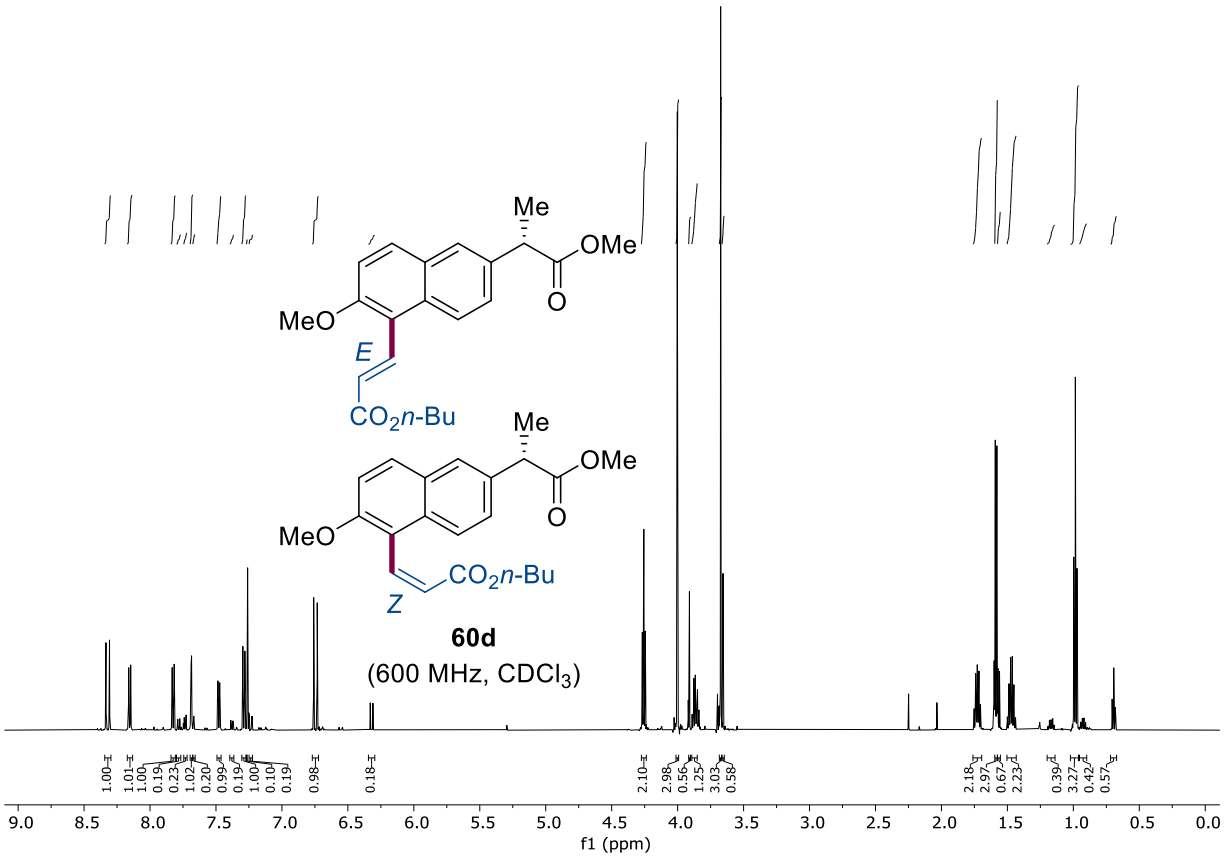

174.95
167.47
156.09
140.29
136.32
134.34
129.43
128.34
127.33
126.86
126.42
125.48
120.16
105.53
64.37
55.50
52.09
45.29
30.81
19.21
18.50
13.76
n-BuO2C
Me
OMe
O
MeO
60a
(125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

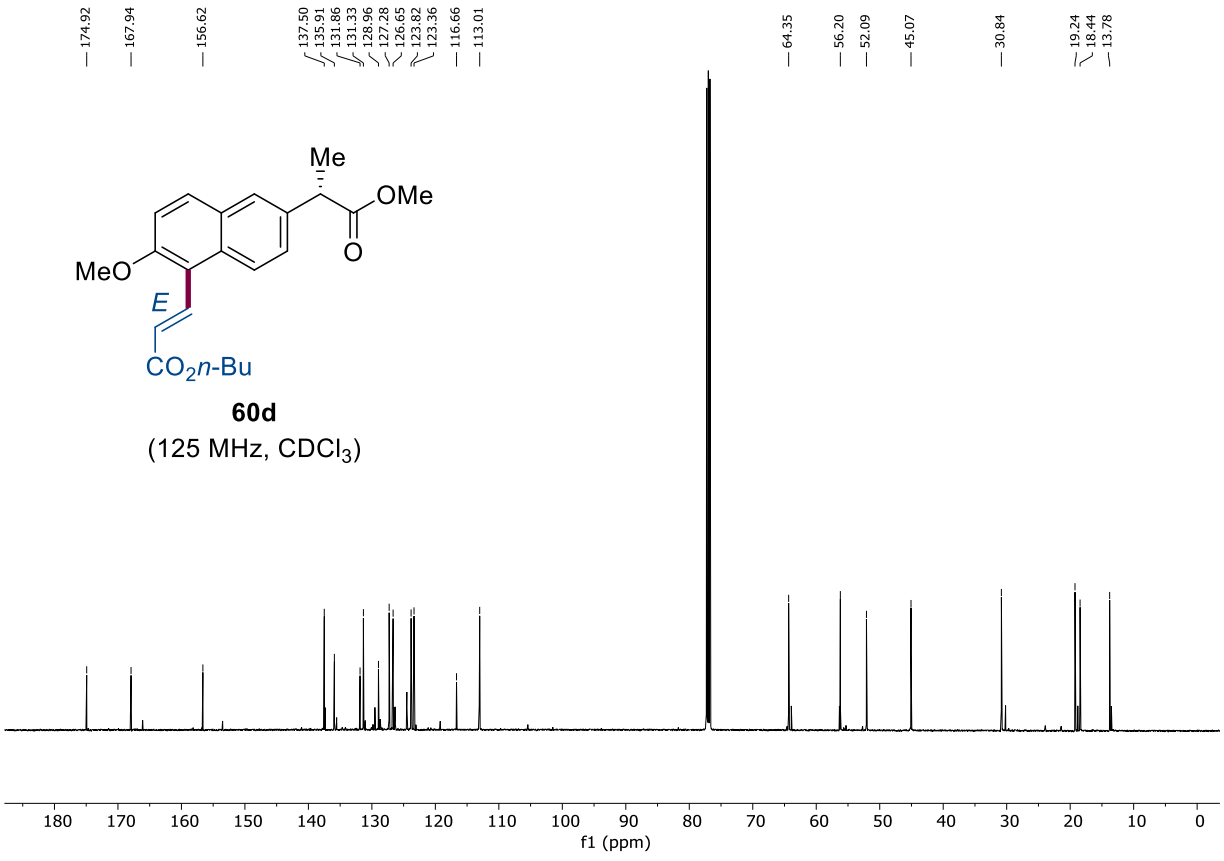

n-BuO2C
Me
OMe
O
MeO
NOESY
f2 (ppm)
f1 (ppm)

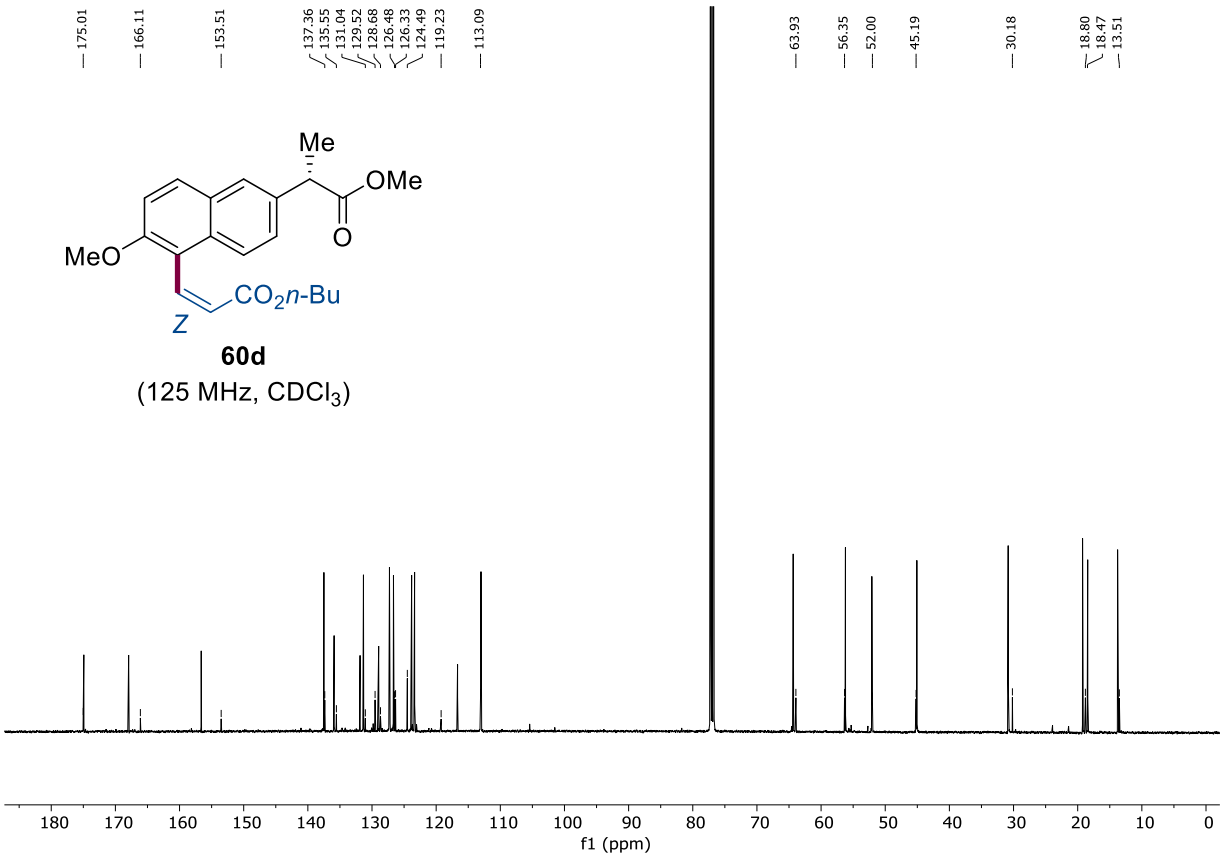

H
β
Me
OMe
O
MeO
γ
CO2n-Bu
60b : 60c = 1:5
(600 MHz, CDCl3)
f1 (ppm)

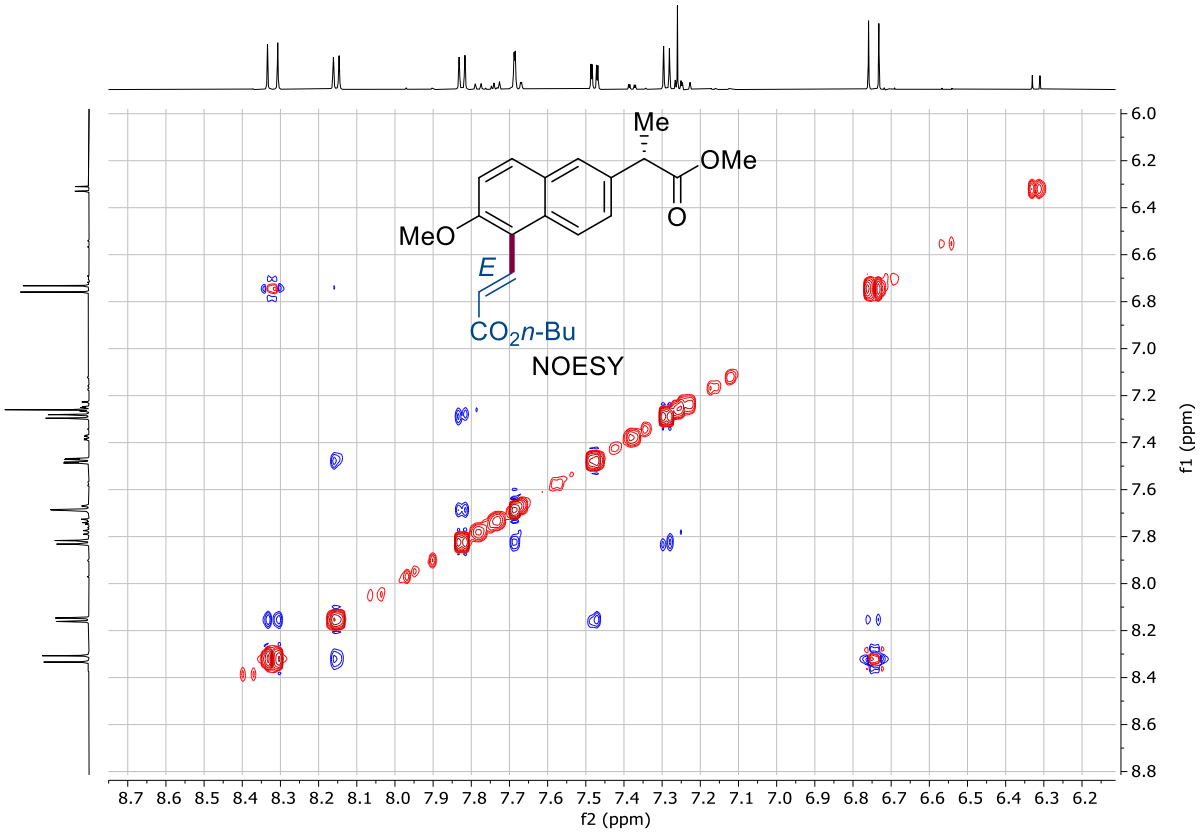

174.92
167.94
156.62
137.50
135.91
131.86
131.33
128.96
127.28
126.65
123.82
123.36
116.66
113.01
64.35
56.20
52.09
45.07
30.84
19.24
18.44
13.78
H
Me
β
OMe
O
MeO
γ
CO2n-Bu
60c
(125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

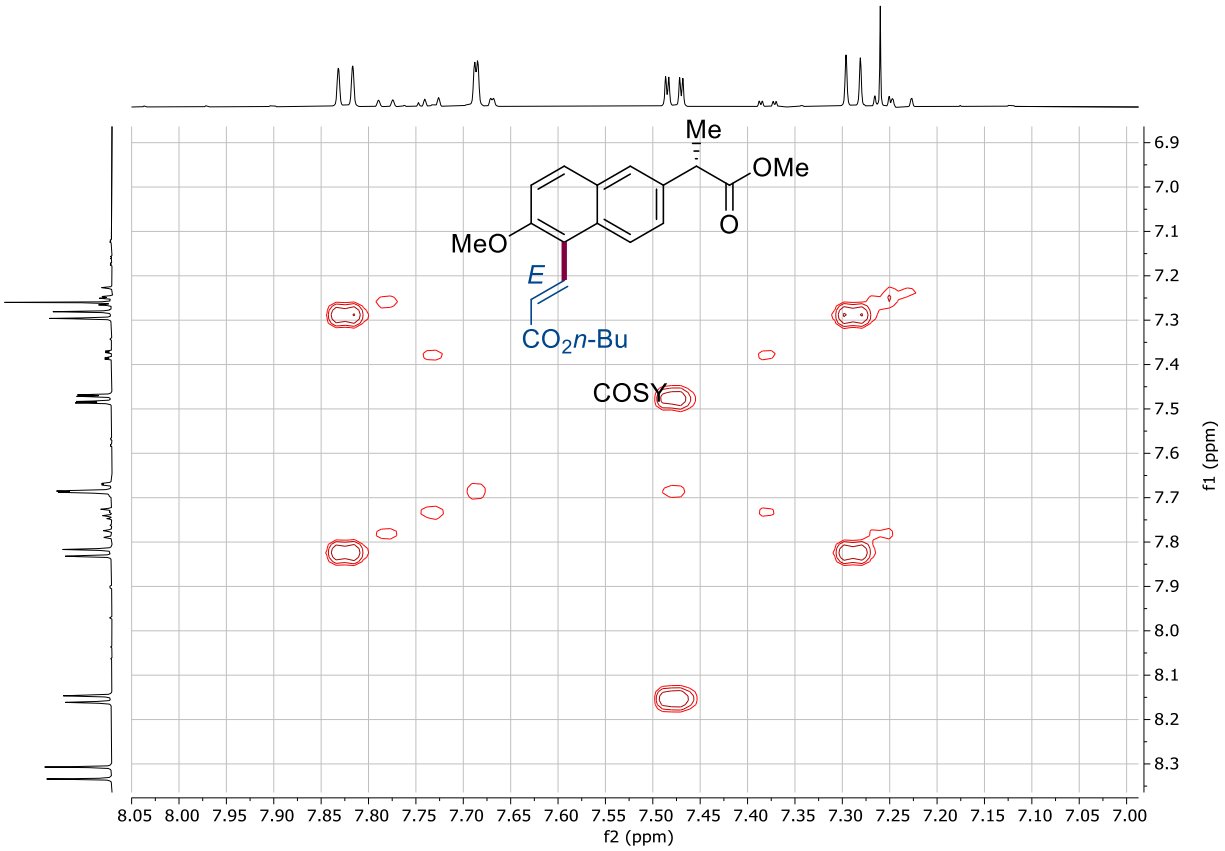

H
Me
β
OMe
O
MeO
γ
CO2n-Bu
NOESY
3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0
f1 (ppm)
9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8
f2 (ppm)

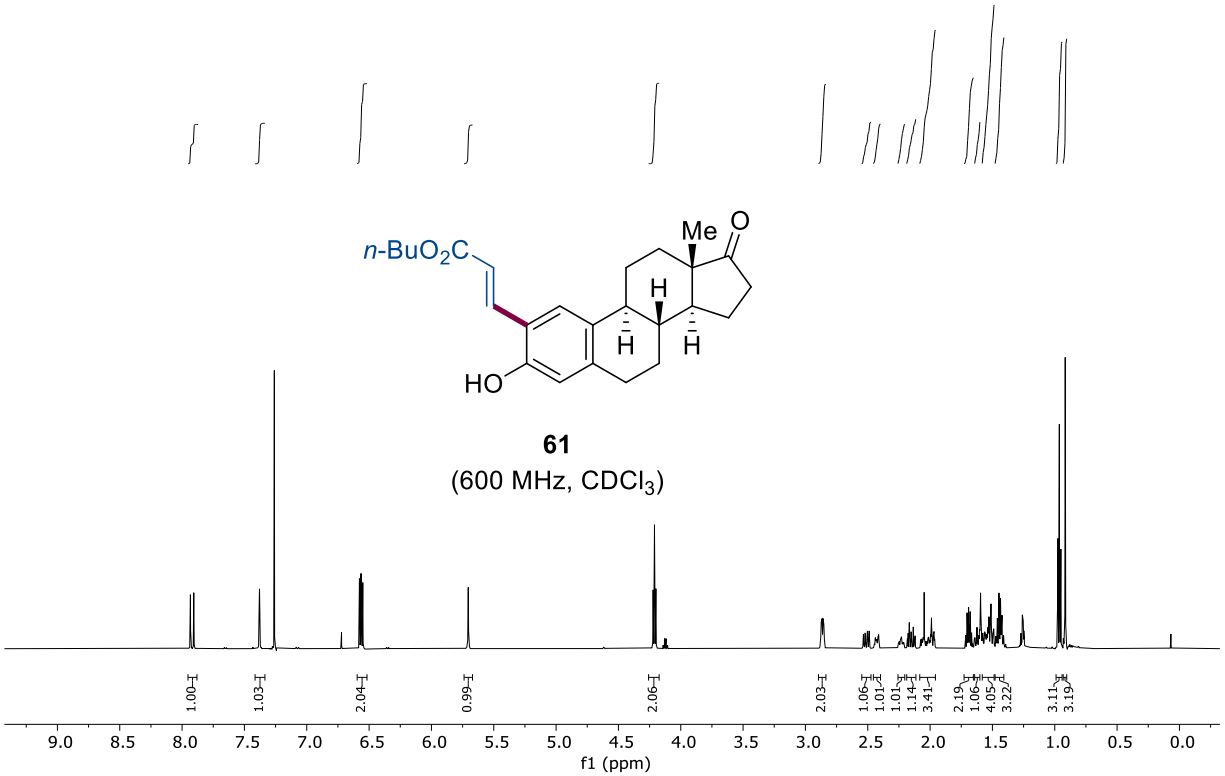

Me
OMe
O
MeO
E
CO2n-Bu
Me
OMe
O
MeO
CO2n-Bu
Z
60d
(600 MHz, CDCl3)
f1 (ppm)


174.92
167.94
156.62
137.50
135.91
131.86
131.33
128.96
127.28
126.65
123.82
123.36
116.66
113.01
64.35
56.20
52.09
45.07
30.84
19.24
18.44
13.78
Me
OMe
O
MeO
E
CO2n-Bu
60d
(125 MHz, CDCl3)
f1 (ppm)


175.01
166.11
153.51
137.36
135.55
131.04
129.52
128.68
126.48
126.33
124.49
119.23
113.09
63.93
56.35
52.00
45.19
30.18
18.80
18.47
13.51
Me
OMe
O
MeO
CO2n-Bu
Z
60d
(125 MHz, CDCl3)
f1 (ppm)

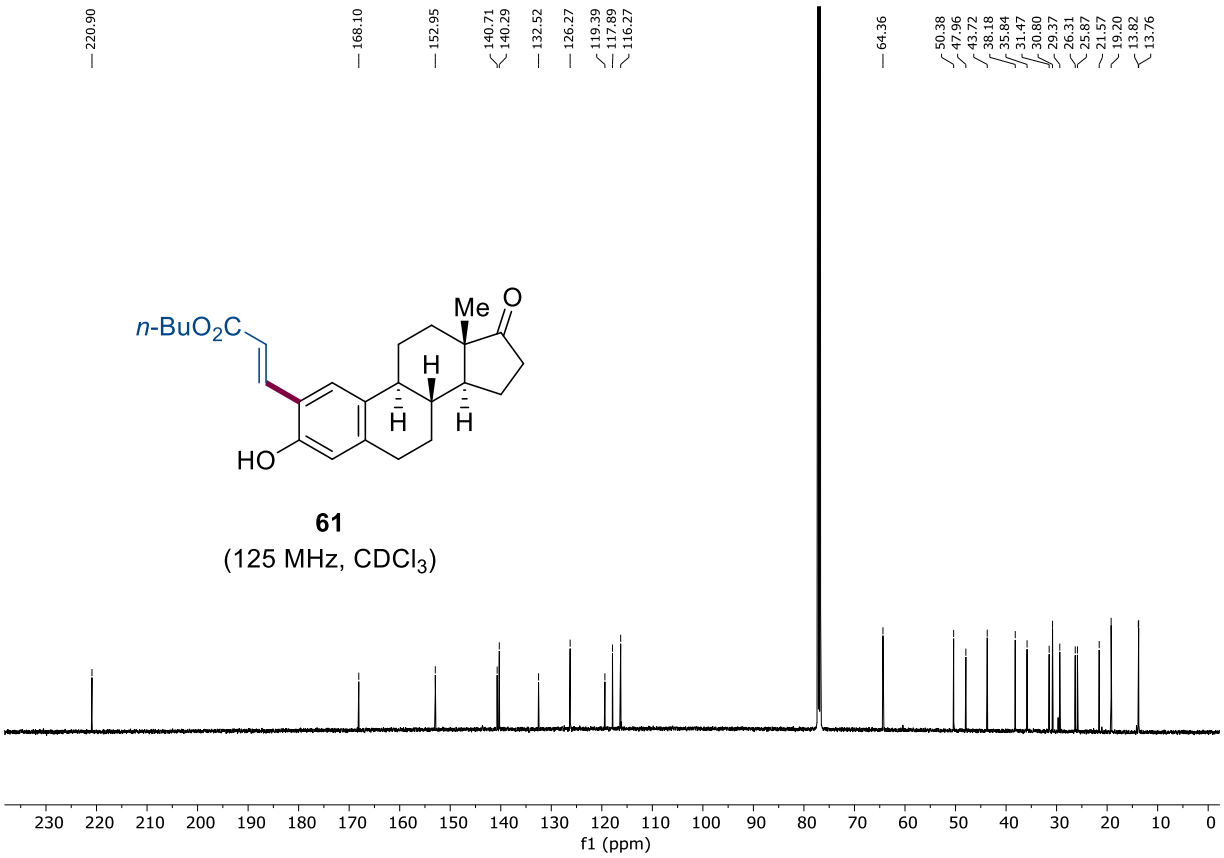

Me
OMe
O
MeO
E
CO2n-Bu
NOESY
f1 (ppm)
f2 (ppm)

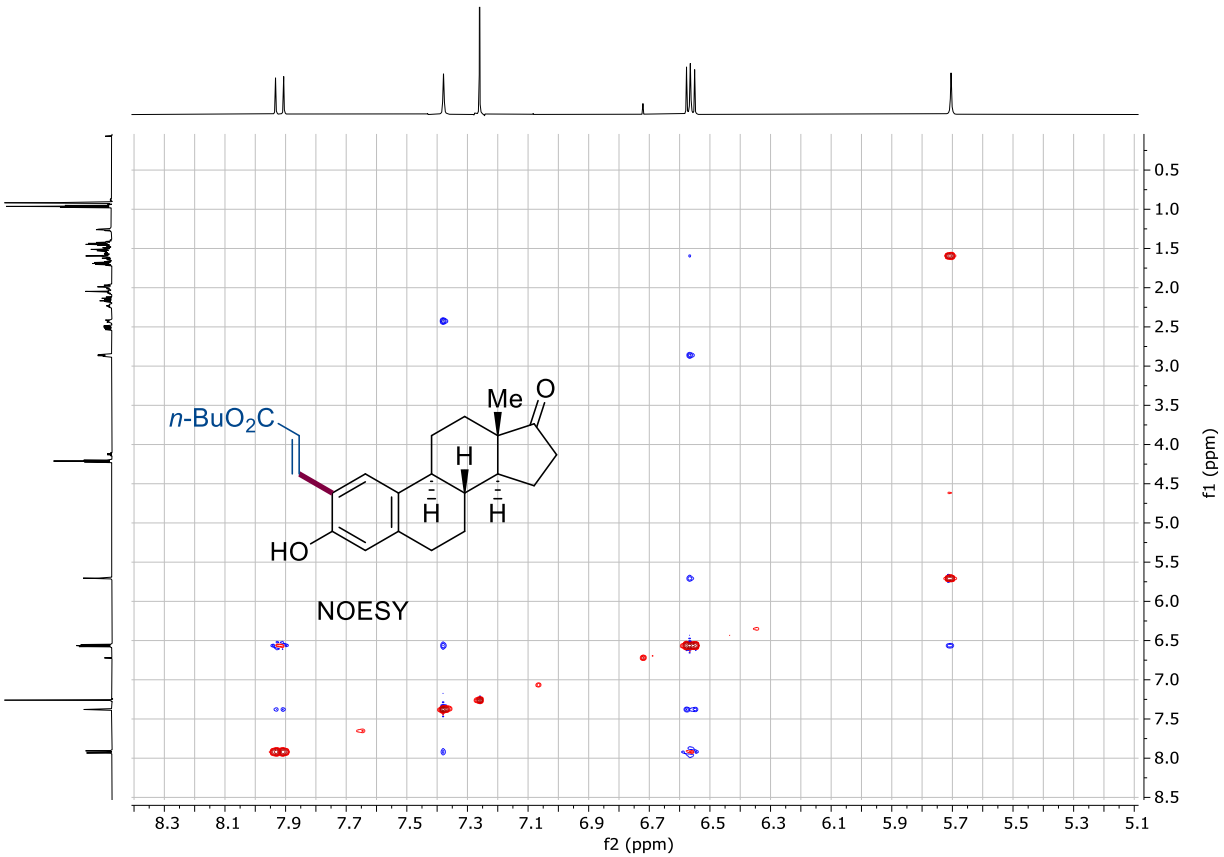


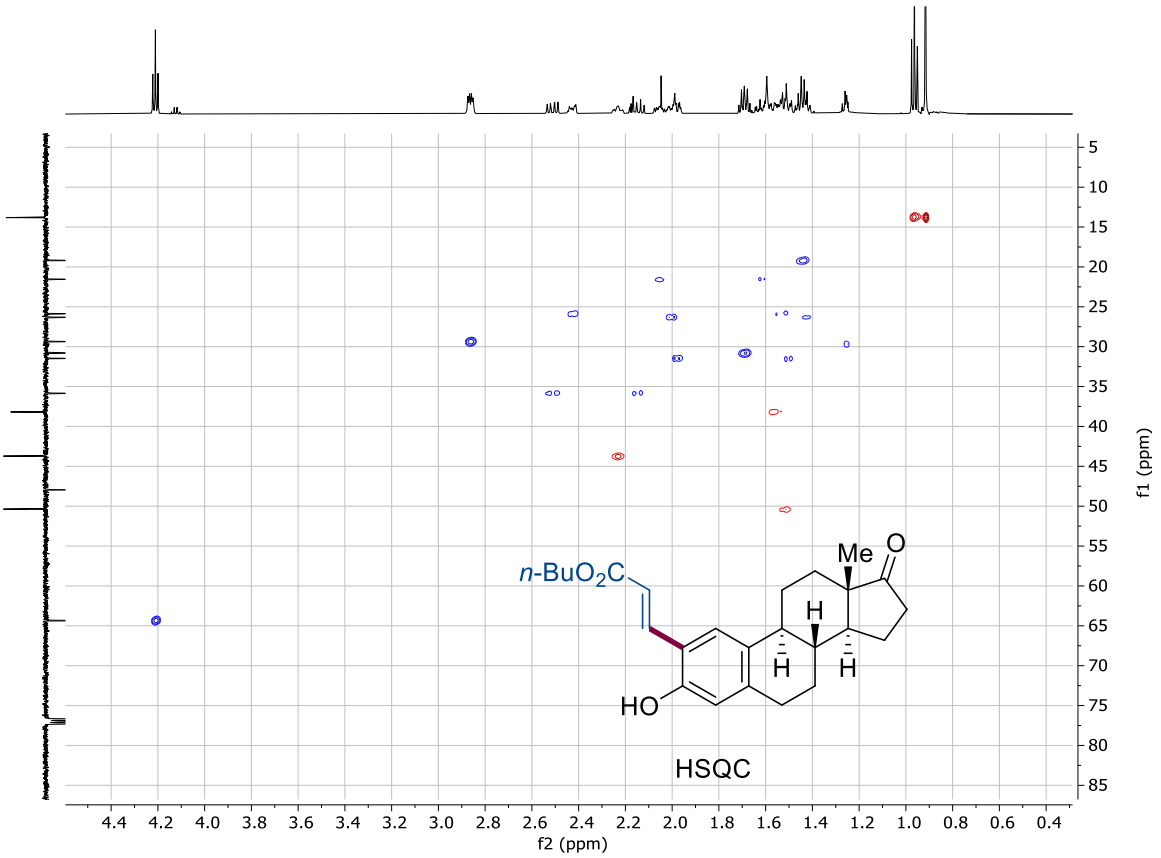


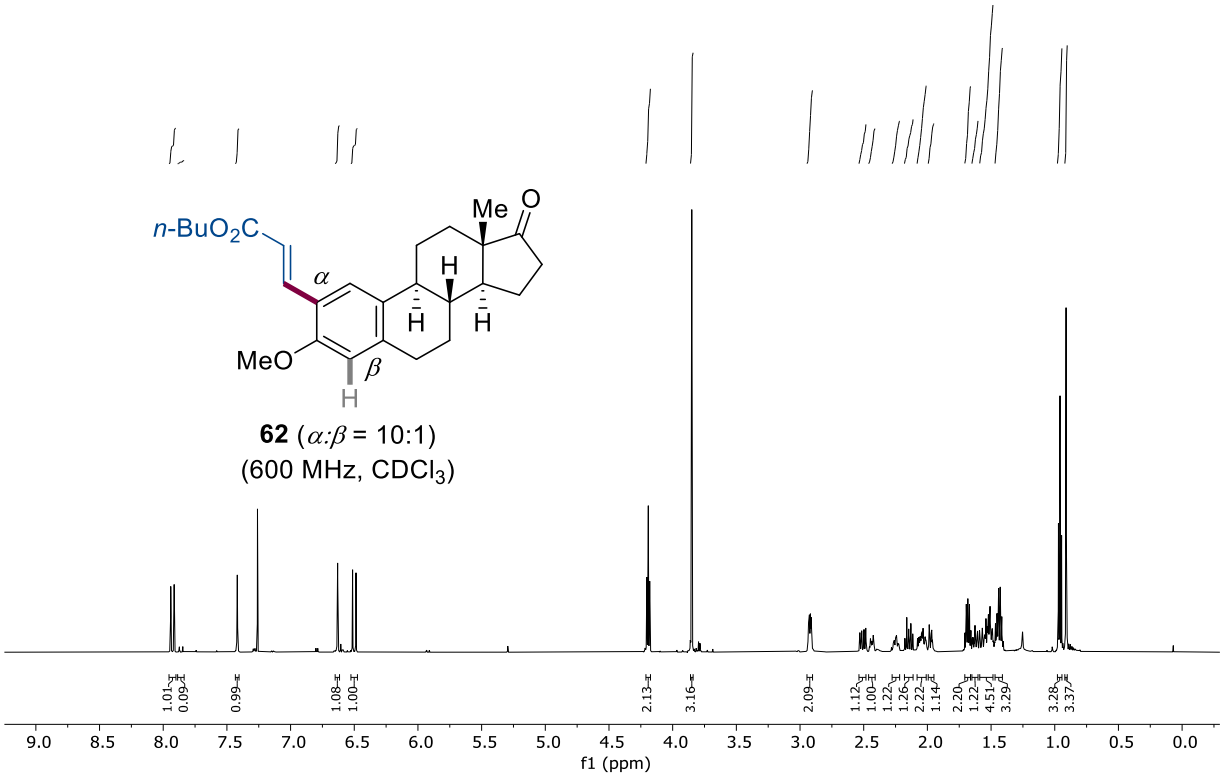
61

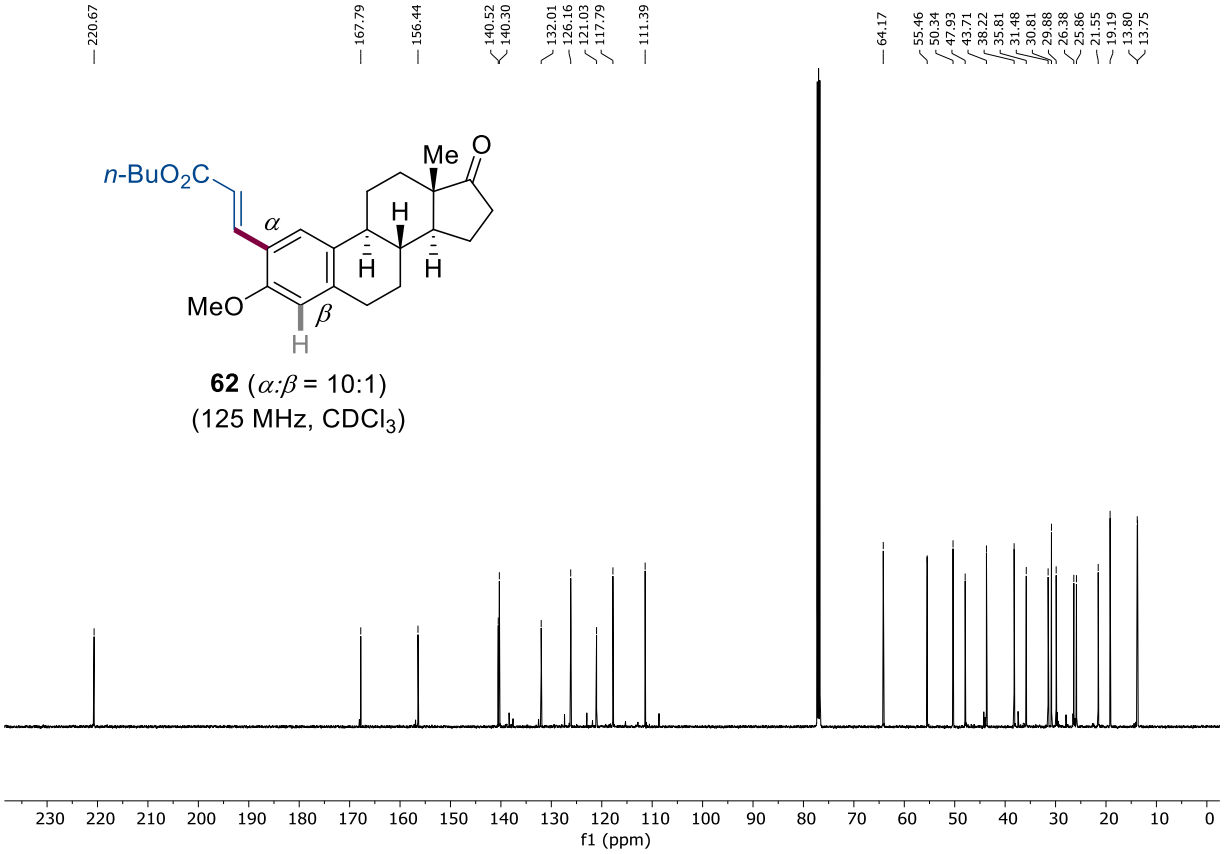
(600 MHz, $CDCl_3$)


220.90
168.10
152.95
140.71
140.29
132.52
126.27
119.39
117.89
116.27
64.36
50.38
47.96
43.72
38.18
35.84
31.47
30.80
29.37
26.31
25.87
21.57
19.20
13.82
13.76
n-BuO2C
Me
O
H
H
H
HO
61
(125 MHz, CDCl3)
f1 (ppm)

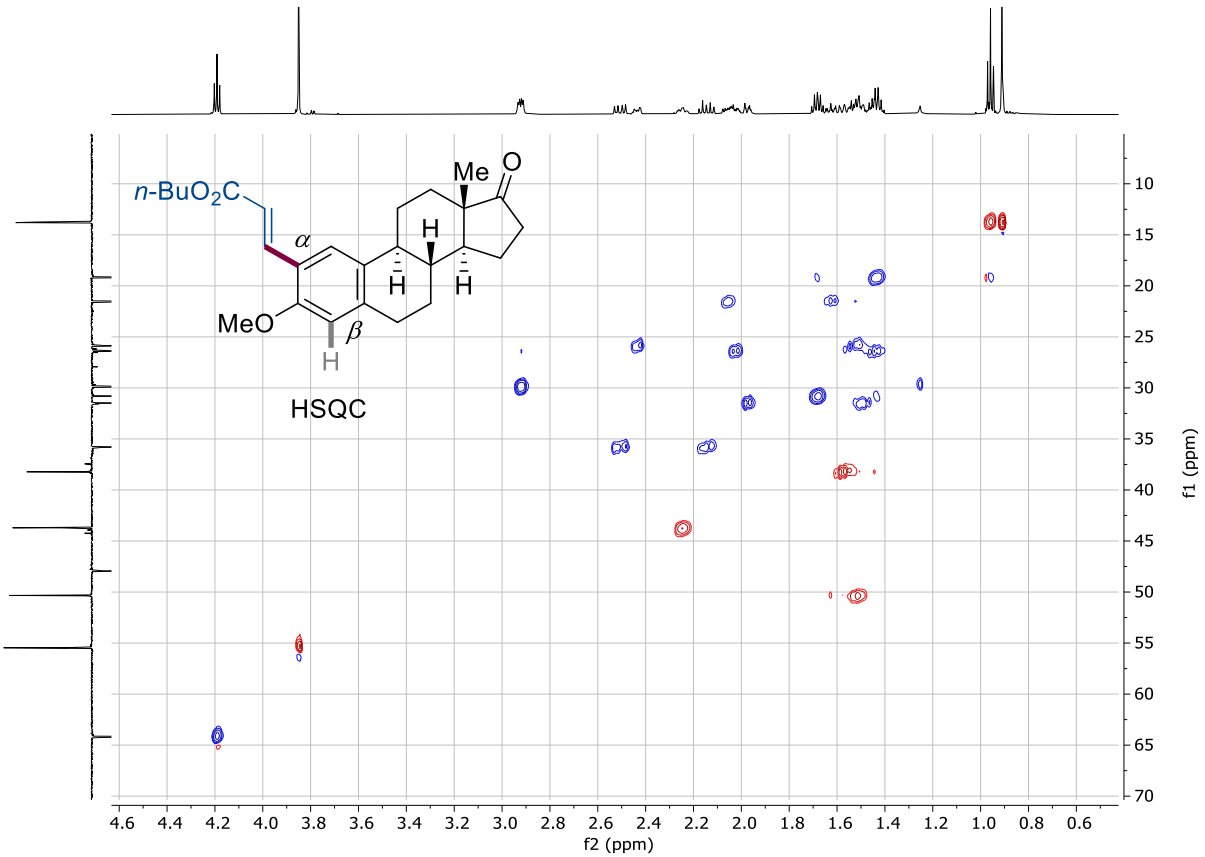

n-BuO2C
Me
O
H
H
H
HO
NOESY
f2 (ppm)
f1 (ppm)

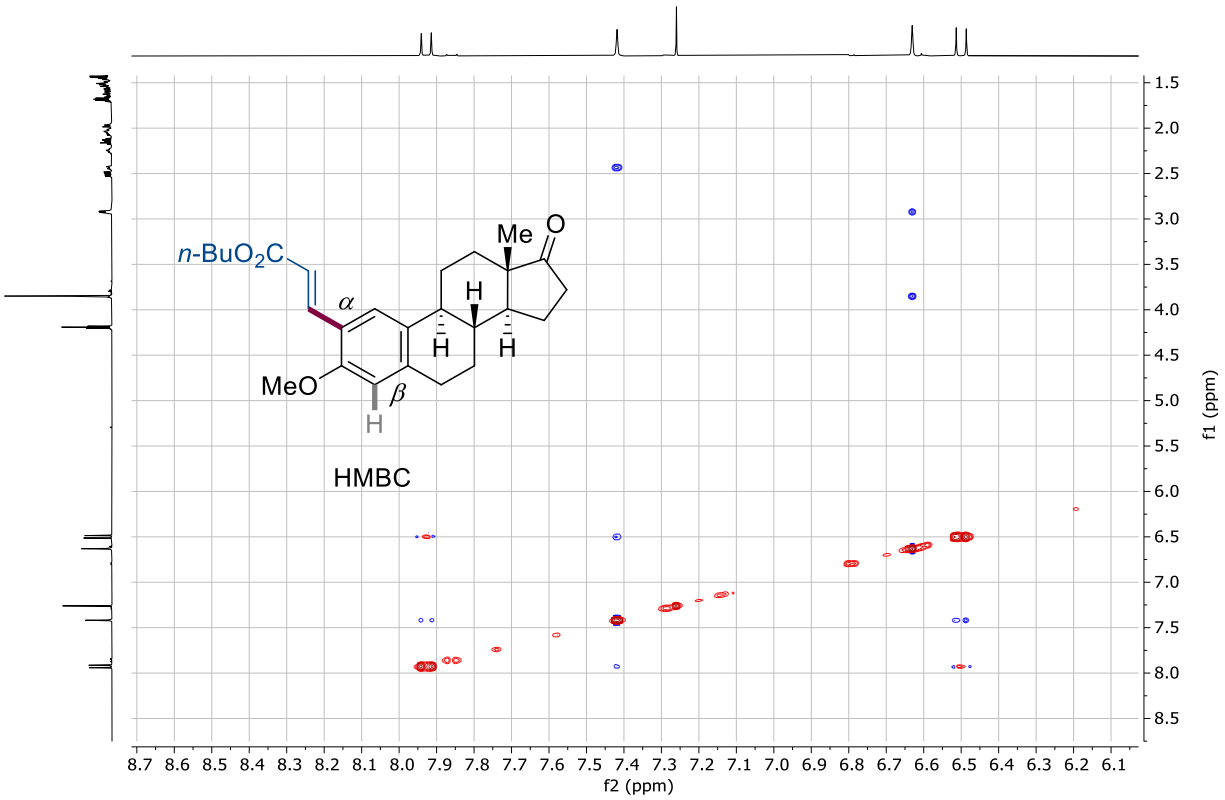

n-BuO2C
Me
O
H
HO
HSQC
f2 (ppm)
f1 (ppm)

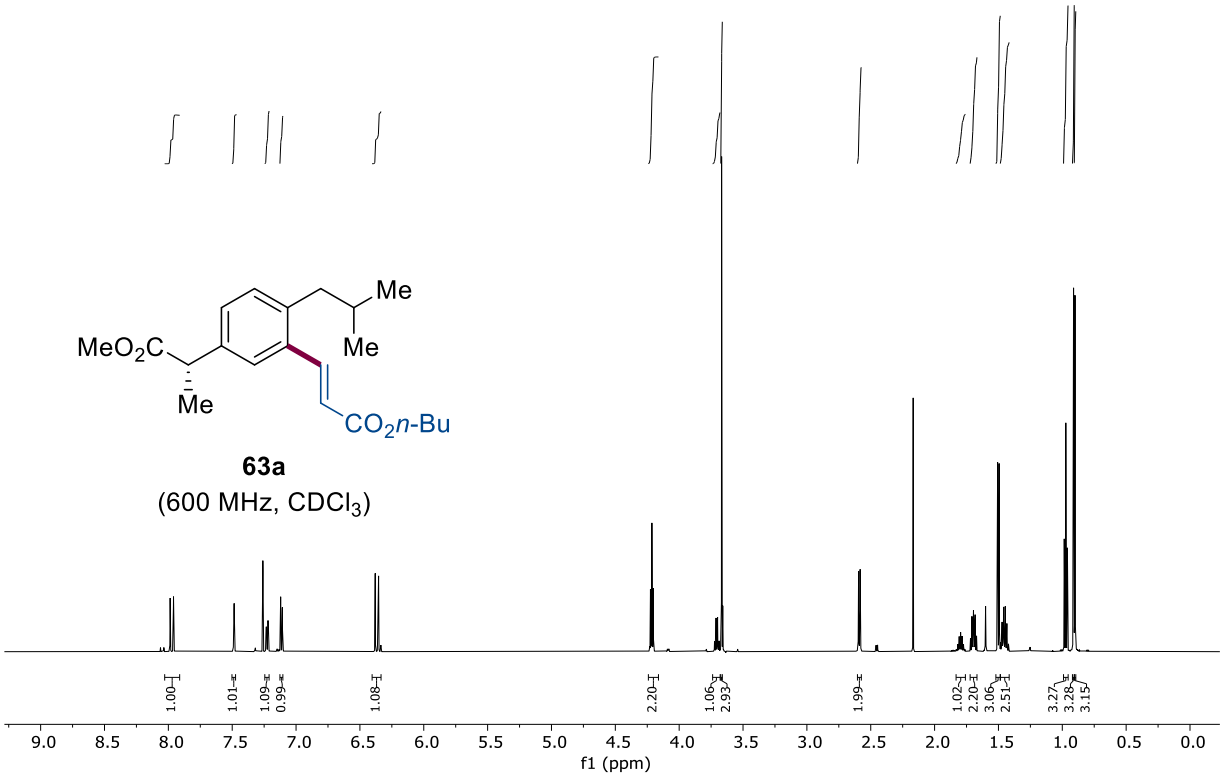

n-BuO2C
α
Me
O
H
MeO
β
H
62 (α:β = 10:1)
(600 MHz, CDCl3)
f1 (ppm)

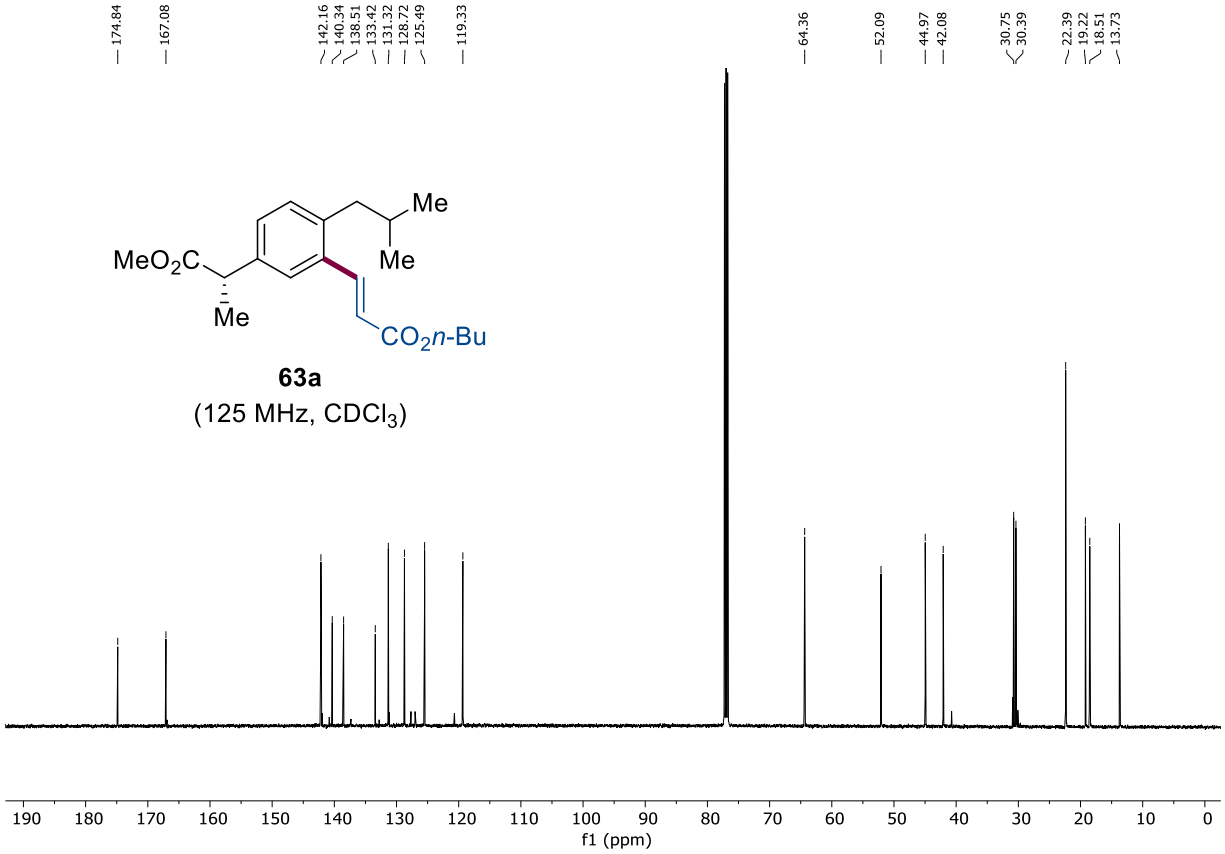


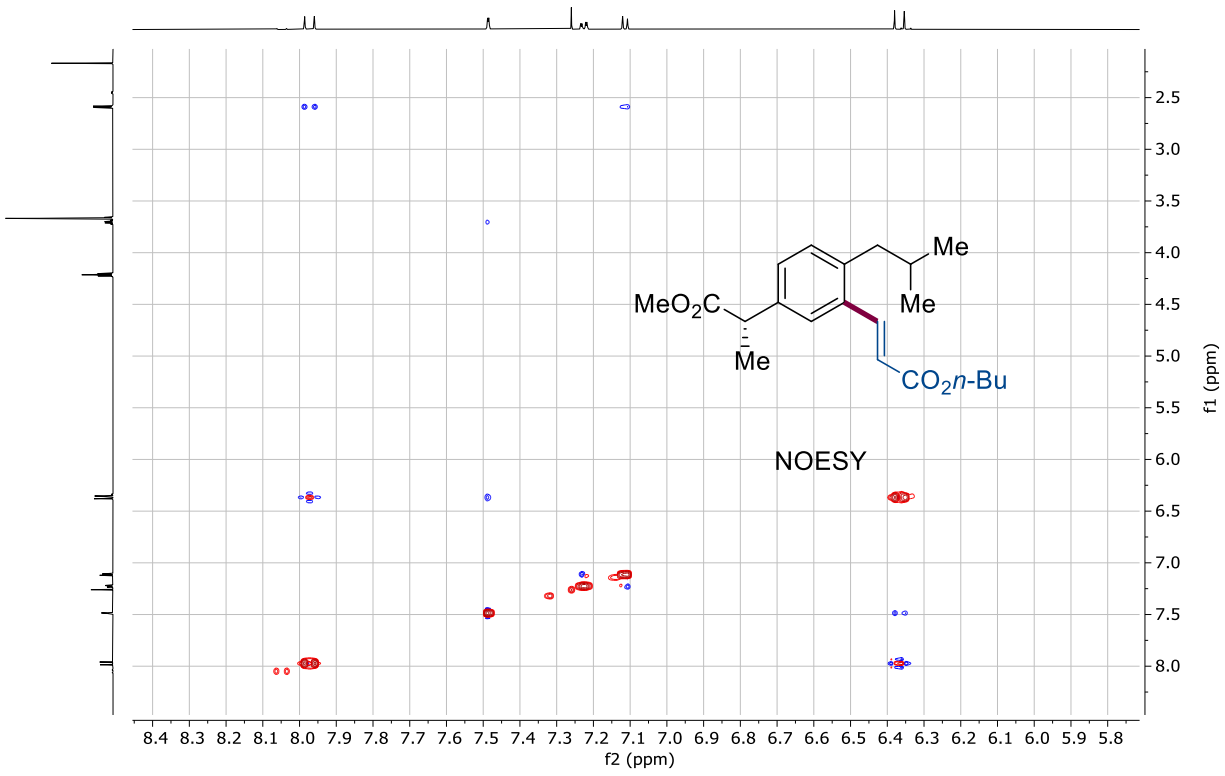
62 (α:β = 10:1)
(125 MHz, $CDCl_3$)

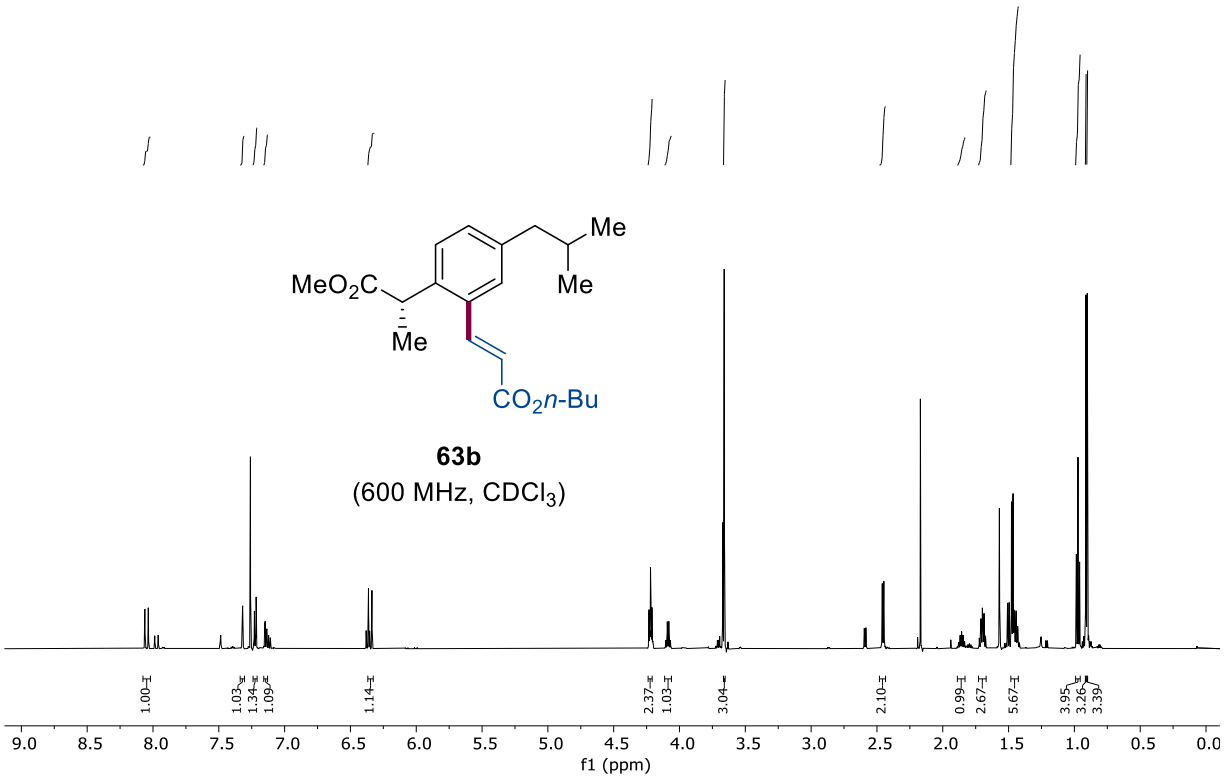



n-BuO2C
α
MeO
β
H
Me
O
H
H
H
HMBC
f2 (ppm)
f1 (ppm)


MeO2C
Me
Me
Me
CO2n-Bu
63a
(600 MHz, CDCl3)
f1 (ppm)

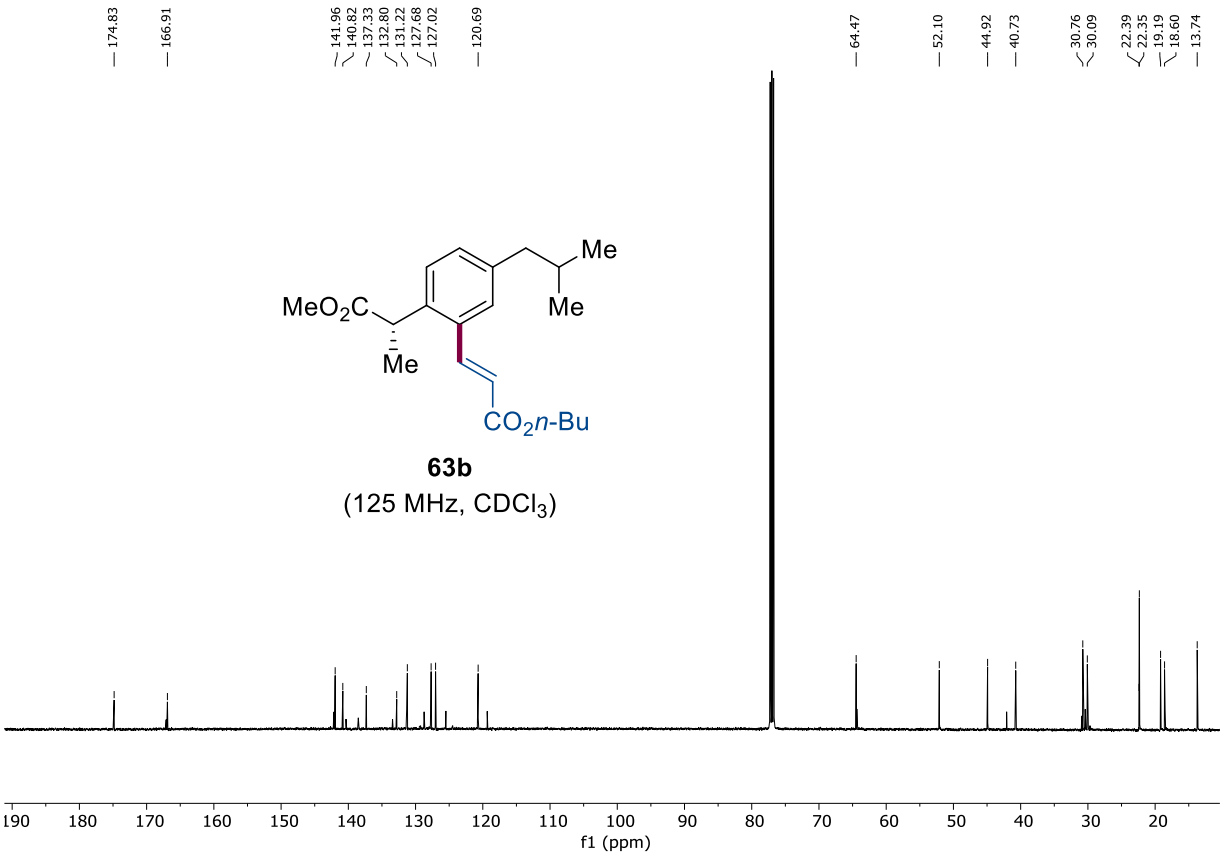

174.84
167.08
142.16
140.34
138.51
133.42
131.32
128.72
125.49
119.33
64.36
52.09
44.97
42.08
30.75
30.39
22.39
19.22
18.51
13.73
Me
MeO2C
Me
Me
CO2n-Bu
63a
(125 MHz, CDCl3)
f1 (ppm)


Me
MeO2C
Me
Me
CO2n-Bu
NOESY
f1 (ppm)
f2 (ppm)



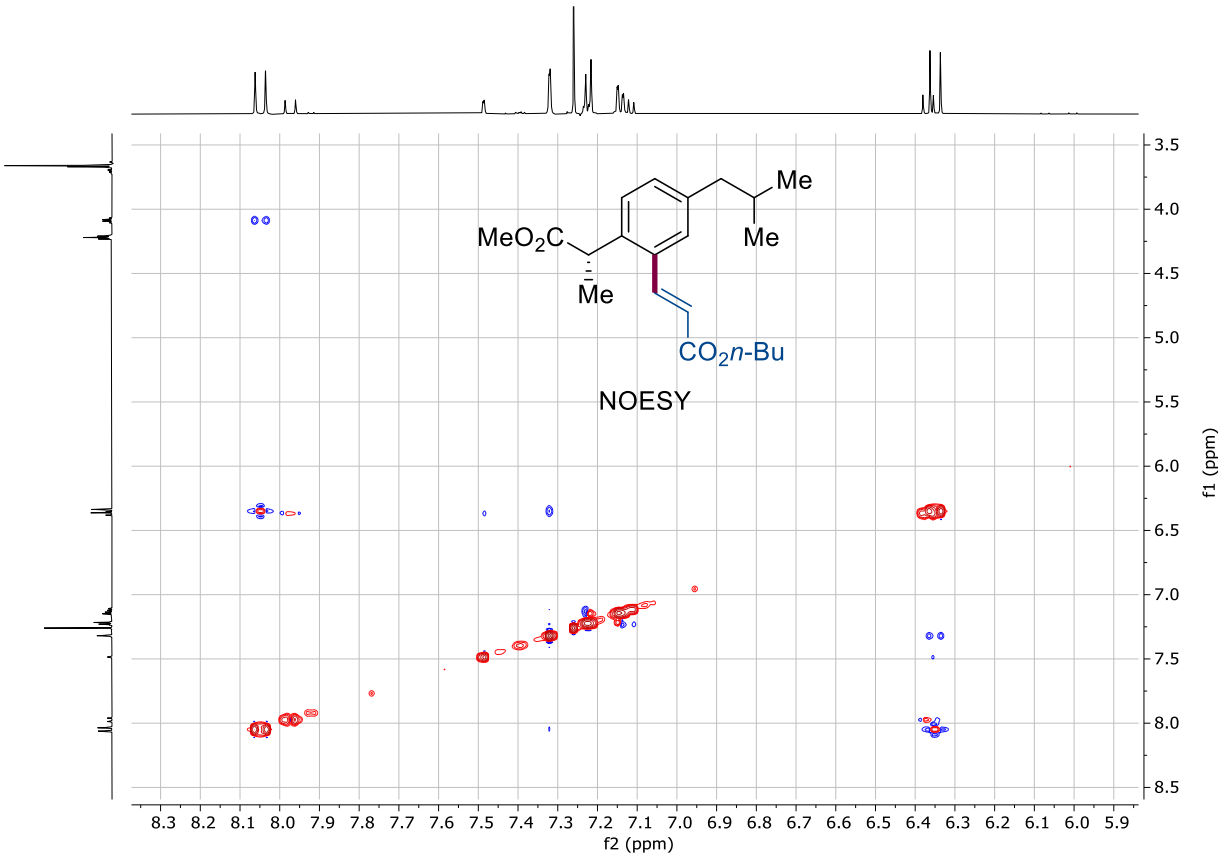
63b

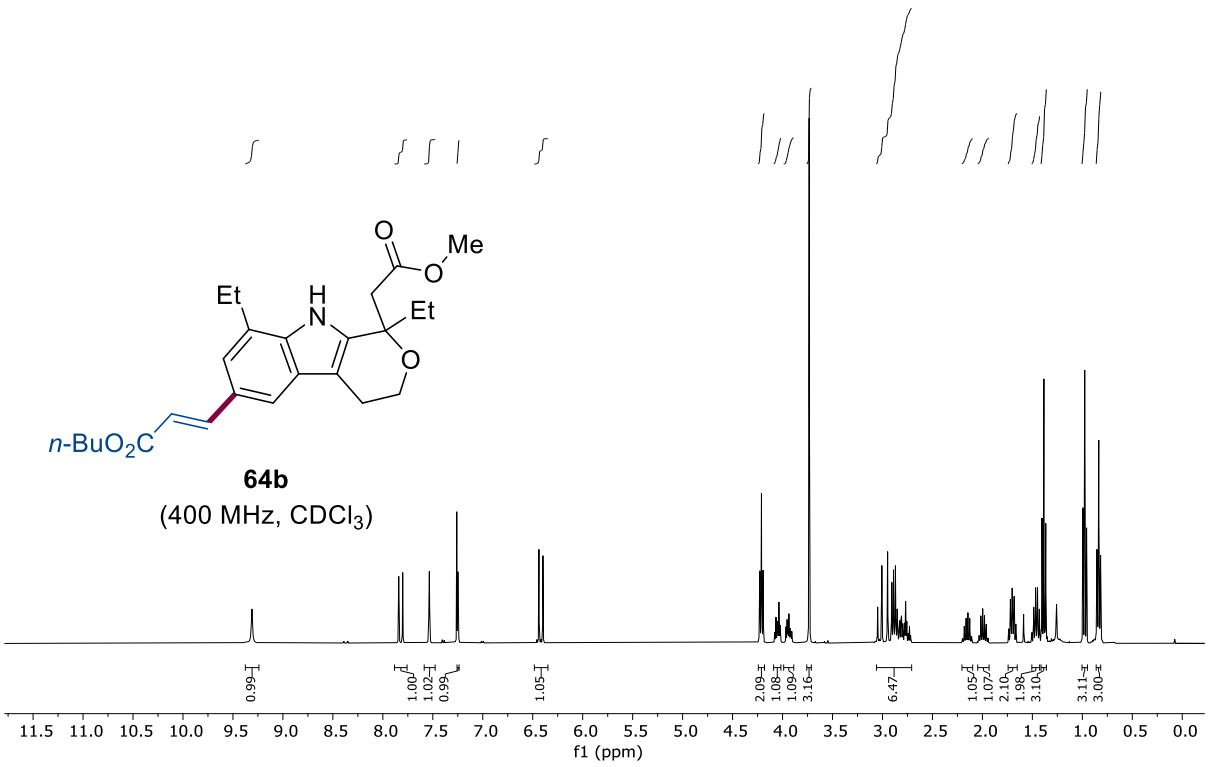
(600 MHz, $CDCl_3$)

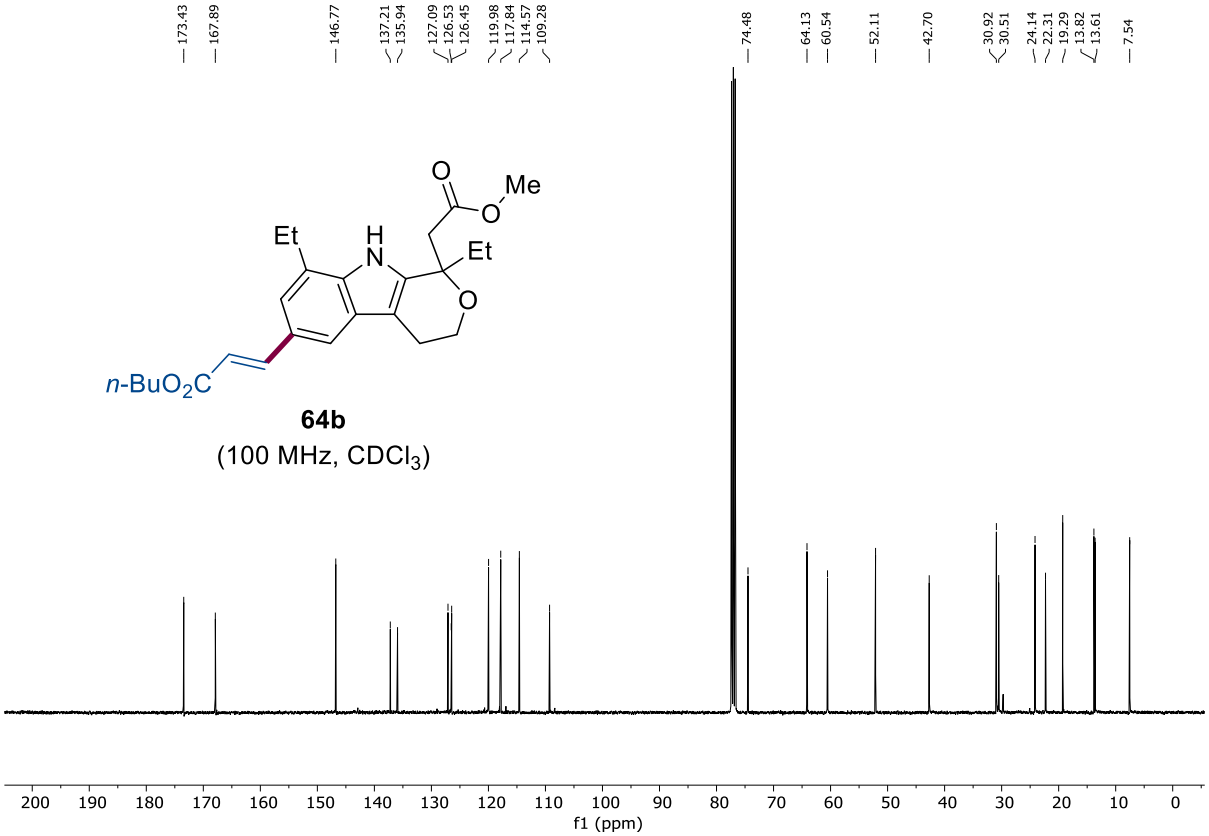


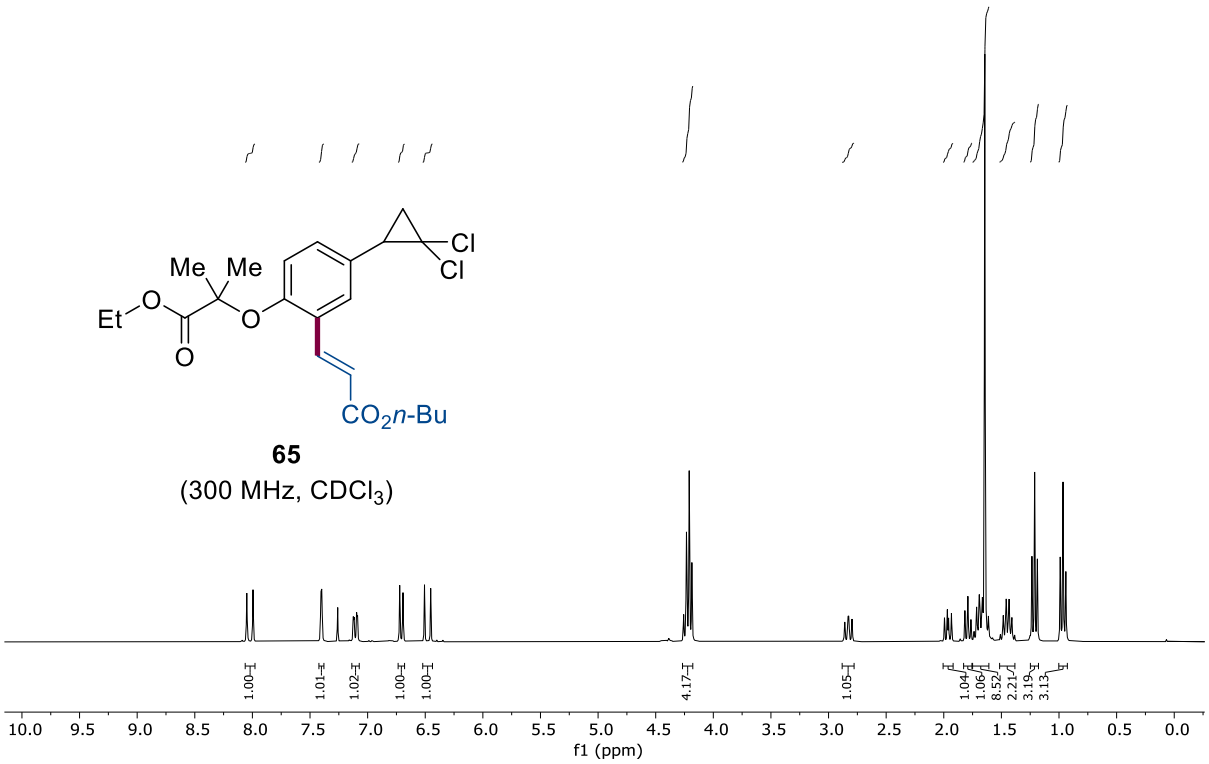
63b

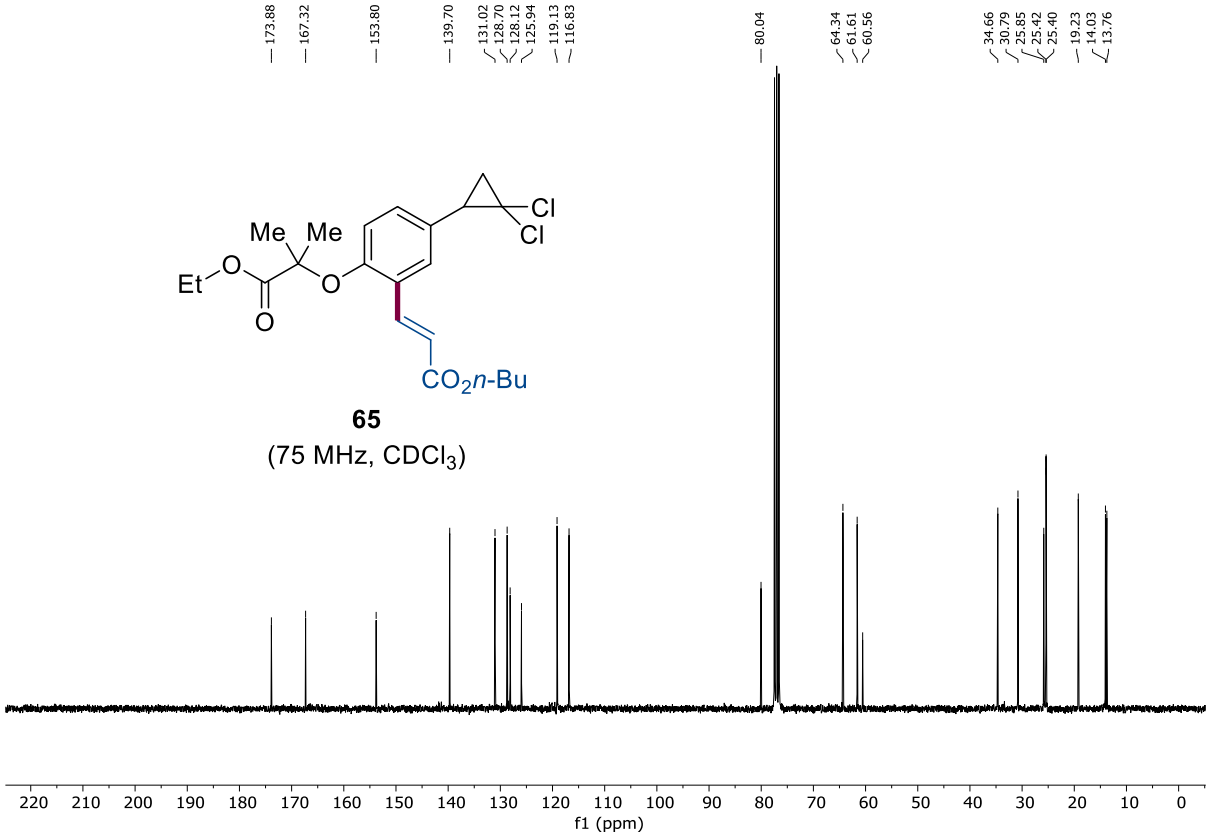
(125 MHz, $CDCl_3$)

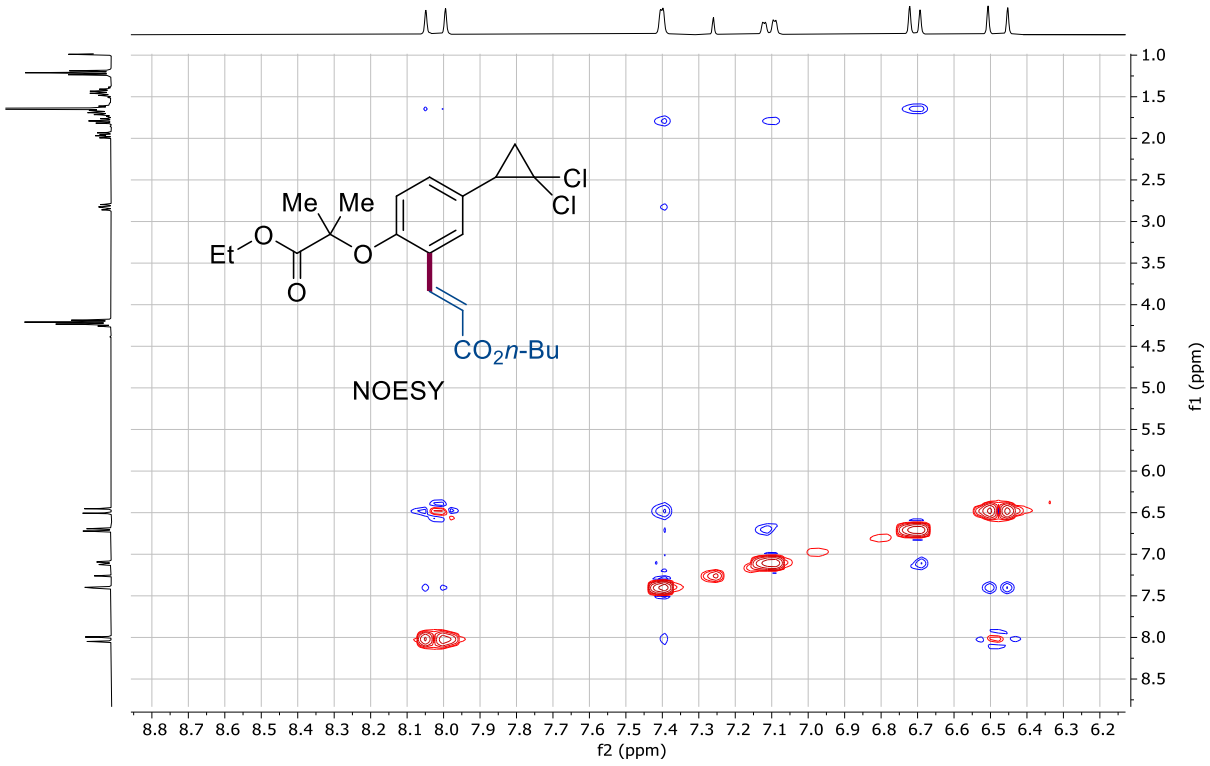

MeO2C
Me
Me
Me
CO2n-Bu
NOESY
f2 (ppm)
f1 (ppm)

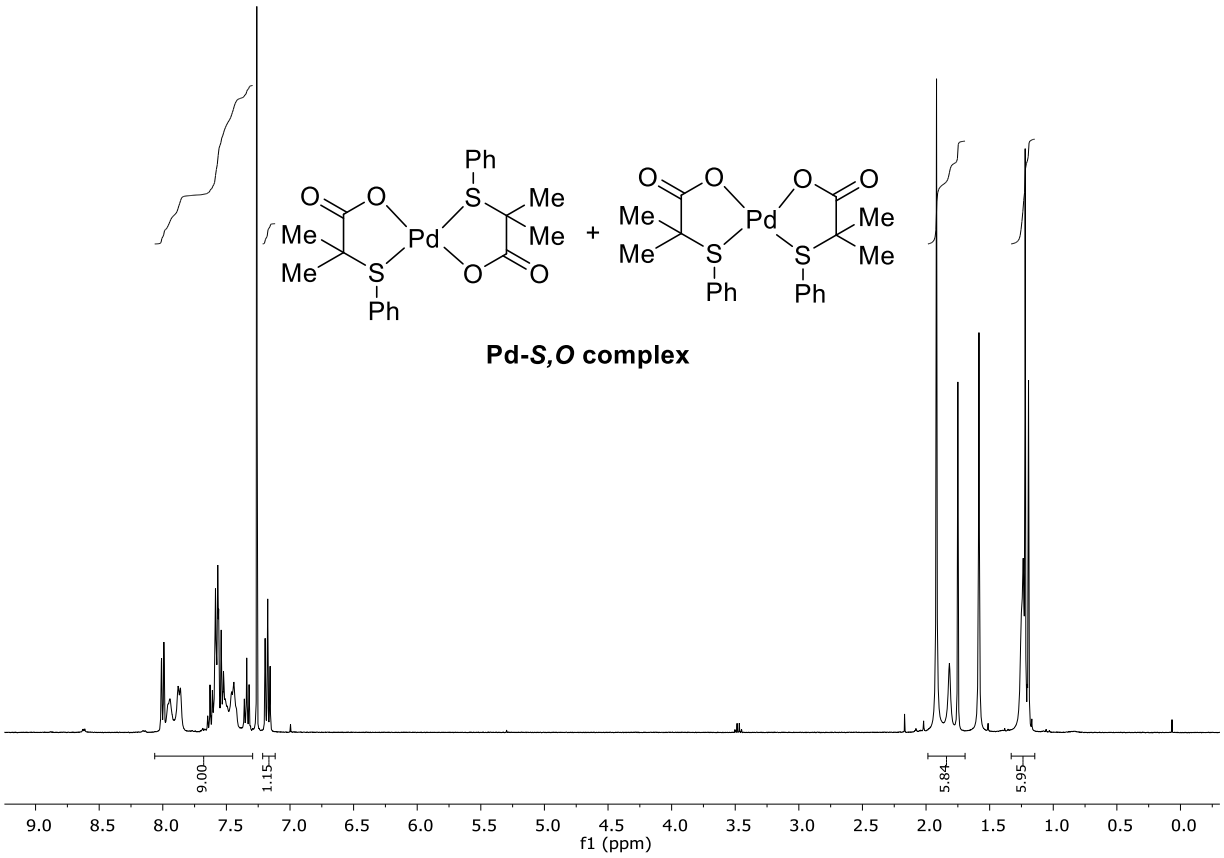

O
Me
O
Et
H
N
Et
O
n-BuO2C
64b
(400 MHz, CDCl3)
f1 (ppm)


173.43
167.89
146.77
137.21
135.94
127.09
126.53
126.45
119.98
117.84
114.57
109.28
74.48
64.13
60.54
52.11
42.70
30.92
30.51
24.14
22.31
19.29
13.82
13.61
7.54
O
Me
O
Et
H
N
Et
O
n-BuO2C
64b
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
Cl
Me
Me
Et
O
O
O
CO2n-Bu
65
(300 MHz, CDCl3)
1.00
1.01
1.02
1.00
1.00
4.17
1.05
1.04
1.06
8.52
2.21
3.19
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.88
167.32
153.80
139.70
131.02
128.70
128.12
125.94
119.13
116.83
80.04
64.34
61.61
60.56
34.66
30.79
25.85
25.42
25.40
19.23
14.03
13.76
Cl
Cl
Me
Me
Et
O
O
O
CO2n-Bu
65
(75 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
Cl
Me
Me
Et
O
O
O
CO2n-Bu
NOESY
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5
f1 (ppm)
8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2
f2 (ppm)


Ph
S
Me
Me
O
O
Me
Pd
Me
S
O
O
Ph
+
O
O
O
O
Me
Pd
Me
Me
S
S
Me
Ph
Ph
Pd-S,O complex
9.00
1.15
5.84
5.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

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