

Photocatalytic Radical Alkylation of Electrophilic Olefins by Benzylic and Alkyl Zinc-Sulfonates

Andrea Gualandi,^{*‡} Daniele Mazzarella,^{‡†} Aitor Ortega-Martínez,^{‡±} Luca Mengozzi,[‡] Fabio Calcinelli,[‡] Elia Matteucci,[§] Filippo Monti,^{*#} Nicola Armaroli,[#] Letizia Sambri,[§] and Pier Giorgio Cozzi^{*‡}

[‡] Dipartimento di Chimica “G. Ciamician”, ALMA MATER STUDIORUM Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

[§] Dipartimento di Chimica Industriale “Toso Montanari”, ALMA MATER STUDIORUM Università di Bologna, Viale Risorgimento 4, Bologna, Italy

[#] Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, Via P. Gobetti 101, 40129 Bologna, Italy

[†] Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain

[±] Departamento de Química Orgánica, Centro de Innovación en Química Avanzada (ORFEO-CINQA) and Instituto de Síntesis Orgánica (ISO), Facultad de Ciencias, Universidad de Alicante, 03080 Alicante, Spain.

Corresponding Authors

[‡]Dipartimento di Chimica “G. Ciamician” ALMA MATER STUDIORUM, Università di Bologna Via Selmi 2, 40126, Bologna, Italy. Email: andrea.gualandi10@unibo.it; piergiorgio.cozzi@unibo.it.

[#]Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, Via P. Gobetti 101, 40129 Bologna, Italy. Email: filippo.monti@isof.cnr.it.

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General methods

¹H NMR spectra were recorded on Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuteriochloroform: $\delta = 7.27$ ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, dd = double duplet, dt = double triplet, bs = broad signal, m = multiplet), coupling constants (Hz). ¹³C NMR spectra were recorded on Varian MR400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuteriochloroform: $\delta = 77.0$ ppm). LC-electrospray ionization mass spectra (ESI-MS) were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. Purification on preparative thin layer chromatography was done on Merck TLC silica gel 60 F₂₅₄.

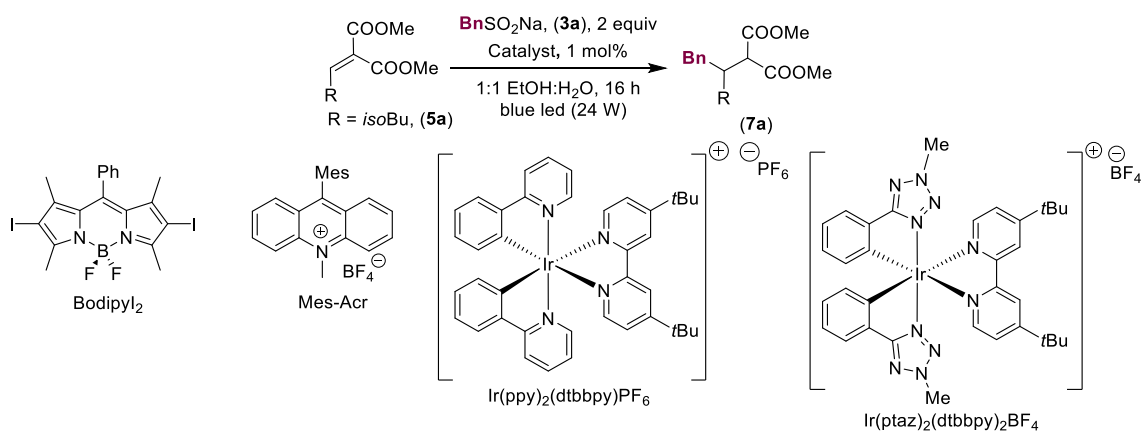
All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques. Synthesis grade solvents were used as purchased and the reaction mixtures were degassed by three cycles of freeze-pump-thaw.

Materials

Anhydrous solvents were supplied by Aldrich in Sureseal® bottles and were used as received avoiding further purification.

Compounds **1a**, **1d**, **2a-f**, **5d**, **5n**, **5j**, **5k**, **5p** and **10** are commercially available or prepared by the procedure reported (see *infra*).

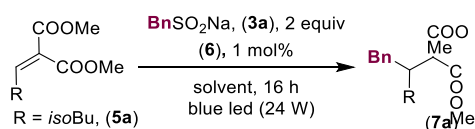
Screening tests: Scheme S1



Catalyst ^a	Conversion (%) ^b
BodipyI ₂	0
Mes-Acr	0
Eosin Y ^c	Traces
Ir(ppy) ₂ (dtbbpy)PF ₆	0
Ir(ptaz) ₂ (dtbbpy)BF ₄	Traces
Ru(bpy) ₃ Cl ₂	0

a All the reactions were carried out under argon. The reaction mixtures were degassed by three cycles of freeze-pump-thaw. The reactions were performed using (3a) (0.2 mmol), (5a) (0.1 mmol) in 1 mL of solvent mixture, in the presence of 1 mol% of the catalyst. b Determined by ¹H-NMR of the crude reaction mixture. c Green LEDs were used.

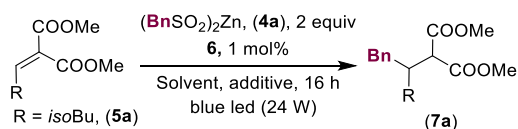
Scheme S2.



Solvent ^a	Conversion (%) ^b
1:4 H ₂ O:EtOH	69
1:1 H ₂ O:EtOH	96
4:1 H ₂ O:EtOH	94
1:1 H ₂ O:DMSO	92
1:1 H ₂ O:TFE	0
1:1 H ₂ O: <i>i</i> PrOH	0

a All the reactions were carried out under argon. The reaction mixtures were degassed by three cycles of freeze-pump-thaw. The reactions were performed using (3a) (0.2 mmol), (5a) (0.1 mmol) in 1 mL of solvent mixture, in the presence of 1 mol% of the catalyst. b Determined by ¹H-NMR of the crude reaction mixture.

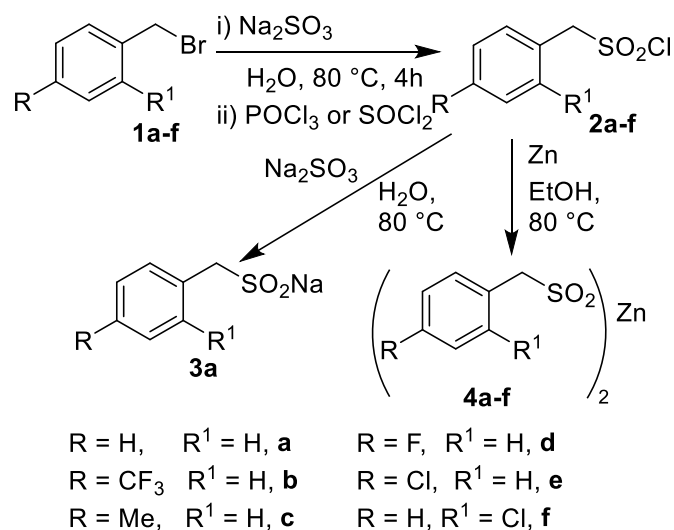
Scheme S3.



Solvent ^a	Additive	Conversion (%) ^b
EtOH	-	27
DMSO	-	48
DMSO	PhCOOH (1 equiv.)	14
DMSO	K ₂ HPO ₄ (1 equiv.)	33
DMF	-	19

a All the reactions were carried out under argon. The reaction mixtures were degassed by three cycles of freeze-pump-thaw. The reactions were performed using (4a) (0.2 mmol), (5a) (0.1 mmol) in 1 mL of solvent, in the presence of 1 mol% of the catalyst 6. b Determined by ¹H-NMR of the crude reaction mixture.

Synthesis of benzyl sulfinates



(2a): In a Schlenk tube under N₂, were added Na₂SO₃ (6.35 g, 50.4 mmol, 1.2 equiv), H₂O (34 mL) and benzyl bromide **1a** (5 mL, 42 mmol) in this order. The reaction mixture was heated and kept at reflux until TLC analysis confirmed complete conversion. The crude reaction mixture was washed with Et₂O (2 x 10 mL) and water phase was evaporated under reduced pressure. The crude was used in the next step without any purification. Spectroscopic data were according to the literature.¹

In a Schlenk tube under N₂, were added sodium benzyl sulfonate (8.148 g, 42 mmol) and POCl₃ (15 mL, 160 mmol, 3.8 equiv). The reaction mixture was stirred at room temperature for 5 hours. POCl₃ was removed under reduced pressure, the residue was dissolved in DCM (50 mL), and washed with H₂O (2 x 10 mL) and brine (2 x 10 mL). The organic phase was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. The desired product was obtained in 73% yield (5.87 g, 30.8 mmol) and used in the next step without any purification.

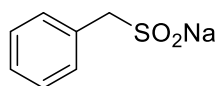
Spectroscopic data were according to the literature.²

(2d): In a Schlenk tube under N₂, were added Na₂SO₃ (756 mg, 6 mmol, 1.2 equiv), H₂O (5 mL) and 4-fluorobenzyl bromide **1d** (615 μL, 5 mmol) in this order. The reaction mixture was heated and kept at reflux until TLC analysis confirmed complete conversion. The crude reaction mixture was washed with Et₂O (2 x 10 mL) and water phase was evaporated under reduced pressure to give the corresponding sodium sulfonate. The crude was used in the next step without any purification.

In a Schlenk tube, dried by heating under reduced pressure and kept under N₂, were added sodium 4-fluorobenzyl sulfonate (5 mmol) and SOCl₂ (1.45 mL, 20 mmol, 4 equiv). The reaction mixture

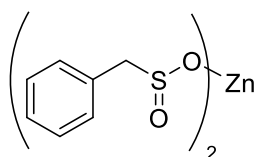
was heated at 70°C for 1.5 hours. SOCl₂ was removed under reduced pressure. The product was dissolved in DCM, and washed with H₂O (2 x 10 mL) and brine (2 x 10 mL). The organic phase was dried over Na₂SO₄, and the solvent was evaporated under reduced pressure. The desired product was obtained in 98% yield (1.02 g, 4.9 mmol).

Spectroscopic data were according to the literature.³



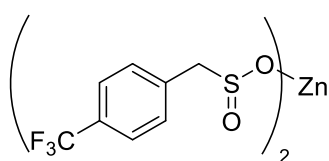
(3a): In a Schlenk tube, were added sulfonyl chloride (5.86 g, 30.8 mmol), Na₂SO₃, (7.76 g, 61.6 mmol, 2 equiv) and NaHCO₃ (5.17 g, 61.6 mmol, 2 equiv) to H₂O (30 mL). The reaction mixture was heated and kept at 80°C for 4 hours and 30 minutes. The crude reaction mixture was cooled at room temperature and washed with AcOEt (3 x 10mL) The water phase was concentrated to dryness under reduced pressure. The obtained solid was washed with ethanol (3 x 10 mL), and dried under vacuum. The desired product was obtained in 47% yield (3.08 g, 14.5 mmol).

Spectroscopic data were according to the literature.⁴



(4a): To a suspension of zinc powder (373 mg, 5.7 mmol, 1.1 equiv) in THF (0.4 mL), dibromoethane (15.5 μL, 0.18 mmol, 0.03 equiv) was added under N₂. The mixture was heated to reflux and returned to room temperature for three times. TMSCl (12.7 μL, 0.1 mmol, 0.02 equiv) was added at room temperature and the mixture was stirred for 10 minutes. The solvent was removed under reduced pressure and EtOH (7 mL) was added. After degassing by bubbling N₂ for 5 minutes, sulfonyl chloride (1.00 g, 5.24 mmol) was added. The mixture was refluxed for 45 minutes, cooled at room temperature and stirred for other 45 minutes. The solid was collected by filtration, and washed with a 1:1 mixture of DCM/EtOAc (3 x 10 mL). The solid was then dissolved in 15 mL of H₂O, the remaining zinc was filtered off and the water solution was concentrated to dryness under reduced pressure. The desired product was obtained in 71% yield (0.70 g, 1.87 mmol) and used in the next step without any further purification.

¹H-NMR (400 MHz, D₂O, 25°C): δ 3.66 (s, 2H), 7.28-7.47 (m, 5H). Spectroscopic data were according to the commercially available compound.⁵

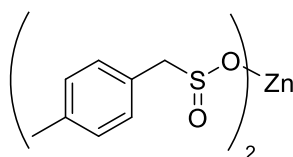


(4b): 21% yield (210 mg, 0.41 mmol). Compound was prepared according to the procedure reported for **4a** using: zinc powder (139 mg, 2.13 mmol, 1.1 equiv), THF (0.2 mL), dibromoethane (5.7 μL, 0.06 mmol, 0.03 equiv), TMSCl (4.7 μL, 0.04 mmol, 0.02 equiv); EtOH (2.6

mL); 4-trifluoromethylbenzyl sulfonyl chloride (500 mg, 1.93 mmol).

$^1\text{H-NMR}$ (400 MHz, D_2O , 25°C): δ 3.71 (s, 2H), 7.47-7.71 (m, 4H).

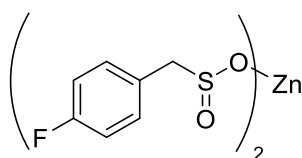
$^{19}\text{F-NMR}$ (400 MHz, D_2O , 25°C): 58.6.



(4c): 58% yield (171 mg, 0.42 mmol) as mixture of corresponding sulfonate in 1.0:2.7 (sulfonate:**4c**); Compound was prepared according to the procedure reported for **4a** using: zinc powder (106 mg, 1.61 mmol, 1.1 equiv), THF (0.2 mL), dibromoethane (4.5 μL , 0.05 mmol, 0.03 equiv),

TMSCl (3.4 μL , 0.03 mmol, 0.02 equiv); EtOH (2.3 mL); 4-methylbenzyl sulfonyl chloride (301 mg, 1.47 mmol).

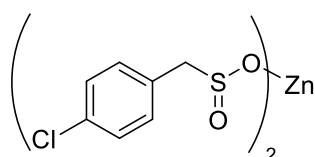
$^1\text{H-NMR}$ (400 MHz, D_2O , 25°C): δ 2.35 (s, 3H), 3.62 (s, 2H), 7.21-7.37 (m, 4H).



(4d): 34% yield (688 mg, 1.67 mmol) as mixture of corresponding sulfonate in 1.0:3.6 (sulfonate:**4d**); Compound was prepared according to the procedure reported for **4a** using: zinc powder (353 mg, 5.4 mmol, 1.1 equiv), THF (0.5 mL), dibromoethane (12.6 μL , 0.17 mmol, 0.03 equiv),

TMSCl (11.5 μL , 0.09 mmol, 0.02 equiv); EtOH (6 mL) 4-fluorobenzyl sulfonyl chloride (1.02 g, 4.91 mmol).

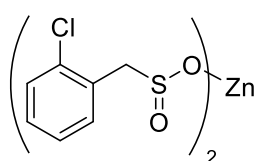
$^1\text{H-NMR}$ (400 MHz, D_2O , 25°C): δ 3.62 (s, 2H), 7.10-7.20 (m, 2H) 7.26-7.33 (m, 2H).



(4e): 23% yield (245 mg, 46% wt, 0.25 mmol) as mixture of corresponding sulfonate in 1.1:1.0 (sulfonate:**4e**); Compound was prepared according to the procedure reported for **4a** using: zinc powder (160 mg, 2.44 mmol, 1.1 equiv), THF (0.3 mL), dibromoethane (6.7 μL ,

0.08 mmol, 0.03 eq), TMSCl (5.2 μL , 0.04 mmol, 0.017 eq); EtOH (3.8 mL), 4-chlorobenzyl sulfonyl chloride (500 mg, 2.22 mmol, 1 equiv).

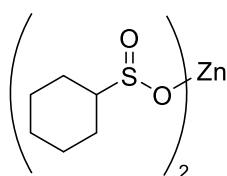
$^1\text{H-NMR}$ (400 MHz, D_2O , 25°C): δ 3.63 (s, 2H), 7.23-7.30 (m, 1H), 7.36-7.48 (m, 3H).



(4f): 70% yield (431 mg, 80% wt, 0.80 mmol) as mixture of corresponding sulfonate in 1.0:4.4 (sulfonate:**4f**); Compound was prepared according to the procedure reported for **4a** using: zinc powder (160 mg, 2.44 mmol, 1.1 equiv), THF (0.3 mL), dibromoethane (6.7 μL , 0.08 mmol, 0.03 eq), TMSCl (5.2 μL ,

0.04 mmol, 0.02 eq); EtOH (3.8 mL) 2-chlorobenzyl sulfonyl chloride (500 mg, 2.22 mmol).

$^1\text{H-NMR}$ (400 MHz, D_2O , 25°C): δ 3.84 (s, 2H), 7.27-7.44 (m, 3H) 7.46-7.57 (m, 1H).



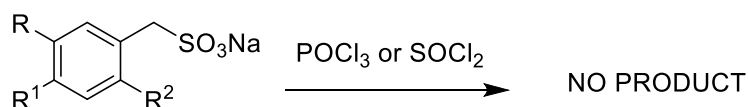
(**11**): 88% yield (173 mg, 0.48 mmol); Compound was prepared according to the procedure reported for **4a** using: zinc powder (78 mg, 1.2 mmol, 1.1 equiv), THF (0.1 mL), dibromoethane (3.3 μ L, 0.04 mmol, 0.03 equiv), TMSCl (2.5 μ L, 0.02 mmol, 0.02 equiv); EtOH (1.5 mL), cyclohexyl sulfonyl chloride

(158.9 μ L, 1.1 mmol).

$^1\text{H-NMR}$ (400 MHz, D_2O , 25°C): δ 1.16-1.34 (m, 5H), 1.63-1.67 (m, 1H), 1.81-1.95 (m, 4H), 1.95-2.03 (m, 1H).

Attempted synthesis of zinc sulfinates

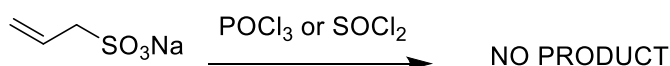
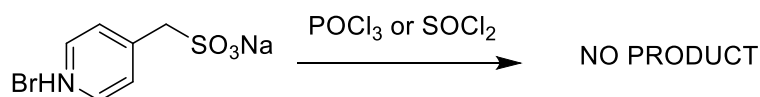
The formation of the following chlorides failed due to the occurring of side reactions.



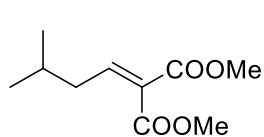
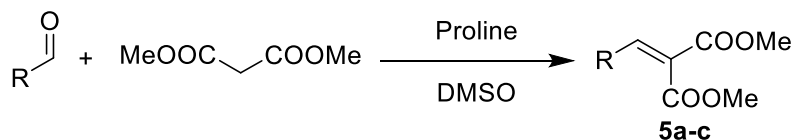
R = H, R¹ = OMe, R² = H

R = Me, R¹ = H, R² = Me

R = H, R¹ = *t*Bu, R² = H



Synthesis of **5a-c**⁶



(**5a**): In a Schlenk tube under N_2 , were added proline (0.230 g, 2 mmol, 10 mol%), DMSO (6 mL) and 3-methylbutanal (2 mL, 20 mmol) for 5 minutes.

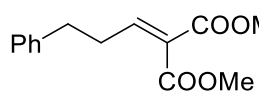
Dimethyl malonate (2.29 mL, 20 mmol, 1 equiv) was added and the reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with Et_2O (40 mL), and washed with H_2O (2 x 10 mL), saturated NaHCO_3 solution (2 x 10 mL) and brine (2 x 10 mL). The organic phase was dried over with Na_2SO_4 and the solvent was removed under reduced

pressure. The product was purified by distillation with a Kugelrohr (140 °C, 8·10⁻² bar). The product **5a** was obtained as transparent oil in 77% yield (3.10 g, 15.5 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 0.92 (d, *J* = 6.7 Hz, 6H), 1.87–1.68 (m, 1H), 2.17 (dt, *J* = 8.7, 4.3 Hz, 1H), 3.76 (s, 3H), 3.81 (s, 3H), 7.04 (t, *J* = 7.9 Hz, 1H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 22.3 (2C), 28.1, 38.6, 52.2, 52.3, 128.5, 149.4, 164.3, 166.0.

ESI-MS (*m/z*): 201.1 [M+H]⁺, 218.1 [M+H₂O]⁺.

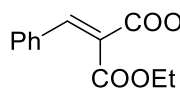


5b: 38% yield (471 mg, 1.90 mmol); Compound **5b** was prepared using the procedure reported for **5a** using: proline (58 mg, 0.5 mmol, 10 mol%), DMSO (1.5 mL), 3-phenylpropanal (664 μL, 5 mmol) and dimethyl malonate (1.14 mL, 10 mmol, 2 equiv). The product was purified by flash chromatography (SiO₂; cyclohexane:AcOEt 90:10 mixture).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 2.62 (q, *J* = 7.6 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 3.76 (s, 3H), 3.78 (s, 3H) 7.05 (t, *J* = 7.6 Hz, 1H), 7.13-7.22 (m, 3H), 7.23-7.31 (m, 2H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 31.5, 34.4, 52.2, 52.3, 126.3, 128.3 (2C), 128.3, 128.5 (2C), 140.2, 149.2, 164.3, 165.7.

ESI-MS (*m/z*): 249.1 [M+H]⁺.



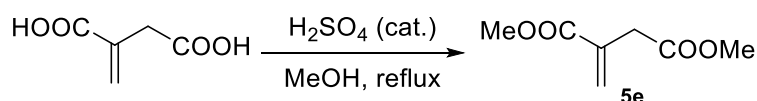
5c: 90% yield (979 mg, 4.5 mmol); Compound **5c** was prepared using the procedure reported for **5a** using: proline (58 mg, 0.5 mmol, 10 mol%), DMSO (1.5 mL), benzaldehyde (427 μL, 5 mmol) and dimethyl malonate (1.14 mL, 10 mmol, 2 equiv). The product was purified by flash chromatography (SiO₂; cyclohexane:AcOEt 90:10 mixture).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 1.16–1.44 (m, 6H), 4.21–4.41 (m, 4H), 7.33–7.40 (m, 3H), 7.44 (dd, *J* = 7.2, 2.1 Hz, 2H), 7.72 (s, 1H).

¹³C-NMR (100 MHz, CDCl₃, 25 °C): δ 13.8, 14.1, 61.6, 61.6, 126.3, 128.7 (2C), 129.4 (2C), 130.5, 132.9, 142.1, 164.1, 166.6.

ESI-MS (*m/z*): 249.0 [M+H]⁺, 266.1 [M+H₂O]⁺.

Synthesis of **5e**



To a solution of itaconic acid (3.9 mmol, 0.500 g) in MeOH (10 mL) some drops of concentrated sulfuric acid were added. The reaction was refluxed for 8 hours, cooled at room temperature and the

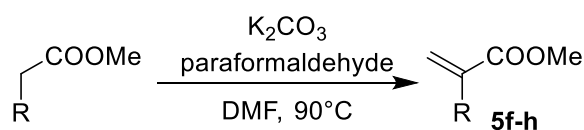
solvent was evaporated under reduced pressure. The residue was dissolved in Et₂O (30 mL) and washed with saturated NaHCO₃ solution (2 x 10 mL) and brine (20 mL). The organic phase was concentrated under reduced pressure to give **5e** (94%, 3.7 mmol, 0.576 g) as colorless oil. The product was used in the next step without purification.

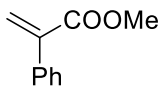
¹H NMR (400 MHz, CDCl₃, 25°C): δ 3.29 (d, *J* = 0.8 Hz, 2H), 3.64 (s, 3H), 3.71 (s, 3H), 5.67 (dd, *J* = 2.2 Hz, *J* = 0.8 Hz, 1H), 6.27 (d, *J* = 1.0 Hz, 1H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 37.4, 51.9, 52.0, 128.4, 133.6, 166.5, 171.0.

ESI-MS (*m/z*): 159.1 [M+H]⁺, 181.0 [M+Na]⁺.

Synthesis of **5f-h**⁷

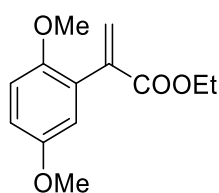


 (**5f**): In a Schlenk tube under N₂, were added methyl 2-phenylacetate (2 mL, 13.9 mmol), paraformaldehyde (0.585 g, 19.5 mmol, 1.5 equiv), K₂CO₃ (1.92 g, 13.9 mmol, 1 equiv) in DMF (10 mL). The reaction mixture was stirred at 100°C for 3 hours and at room temperature overnight. The reaction crude was diluted with H₂O (20 ml) and extracted with AcOEt (3 x 20 mL). The collected organic phases were washed with aqueous 1 M HCl (2 x 10 mL), NaHCO₃ sat. sol. (2 x 10 mL) and brine (2 x 10 mL). The organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The product was purified by flash chromatography (SiO₂; cyclohexane:AcOEt 99:1 mixture) as colorless oil in 40% yield (0.90 g, 5.6 mmol).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 3.81 (s, 3H), 5.89 (d, *J* = 1.3 Hz, 1H), 6.35 (d, *J* = 1.3 Hz, 1H), 7.30-7.67 (m, 5H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 52.1, 126.8, 128.1 (2C), 128.1, 128.2 (2C), 136.6, 141.3, 167.2.

ESI-MS (*m/z*): 163.1 [M+H]⁺, 185.0 [M+Na]⁺.



(**5g**): In a round bottom flask, (2,5-dimethoxyphenyl)acetic acid (2 g, 10.2 mmol) was added in 40 ml of EtOH. The mixture is cooled in an ice-water bath for 10 minutes and SOCl₂ (2.3 mL, 30 mmol, 3 eq.) was added dropwise. The reaction was stirred overnight at room temperature. Then solvent was removed under reduced pressure. The residue was diluted with DCM (50 mL) and the solution was washed

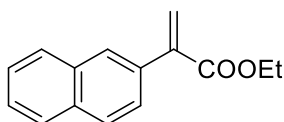
with saturated solution of NaHCO₃ (3 x 15 mL). The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The ester product was used in the next step without any purification.

Compound **5g** was prepared applying the procedure adopted for **5f** on the residue of the previous reaction. The product was purified by flash chromatography (SiO₂; cyclohexane:AcOEt 95:5 mixture) as colorless oil in 68% yield.

¹H-NMR (400 MHz, CDCl₃, 25 °C) present as mixture of two rotamers a and b in 4.6:1.0 ratio: δ 1.23 (t, *J* = 7.1 Hz, 3Hb), 1.26 (t, *J* = 7.1 Hz, 3Ha), 3.72 (s, 3Ha), 3.72 (s, 3Hb), 3.75 (s, 3Hb), 3.77 (s, 3Ha), 4.14 (q, *J* = 7.1 Hz, 2Hb), 4.22 (q, *J* = 7.1 Hz, 2Ha), 5.72 (d, *J* = 1.5 Hz, 1Ha+b), 6.25 (d, *J* = 1.5 Hz, 1Ha+b), 6.86 – 6.75 (m, 3Ha+b).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 14.1, 55.6, 56.0, 60.7, 111.7, 114.0, 116.0, 126.0, 127.8, 140.1, 151.1, 153.4, 166.7.

ESI-MS (*m/z*): 237.0 [M+H]⁺, 254.1 [M+H₂O]⁺.



(**5h**): In a round bottom flask, 2-(naphthalen-2-yl)acetic acid (2 g, 10.8 mmol) was added in 40 ml of EtOH. The mixture is cooled in an ice-water bath for 10 minutes and SOCl₂ (2.35 mL, 32 mmol, 3 eq.) was added

dropwise. The reaction was stirred overnight at room temperature. Then solvent was removed under reduced pressure. The residue was diluted with DCM (50 mL) and the solution was washed with saturated solution of NaHCO₃ (3 x 15 mL). The organic layer was dried over Na₂SO₄, and the solvent was removed under reduced pressure. The ester product was used in the next step without any purification.

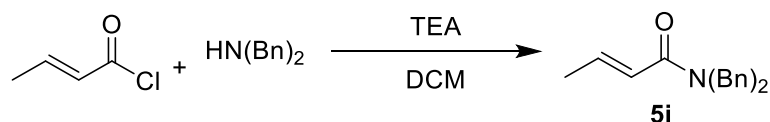
Compound **5h** was prepared applying the procedure adopted for **5f** on the residue of the previous reaction. The product was purified by flash chromatography (SiO₂; cyclohexane:AcOEt 95:5 mixture) as colorless oil in 68% yield.

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 1.34 (t, *J* = 7.1 Hz, 3H), 4.32 (q, *J* = 7.1 Hz, 2H), 6.00 (d, *J* = 1.2 Hz, 1H), 6.42 (d, *J* = 1.2 Hz, 1H), 7.44-7.50 (m, 2H), 7.50–7.55 (m, 1H), 7.79-7.86 (m, 3H), 7.91 (d, *J* = 1.2 Hz, 1H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 14.2, 61.2, 126.1, 126.2, 126.3, 126.7, 127.4, 127.5, 127.6, 128.3, 133.0, 133.1, 134.2, 141.5, 166.9.

ESI-MS (*m/z*): 227.1 [M+H]⁺, 244.1 [M+H₂O]⁺.

Synthesis of 5i



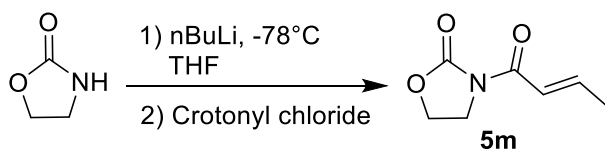
In a round bottom flask under N₂, were added *N,N*-dibenzylamine (481 μL, 2.5 mmol) and Et₃N (871 μL, 6.25 mmol, 2.5 eq) in dry DCM (10 mL). After 5 minutes, crotonyl chloride (266 μL, 2.5 mmol, 1 equiv) was added dropwise. After 20 hours, H₂O (20 mL) was added and the mixture was extracted with DCM (3 x 20 mL). The collected organic phases were washed with NH₄Cl sat. sln. (1 x 20 mL) and brine (1 x 20 mL). The organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The product was isolated by flash chromatography (SiO₂; cyclohexane:AcOEt 80:20 mixture) in 94% yield (620 mg, 2.34 mmol).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 1.85 (dd, *J* = 6.80 Hz, *J* = 1.6 Hz, 3H), 4.49 (s, 2H), 4.62 (s, 2H), 6.29 (dq, *J* = 14.8 Hz, *J* = 1.6 Hz, 1H), 7.02-7.10 (m, 1H), 7.15-7.37 (m, 10H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 18.1, 48.2, 49.7, 121.4, 126.4 (2C), 127.2, 127.5, 128.2 (2C), 128.4 (2C), 128.7 (2C), 136.6, 137.3, 142.8, 167.1.

ESI-MS (*m/z*): 266.1 [M+H]⁺, 288.0 [M+Na]⁺.

Synthesis of 5m



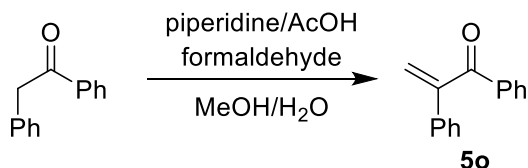
To a solution of oxazolidin-2-one (1 g, 11.5 mmol) in THF (12 mL) under N₂, *n*BuLi (2.5 M in hexanes, 4.60 mL, 11.5 mmol, 1 equiv) was added dropwise at -78 °C. After 30 minutes, crotonyl chloride (12.6 mmol, 1.1 eq) was added dropwise and the reaction mixture was stirred for 30 minutes. Saturated solution of NH₄Cl (20 mL) was added and the mixture was extracted with AcOEt (2 x 15 mL). The organic phases were dried over with Na₂SO₄, and the solvent was removed under reduced pressure. The product was isolated by flash chromatography (SiO₂; eluent: cyclohexane:AcOEt 60:40 mixture) in 70% yield (1.25 g, 8.0 mmol).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 1.91 (dd, *J* = 6.5 Hz, *J* = 1.5 Hz, 3H), 4.01 (t, *J* = 8.1 Hz, 2H), 4.37 (t, *J* = 8.1 Hz, 2H), 7.05-7.25 (m, 2H).

¹³C NMR (100 MHz, CDCl₃, 25°C): δ 18.4, 42.6, 61.9, 121.3, 146.6, 153.4, 165.0.

ESI-MS (*m/z*): 156.1 [M+H]⁺.

Synthesis of 5o⁸



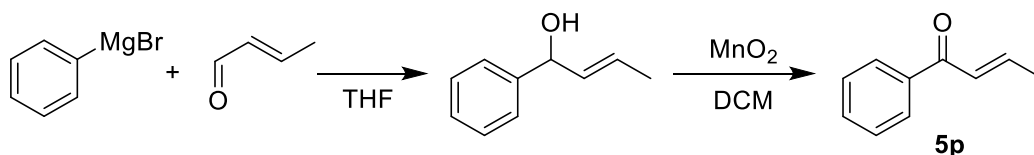
In a Schlenk tube under N₂, were added 1,2-diphenylethan-1-one (1 g, 5.1 mmol), formaldehyde (1.8 ml, 37% in H₂O), piperidine (65 μL, 0.66 mmol, 0.13 equiv), acetic acid (63 μL, 1.1 mmol, 0.22 equiv) in 13 mL of MeOH. The reaction mixture was refluxed for 6 hours, diluted with brine (20 ml), and extracted with AcOEt (3 x 20 mL). The collected organic phases were washed with aqueous 1 M HCl (2 x 10 mL), NaHCO₃ sat. sln. (2 x 10 mL) and brine (2 x 10 ml), dried over Na₂SO₄, and the solvent was removed under reduced pressure. The product was isolated by flash chromatography (SiO₂; cyclohexane:Et₂O 95:5 mixture) in 58% yield (616 mg, 2.96 mmol).

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 5.64 (s, 1H), 6.06 (s, 1H), 7.28-7.56 (m, 8H), 7.89-7.92 (m, 2H).

¹³C NMR (100 MHz, CDCl₃, 25°C): δ 120.9, 127.0 (2C), 128.4 (2C), 128.4, 128.6 (2C), 130.0 (2C), 133.1, 137.0, 137.1, 148.3, 197.5.

ESI-MS (*m/z*): 209.1 [M+H]⁺, 231.0 [M+Na]⁺.

Synthesis of 5p⁹



To a solution of phenylmagnesium bromide (1M in THF, 7 mL, 7 mmol) in THF (21 ml) crotonaldehyde (580 μL, 7mmol, 1 equiv) was added dropwise at 0°C under N₂. The reaction was stirred for 30 minutes at the same temperature and then quenched with a saturated solution of NH₄Cl (5 mL). The organic solvent was removed under reduced pressure and the aqueous phase was extracted with Et₂O (2 x 20 mL). The organic phases were washed with aqueous 1 M HCl (2 x 10 mL) and brine (2 x 10 mL), dried over Na₂SO₄, and concentrated to dryness under reduced pressure obtaining a yellow oil. The oil was dissolved in DCM (15 mL) and MnO₂ (6.5 g, 74 mmol, 10.5 equiv) was added under vigorous stirring. After complete conversion (TLC analysis), the mixture was filtered through a Celite pad washing with DCM.

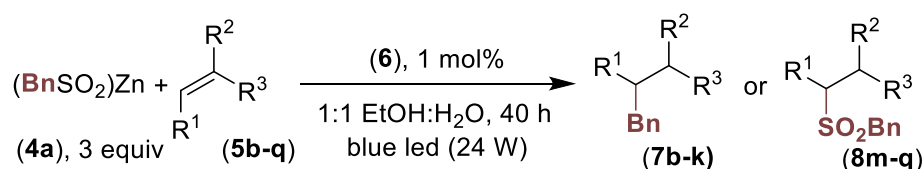
The product was isolated by flash chromatography (SiO₂; cyclohexane:AcOEt 95:5 mixture) in 53% yield (541 mg, 3.70 mmol) as colorless oil.

¹H-NMR (400 MHz, CDCl₃, 25 °C): δ 1.93 (dd, *J* = 6.8 Hz, *J* = 1.7 Hz, 3H), 6.85 (ddd, *J* = 15.3, *J* = 3.0, *J* = 1.5 Hz, 1H), 7.02 (dq, *J* = 15.2, *J* = 6.8 Hz, 1H), 7.36-7.43 (m, 2H), 7.44-7.53 (m, 1H), 7.88 (dt, *J* = 8.6, 1.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃, 25°C): δ 18.4, 127.3, 128.3 (2C), 128.3 (2C), 132.4, 137.7, 144.8, 190.4.

ESI-MS (*m/z*): 147.1 [M+H]⁺.

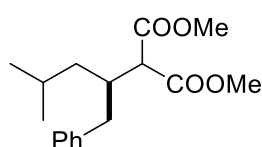
General procedure for photocatalytic reactions



All photocatalytic reactions were conducted under inert argon atmosphere using Schlenk techniques.

Sulfinate salts, iridium complex, substrates and solvents were introduced in the Schlenk flask in this order. The reaction mixture was then subjected to a freeze-pump-thaw procedure (three cycles). The reaction was irradiated with blue LED (approx. 10 cm distance) and stirred for 40 hours.

After that the reaction mixture was diluted with H₂O (5 mL) extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na₂SO₄, and the solvent was removed under reduced pressure. The desired product was isolated by flash chromatography or by preparative TLC.



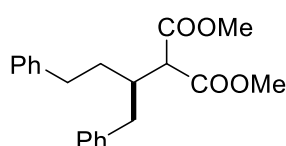
(7a): The general procedure was applied using sodium benzyl sulfinate (53.4 mg, 0.3 mmol, 3 equiv), **5a** (20.0 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.25 mL) and H₂O (0.25 mL).

Otherwise, the general procedure was applied using: zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5a** (20.0 mg, 0.1 mmol, 1 equiv), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was isolated by flash chromatography (SiO₂; cyclohexane:AcOEt 95:5 mixture) in 57% yield (33.2 mg, 0.057 mmol) as yellowish oil.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 0.82 (d, *J* = 11.3 Hz, 3H), 0.88 (d, *J* = 13.4 Hz, 3H), 1.25-1.28 (m, 2H), 1.57-1.65 (m, 1H), 2.43-2.49 (m, 1H), 2.69 (d, *J* = 7.1 Hz, 2H), 3.41 (d, *J* = 5.1 Hz, 1H), 3.66 (s, 3H), 3.71 (s, 3H), 7.16-7.19 (m, 3H), 7.23-7.28 (m, 2H).

¹³C NMR (100 MHz, CDCl₃, 25°C): δ 22.1, 22.9, 25.5, 38.0, 38.4, 40.5, 52.1 (2C), 53.9, 126.1, 128.3 (2C), 129.3 (2C), 140.0, 169.4 (2C).

ESI-MS (*m/z*): 293.0 [M+H]⁺, 310.2 [M+H₂O]⁺.



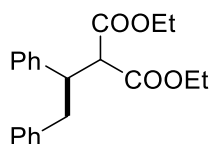
(7b): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5b** (24.8 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was purified by

flash chromatography (SiO₂; cyclohexane/Et₂O 95:5 mixture) in 62% yield (21.1 mg, 0.062 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 1.65-1.83 (m, 2H), 2.47-2.55 (m, 1H), 2.58-2.70 (m, 2H), 2.76 (d, *J* = 7.3 Hz, 2H), 3.51 (d, *J* = 6.6 Hz, 1H), 3.70 (s, 3H), 3.75 (s, 3H), 7.10-7.32 (m, 10H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 32.8, 33.2, 37.7, 40.1, 52.3 (2C), 54.0, 125.8, 126.3, 128.3 (4C), 128.4 (2C), 129.2 (2C), 139.7, 141.8, 169.2, 169.3.

ESI-MS (*m/z*): 341.0 [M+H]⁺, 358.2 [M+H₂O]⁺.



(7c): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5c** (16.2 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL).

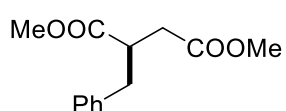
The product was purified by preparative TLC (stationary phase: silica; cyclohexane:Et₂O 95:5 mixture) and obtained as an inseparable mixture with **5c** (15 mg, **5c**:**7c**, 1.4:1.0): yield estimated by

¹H-NMR 11% yield.

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 0.91 (t, *J* = 7.2, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 2.81 (dd, *J* = 13.3, *J* = 10.2, 1H), 3.08 (dd, *J* = 13.3, *J* = 4.0, 1H), 3.65 (td, *J* = 10.4, *J* = 4.0, 1H), 3.77 (d, *J* = 10.7, 1H), 3.86 (q, *J* = 7.1, 2H), 4.23 (q, *J* = 7.1, 2H), 6.88-6.93 (m, 2H), 6.99-7.20 (m, 8H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 13.6, 14.1, 40.7, 47.6, 57.9, 61.2, 61.6, 126.0, 126.8, 127.9 (2C), 128.0 (2C), 128.5 (2C), 129.2 (2C), 138.9, 140.0, 167.7, 168.4.

ESI-MS (*m/z*): 341.1 [M+H]⁺, 363.0 [M+Na]⁺.



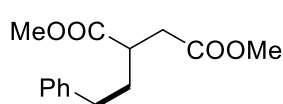
(7d): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5d** (14.4 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was isolated by

flash chromatography (SiO₂; cyclohexane:AcOEt 90:10 mixture) in 60% yield (14 mg, 0.06 mmol).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ 2.39 (dd, $J = 16.7$ Hz, $J = 5.0$ Hz, 1H), 2.67-2.77 (m, 2H), 3.01-3.06 (m, 1H), 3.08-3.15 (m, 1H), 3.63 (s, 3H), 3.65 (s, 3H), 7.13-7.15 (m, 2H), 7.18-7.22 (m, 1H), 7.24-7.29 (m, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): δ 34.9, 37.7, 43.0, 51.7, 51.9, 126.7, 128.5 (2C), 129.0 (2C), 138.1, 172.2, 174.6.

ESI-MS (m/z): 237.0 $[\text{M}+\text{H}]^+$, 259.0 $[\text{M}+\text{Na}]^+$.

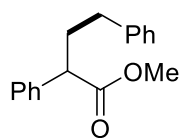


(7e): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5e** (15.8 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by flash chromatography (SiO_2 ; cyclohexane:Et $_2$ O 95:5 mixture) in 40% yield (10 mg, 0.04 mmol).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ 1.77-1.84 (m, 1H), 1.93-2.03 (m, 1H), 2.47 (dd, $J = 17.1$ Hz, $J = 5.1$ Hz, 1H), 2.59-2.64 (m, 2H), 2.75 (dd, $J = 15.9$ Hz, $J = 9.3$ Hz, 1H), 2.85-2.90 (m, 1H), 3.65 (s, 3H), 3.69 (s, 3H), 7.14-7.19 (m, 3H), 7.24-7.28 (m, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): δ 33.2, 33.5, 35.9, 40.8, 51.8, 51.9, 126.1, 128.3 (2C), 128.4 (2C), 141.0, 172.2, 175.1.

ESI-MS (m/z): 251.0 $[\text{M}+\text{H}]^+$, 273.0 $[\text{M}+\text{Na}]^+$.

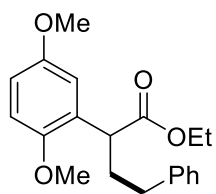


(7f): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5f** (24.8 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by preparative TLC (SiO_2 ; cyclohexane:AcOEt 95:5 mixture) in 53% yield (20 mg, 0.04 mmol).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ 2.05-2.14 (m, 1H), 2.35-2.45 (m, 1H), 2.56 (t, $J = 7.6$ Hz, 2H), 3.55 (t, $J = 7.6$ Hz, 1H), 3.64 (s, 3H), 7.13-7.18 (m, 3H), 7.24-7.34 (m, 7H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): δ 33.5, 34.9, 50.8, 52.0, 126.0, 127.3, 128.0 (2C), 128.4 (2C), 128.5 (2C), 128.7 (2C), 138.8, 141.2, 174.3.

ESI-MS (m/z): 255.0 $[\text{M}+\text{H}]^+$, 272.0 $[\text{M}+\text{H}_2\text{O}]^+$, 273.0 $[\text{M}+\text{H}_2\text{O}+\text{H}]^+$



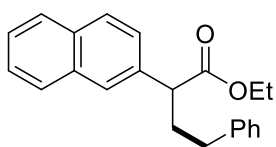
(7g): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5g** (23.6 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by flash chromatography (SiO_2 ; cyclohexane:AcOEt 95:5 mixture) in 40% yield (13 mg, 0.04 mmol).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ 1.19 (t, $J = 7.1$ Hz, 3H), 1.92-2.09 (m, 1H), 2.22-2.42 (m, 1H), 2.48-2.68 (m, 2H), 3.74 (s, 3H), 3.75 (s, 3H), 3.98 (t, $J = 7.5$ Hz, 1H), 4.07-4.16 (m, 2H), 6.74

(dd, $J = 8.9$ Hz, $J = 2.9$ Hz, 1H), 6.79 (d, $J = 8.9$ Hz, 1H), 6.85 (d, $J = 2.9$ Hz, 1H), 7.14-7.18 (m, 3H), 7.22-7.28 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ 14.2, 33.7, 34.1, 44.0, 55.7, 56.2, 60.5, 112.0, 112.4, 114.6, 125.8, 128.2 (2C), 128.4 (2C), 129.1, 141.7, 151.2, 153.7, 174.0.

ESI-MS (m/z): 329.2 $[\text{M}+\text{H}]^+$.



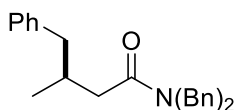
(7h): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5h** (22.6 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by

flash chromatography (SiO_2 ; cyclohexane:AcOEt 95:5 mixture) in 49% yield (15.7 mg, 0.049 mmol).

^1H -NMR (400 MHz, CDCl_3 , 25°C): δ 1.19 (t, $J = 7.1$ Hz, 3H), 2.18-2.25 (m, 1H), 2.48-2.58 (m, 1H), 2.59 (t, $J = 7.7$ Hz, 2H), 3.70 (t, $J = 7.7$ Hz, 1H), 4.02-4.21 (m, 2H), 7.17 (dd, $J = 16.9$, $J = 7.4$ Hz, 3H), 7.22-7.32 (m, 2H), 7.40-7.50 (m, 3H), 7.73 (s, 1H), 7.76-7.85 (m, 3H).

^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ 14.1, 33.6, 34.8, 51.1, 60.8, 125.8, 125.9, 126.0, 126.1, 126.9, 127.6, 127.8, 128.3, 128.4 (2C), 128.5 (2C), 132.6, 133.4, 136.4, 141.3, 173.8.

ESI-MS (m/z): 319.2 $[\text{M}+\text{H}]^+$, 336.0 $[\text{M}+\text{H}_2\text{O}]^+$.



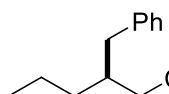
(7i): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5i** (26.5 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by flash

chromatography (SiO_2 ; cyclohexane:AcOEt 90:10 mixture) in 27% yield (9.6 mg, 0.027 mmol).

^1H -NMR (400 MHz, CDCl_3 , 25°C): δ 0.96 (d, $J = 6.0$ Hz, 3H), 2.20-2.26 (m, 1H), 2.38-2.48 (m, 3H), 2.64-2.70 (m, 1H), 4.36 (s, 2H), 4.52 (d, $J = 14.8$ Hz, 1H), 4.64 (d, $J = 14.8$ Hz, 1H), 7.07-7.36 (m, 15H).

^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ 19.8, 32.4, 39.7, 43.2, 48.1, 49.8, 125.9, 126.4 (2C), 127.3, 127.5, 128.2, 128.3 (2C), 128.5 (2C), 128.9 (2C), 129.2 (2C), 136.6, 137.5, 140.5, 172.8.

ESI-MS (m/z): 358.2 $[\text{M}+\text{H}]^+$, 380.2 $[\text{M}+\text{Na}]^+$.



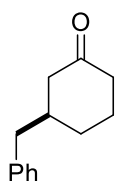
(7j): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5j** (11.6 μL , 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH

(0.5 mL) and H_2O (0.5 mL). The product was purified by flash chromatography (SiO_2 ; cyclohexane:AcOEt 96:4 mixture) in 39% yield (7.5 mg, 0.039 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.17-1.41 (m, 4H), 2.23-2.36 (m, 3H), 2.47 (dd, *J* = 13.6 Hz, *J* = 7.6 Hz, 1H), 2.72 (dd, *J* = 13.2 Hz, *J* = 5.6 Hz, 1H), 7.11-7.29 (m, 5H), 9.64 (t, *J* = 1.6 Hz, 1H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 14.2, 19.9, 35.1, 36.4, 40.6, 47.9, 126.2, 128.4 (2C), 129.2 (2C), 140.1, 202.8.

ESI-MS (*m/z*): 191.1 [M+H]⁺, 214.1 [M+Na]⁺.

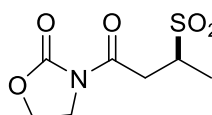


(7k): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5k** (9.7 μL, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was purified by flash chromatography (SiO₂; cyclohexane:AcOEt 95:5 mixture) in 85% yield (16 mg, 0.085 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 1.29-1.43 (m, 1H), 1.54-1.68 (m, 1H), 1.81-1.91 (m, 1H), 1.96-1.12 (m, 3H), 2.18-2.30 (m, 1H), 2.30-2.43 (m, 2H), 2.54-2.67 (m, 2H), 7.07-7.13 (m, 2H), 7.15-7.22 (m, 1H), 7.23 – 7.30 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 25.1, 30.9, 40.8, 41.4, 43.0, 47.8, 126.2, 128.3 (2C), 129.0 (2C), 139.4, 211.5.

ESI-MS (*m/z*): 189.0 [M+H]⁺.



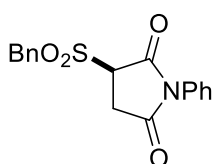
(8m): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5m** (15.5 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was purified by flash

chromatography (SiO₂; cyclohexane:AcOEt 1:1 mixture) in 57% yield (17.7 mg, 0.057 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 1.39 (d, *J* = 6.8 Hz, 3H), 3.06 (dd, *J* = 19.2 Hz, *J* = 8.8 Hz, 1H), 3.63-3.70 (m, 2H), 3.97-4.02 (m, 2H), 4.25 (d, *J* = 13.6 Hz, 1H), 4.29 (d, *J* = 13.6 Hz, 1H), 4.41 (t, *J* = 8.0 Hz, 2H), 7.36-7.42 (m, 5H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 14.7, 35.5, 42.5, 52.7, 57.0, 62.2, 127.2, 128.9 (2C), 129.0, 130.8 (2C), 153.3, 169.6.

ESI-MS (*m/z*): 312.0 [M+H]⁺, 329.0 [M+H₂O]⁺, 334.0 [M+Na]⁺.

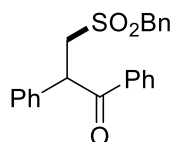


(8n): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5n** (17.3 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was purified by flash chromatography (SiO₂; cyclohexane:AcOEt 60:40 mixture) in 61% yield (20 mg, 0.061 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 3.02 (dd, *J* = 19.2 Hz, *J* = 10.0 Hz, 1H), 3.38 (dd, *J* = 19.2 Hz, *J* = 4.2 Hz, 1H), 4.26 (dd, *J* = 9.6 Hz, *J* = 4.0 Hz, 1H), 4.47 (d, *J* = 14.6 Hz, 1H), 4.95 (d, *J* = 14.6 Hz, 1H), 7.24-7.30 (m, 2H), 7.41-7.52 (m, 6H), 7.58-7.60 (m, 2H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 27.5, 56.9, 58.5, 126.4 (2C), 127.0, 129.3 (2C), 129.4, 129.4 (2C), 129.5, 131.0, 131.3 (2C), 169.1, 172.0.

ESI-MS (*m/z*): 330.0 [M+H]⁺, 347.0 [M+H₂O]⁺, 351.8 [M+Na]⁺.

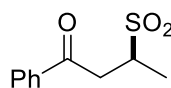


(8o): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5o** (28.8 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was purified by preparative TLC (SiO₂; cyclohexane:AcOEt 95:5 mixture) in 44% yield (31.8 mg, 0.044 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 3.10 (dd, *J* = 14.6 Hz, *J* = 5.0 Hz, 1H), 3.93 (d, *J* = 13.9 Hz, 1H), 3.98-4.07 (m, 2H), 5.12 (dd, *J* = 8.3 Hz, *J* = 5.0 Hz, 1H), 7.10-7.25 (m, 6H), 7.25-7.34 (m, 6H), 7.36-7.42 (m, 1H), 7.81-7.86 (m, 2H).

¹³C NMR (100 MHz, CDCl₃, 25°C): δ 48.1, 54.9, 60.9, 127.6, 128.2, 128.3 (2C), 128.6 (2C), 128.9 (2C), 129.0 (2C), 129.0, 129.5 (2C), 130.8 (2C), 133.5, 135.3, 136.2, 190.7.

ESI-MS (*m/z*): 365.0 [M+H]⁺, 382.0 [M+H₂O]⁺.



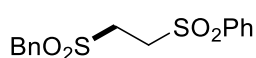
(8p): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5p** (14.6 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL).

The product was purified by flash chromatography (stationary phase: silica; cyclohexane:AcOEt 75:25 mixture) in 63% yield (19.1 mg, 0.063 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 1.44 (d, *J* = 6.8 Hz, 3H), 3.12 (dd, *J* = 18.0 Hz, *J* = 9.4 Hz, 1H), 3.63 (dd, *J* = 18.0 Hz, *J* = 3.2 Hz, 1H), 3.69-3.82 (m, 1H), 4.28 (s, 2H), 7.38-7.47 (m, 7H), 7.55-7.59 (m, 1H), 7.89-7.91 (m, 2H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 14.6, 37.5, 52.0, 57.3, 127.5, 128.1 (2C), 128.8 (2C), 129.1 (3C), 130.7 (2C), 133.7, 136.1, 195.6.

ESI-MS (*m/z*): 303.2 [M+H]⁺.

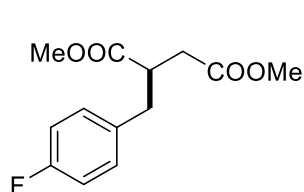
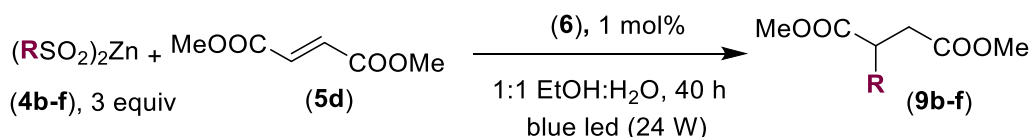


(8q): The general procedure was applied using zinc benzyl sulfinate (112.7 mg, 0.3 mmol, 3 equiv), **5q** (16.8 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was purified by flash chromatography (SiO₂; cyclohexane:AcOEt 70:30 mixture) in 91% yield (29.7 mg, 0.091 mmol).

$^1\text{H-NMR}$ (400 MHz, CD_3CN , 25°C): δ 3.23-3.27 (m, 2H), 3.47-3.53 (m, 2H), 4.34 (s, 2H), 7.33-7.42 (m, 5H), 7.61-7.69 (m, 2H), 7.75-7.81 (m, 1H), 7.86-7.92 (m, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CD_3CN , 25°C): δ 46.0, 49.3, 59.7, 128.7, 129.1 (2C), 129.8 (2C), 129.9, 130.6 (2C), 131.8 (2C), 135.4, 139.0.

ESI-MS (m/z): 325.0 $[\text{M}+\text{H}]^+$, 342.0 $[\text{M}+\text{H}_2\text{O}]^+$, 347.0 $[\text{M}+\text{Na}]^+$.



(9b): The general procedure was applied using **4b** (123.5 mg, 0.3 mmol, 3 equiv), **5d** (14.4 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL).

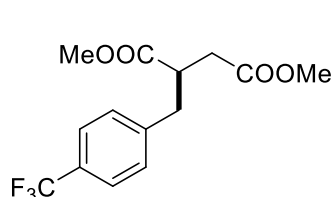
The product was purified by flash chromatography (SiO_2 ; cyclohexane:AcOEt 90:10 mixture) in 51% yield (13.2 mg, 0.051 mmol).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ 2.39 (dd, $J = 16.8$ Hz, $J = 5.2$ Hz, 1H), 2.65 (dd, $J = 16.8$ Hz, $J = 8.9$ Hz, 1H), 2.74 (dd, $J = 13.7$ Hz, $J = 7.9$ Hz, 1H), 2.98 (dd, $J = 13.7$ Hz, $J = 6.7$ Hz, 1H), 3.04-3.12 (m, 1H), 3.63 (s, 3H), 3.64 (s, 3H), 6.93-6.98 (m, 2H), 7.06-7.13 (m, 2H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): δ 34.9, 36.9, 43.1, 51.8, 51.9, 115.3 (d, $J = 20.9$ Hz, 2C), 130.4 (d, $J = 8.2$ Hz, 2C), 133.8 (d, $J = 3.3$ Hz), 161.7 (d, $J = 242.3$ Hz), 172.1, 174.4.

$^{19}\text{F-NMR}$ (400MHz, CDCl_3 , 25°C): δ (-115.1)-(-115.0) (m, 1F).

ESI-MS (m/z): 255.0 $[\text{M}+\text{H}]^+$, 277.0 $[\text{M}+\text{Na}]^+$.



(9c): The general procedure was applied using **4c** (153.5 mg, 0.3 mmol, 3 equiv), **5d** (14.4 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by flash chromatography (SiO_2 ; cyclohexane:AcOEt 85:15 mixture) in 63%

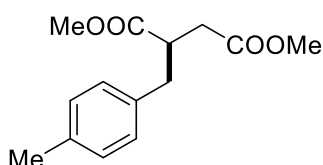
yield (19.2 mg, 0.063 mmol).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C): δ 2.41 (dd, $J = 16.8$ Hz, $J = 5.6$ Hz, 1H), 2.68 (dd, $J = 16.8$ Hz, $J = 8.4$ Hz, 1H), 2.85 (dd, $J = 13.6$ Hz, $J = 7.6$ Hz, 1H), 3.03-3.16 (m, 2H), 3.64 (s, 6H), 7.32-7.48 (m, 4H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C): δ 35.0, 37.4, 42.8, 51.8, 52.0, 123.6 (q, $J = 3.8$ Hz), 124.1 (q, $J = 272.7$ Hz), 125.7 (q, $J = 3.8$ Hz), 129.0, 130.9 (q, $J = 31.8$ Hz), 132.4 (q, $J = 1.3$ Hz), 139.1, 171.9, 174.1.

^{19}F -NMR (400 MHz, CDCl_3 , 25°C): δ -61.5.

ESI-MS (m/z): 305.0 $[\text{M}+\text{H}]^+$, 327.0 $[\text{M}+\text{Na}]^+$.



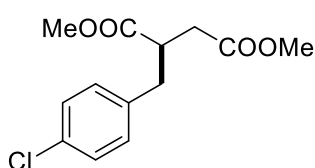
(9d): The general procedure was applied using **4d** (121.1 mg, 0.3 mmol, 3 equiv), **5d** (14.4 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by flash chromatography (SiO_2 ; cyclohexane/AcOEt 90:10 mixture) in 68% yield

(17.1 mg, 0.068 mmol).

^1H -NMR (400 MHz, CDCl_3 , 25°C): δ 2.32 (s, 3H), 2.38 (dd, $J = 16.8$ Hz, $J = 4.8$ Hz, 1H), 2.61-2.72 ppm (m, 2H), 2.97-3.02 (m, 1H), 3.05-3.12 (m, 1H), 3.62 (s, 3H), 3.66 (s, 3H), 7.02 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H).

^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ 21.0, 34.8, 37.3, 43.1, 51.7, 51.9, 128.8 (2C), 129.2 (2C), 135.0, 136.2, 172.3, 174.7.

ESI-MS (m/z): 251.2 $[\text{M}+\text{H}]^+$, 273.2 $[\text{M}+\text{Na}]^+$.



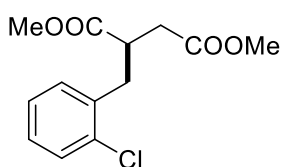
(9e): The general procedure was applied using **4e** (133.4 mg, 0.3 mmol, 3 equiv), **5e** (14.4 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL).

The product was purified by flash chromatography (SiO_2 ; cyclohexane/AcOEt 90:10 mixture) in 64% yield (17.3 mg, 0.064 mmol).

^1H -NMR (400 MHz, CDCl_3 , 25°C): δ 2.38 (dd, $J = 16.7$ Hz, $J = 5.6$ Hz, 1H), 2.66 (dd, $J = 16.7$ Hz, $J = 8.8$ Hz, 1H), 2.75 (dd, $J = 13.6$ Hz, $J = 7.9$ Hz, 1H), 2.99 (dd, $J = 13.6$ Hz, $J = 6.8$ Hz, 1H), 3.05-3.15 (m, 1H), 3.64 (s, 3H), 3.65 (s, 3H), 7.05-7.09 (m, 2H), 7.22-7.26 (m, 2H).

^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ 34.9, 37.0, 42.9, 51.8, 52.0, 128.7 (2C), 130.3 (2C), 132.6, 136.6, 172.0, 174.3.

ESI-MS (m/z): 271.2 $[\text{M}+\text{H}]^+$, 293.2 $[\text{M}+\text{Na}]^+$.



(9f): The general procedure was applied using **4e** (133.4 mg, 0.3 mmol, 3 equiv), **5f** (14.4 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by flash chromatography (SiO_2 ; cyclohexane/AcOEt 90:10 mixture) in 61% yield (16.5 mg, 0.061

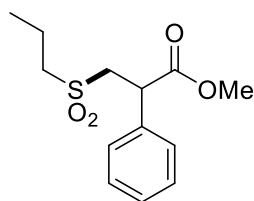
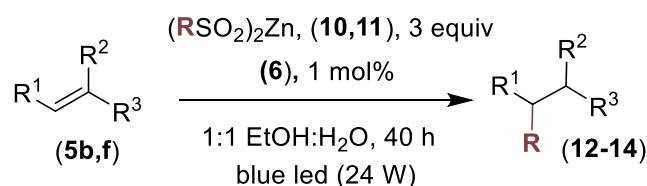
mmol).

^1H -NMR (400 MHz, CDCl_3 , 25°C): δ 2.43 (dd, $J = 16.8$ Hz, $J = 4.4$ Hz, 1H),

2.71 (dd, $J = 16.7$ Hz, $J = 9.2$ Hz, 1H), 2.90 (dd, $J = 13.5$ Hz, $J = 8.2$ Hz, 1H), 3.13 (dd, $J = 13.5$ Hz, $J = 6.9$ Hz, 1H), 3.18-3.28 (m, 1H), 3.61 (s, 3H), 3.63 (s, 3H), 7.12-7.17(m, 3H), 7.32-7.34 (m, 1H).

^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ 35.1, 35.4, 41.2, 51.7, 51.9, 126.8, 128.3, 129.7, 131.2, 134.3, 135.9, 172.0, 174.5.

ESI-MS (m/z): 271.2 $[\text{M}+\text{H}]^+$, 293.2 $[\text{M}+\text{Na}]^+$.

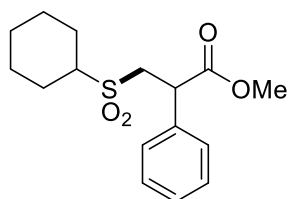


(11): The general procedure was applied using **10** (83.9 mg, 0.3 mmol, 3 equiv), **5f** (24.8 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by flash chromatography (SiO_2 ; cyclohexane/AcOEt 85:15 mixture) in 30% yield (8.0 mg, 0.030 mmol).

^1H -NMR (400 MHz, CDCl_3 , 25°C): δ 0.98 (t, $J = 7.2$ Hz, 3H), 1.71-1.87 (m, 2H), 2.67-2.81 (m, 2H), 3.26 (dd, $J = 14.4$ Hz, $J = 8.4$ Hz, 1H), 3.70 (s, 3H), 3.91 (dd, $J = 14.0$ Hz, $J = 8.4$ Hz, 1H), 4.25 (dd, $J = 8.8$ Hz, $J = 5.1$ Hz, 1H), 7.28-7.34 (m, 5H).

^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ 13.0, 15.8, 45.5, 52.8, 55.6, 55.8, 127.8 (2C), 128.4, 129.2 (2C), 136.1, 172.1.

ESI-MS (m/z): 271.1 $[\text{M}+\text{H}]^+$, 288.2 $[\text{M}+\text{H}_2\text{O}]^+$, 293.2 $[\text{M}+\text{Na}]^+$.

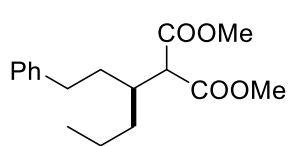


(13): The general procedure was applied using **11** (107.9 mg, 0.3 mmol, 3 equiv), **5f** (24.8 mg, 0.1 mmol), **6** (1.1 mg, 1 μmol , 1 mol%), EtOH (0.5 mL) and H_2O (0.5 mL). The product was purified by flash chromatography (SiO_2 ; cyclohexane:AcOEt 95:15 mixture) in 53% yield (13 mg, 0.053 mmol).

^1H -NMR (400 MHz, CDCl_3 , 25°C): δ 1.07-1.30 (m, 3H), 1.40-1.54 (m, 2H), 1.62-1.70 (m, 1H), 1.81-1.92 (m, 2H), 2.02-2.15 (m, 2H), 2.55 (tt, $J = 12.0$ Hz, $J = 3.6$ Hz, 1H), 3.21 (dd, $J = 14.0$ Hz, $J = 4.8$ Hz, 1H), 3.69 (s, 3H), 3.89 (dd, $J = 13.8$ Hz, $J = 9.0$ Hz, 1H), 4.25 (dd, $J = 8.3$ Hz, $J = 4.8$ Hz, 1H), 7.28-7.36 (m, 5H).

^{13}C -NMR (100 MHz, CDCl_3 , 25°C): δ 24.8, 25.0, 25.0, 25.0, 44.9, 52.4, 52.8, 61.9, 127.8 (2C), 128.3, 129.2 (2C), 136.4, 172.1.

ESI-MS (m/z): 311.2 $[\text{M}+\text{H}]^+$, 328.2 $[\text{M}+\text{H}_2\text{O}]^+$.



(14): The general procedure was applied using **10** (83.9 mg, 0.3 mmol, 3 equiv), **5b** (24.8 mg, 0.1 mmol), **6** (1.1 mg, 1 μ mol, 1 mol%), EtOH (0.5 mL) and H₂O (0.5 mL). The product was purified by flash chromatography

(SiO₂; cyclohexane:AcOEt 90:10 mixture) in 53% yield (15.5 mg, 0.053 mmol).

¹H-NMR (400 MHz, CDCl₃, 25°C): δ 0.89 (t, J = 6.8 Hz, 3H), 1.22-1.42 (m, 4H), 1.59-1.76 (m, 2H), 2.17-2.25 (m, 1H), 2.53-2.65 (m, 2H), 3.49 (d, J = 7.2 Hz, 1H), 3.71 (s, 6H), 7.13-7.17 (m, 3H), 7.24-7.27 (m, 2H).

¹³C-NMR (100 MHz, CDCl₃, 25°C): δ 14.2, 19.8, 33.0, 33.1, 33.3, 37.8, 52.2, 55.0, 125.8, 128.3 (2C), 128.3 (2C), 142.1, 169.3, 169.4.

ESI-MS (m/z): 293.0 [M+H]⁺, 310.0 [M+H₂O]⁺.

Test to determinate the stability of sodium benzy sulfinate

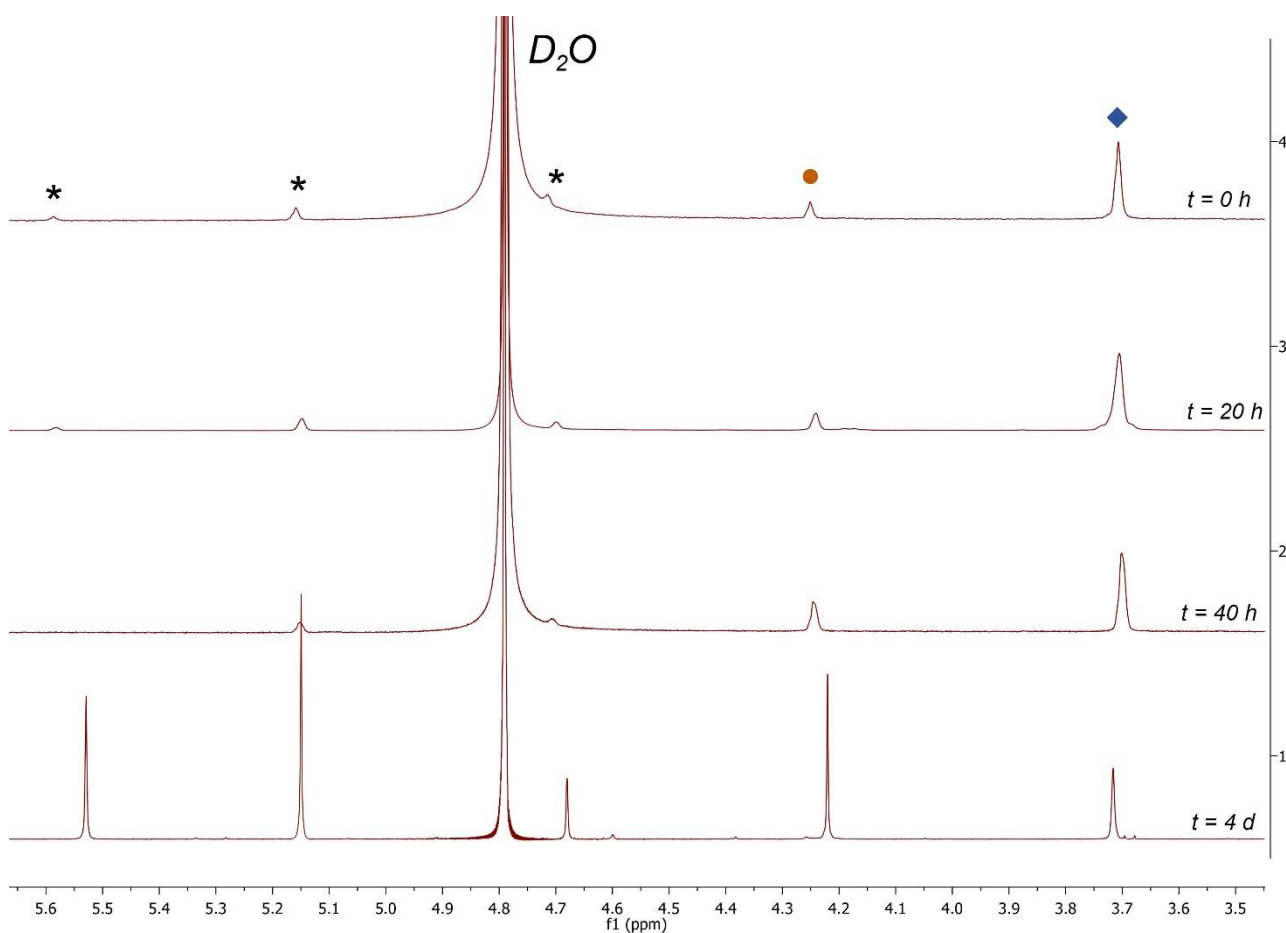


Figure S1. ¹H-NMR (400 MHz, D₂O, 25°C) spectra of sodium benzy sulfinate at different amount of time from preparation. \blacklozenge = sulfinate; \bullet = sulfonate.

NMR spectra of the same batch of sodium benzenesulfonate, stored at -20°C under argon, were collected after different time from the preparation. Decomposition of the sulfinate to sulfonate and some undetermined impurities were observed.

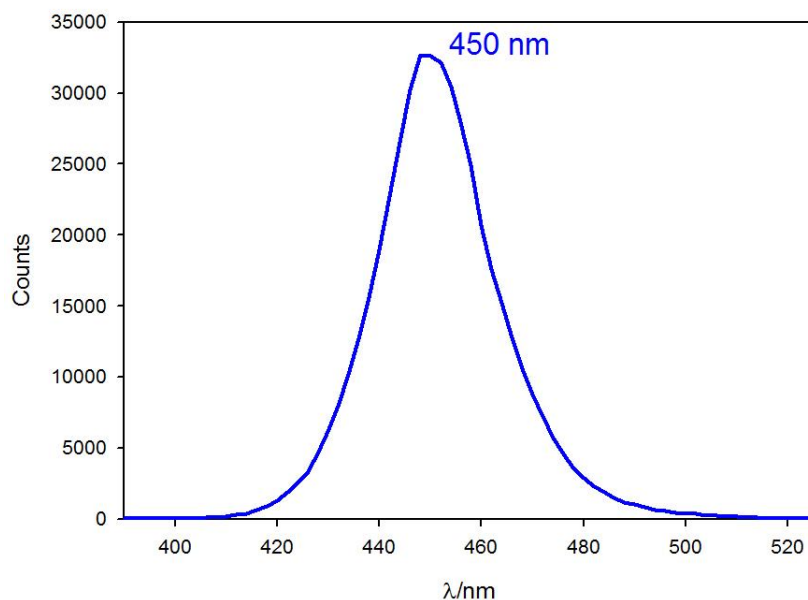


Figure S2. Emission profile of the 24W Blue LED strip used to irradiate the solutions.

Electrochemistry

Voltammetric experiments were performed using a Metrohm AutoLab PGSTAT 302 electrochemical workstation in combination with the NOVA software package. All the measurements were carried out at room temperature in acetonitrile solutions with a sample concentration of approx. 1 mM and using 0.1 M tetrabutylammonium hexafluorophosphate (electrochemical grade, TBAPF₆) as the supporting electrolyte. Oxygen was removed from the solutions by bubbling argon for 20 minutes. All the experiments were carried out using a three-electrode setup (BioLogic VC-4 cell, with a cell volume of 5 ml) with a glassy-carbon working electrode (1.6 mm diameter), the Ag/AgNO₃ redox couple (0.01 M in acetonitrile with 0.1 M TBAClO₄ supporting electrolyte) as reference electrode and a platinum wire as counter electrode. At the end of each measurement, ferrocene was added as the internal reference. All square-wave voltammograms were recorded with a scan rate of 100 mV s⁻¹, a square-wave amplitude of ± 20 mV and a frequency of 25 Hz.

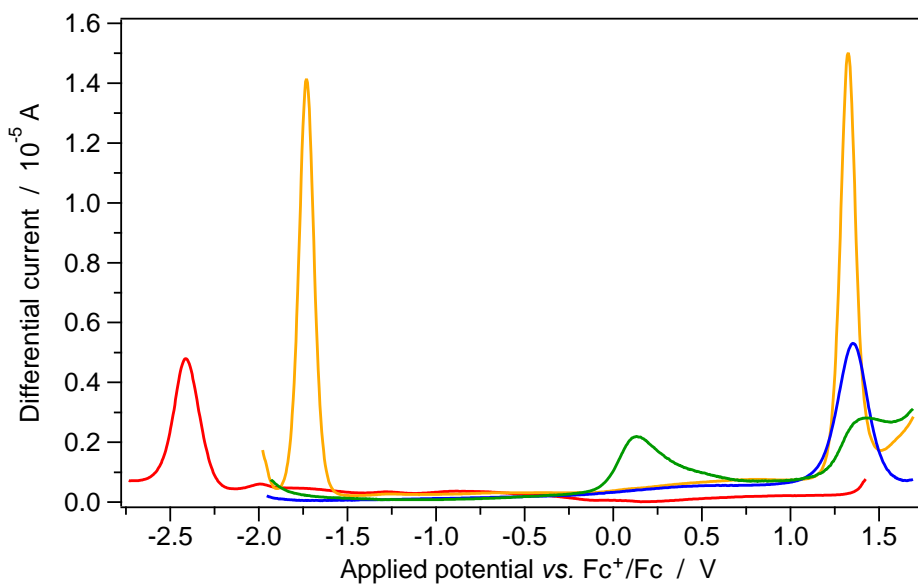


Figure S3. Square-wave voltammograms of the iridium(III) photocatalysts **6** (orange), together with those of the Michael acceptor **5a** (red), of the pure 1-methylimidazole **MI** (blue) and of the benzyl zinc sulfinate **4a** + **4** · **MI** (green); sample concentration: 1 mM. Experiments were carried out in acetonitrile solutions at room-temperature, with TBAPF₆ 0.1 M as supporting electrolyte, and recorded at a scan rate of 100 mV s⁻¹ with a square-wave amplitude of ± 20 mV and a frequency of 25 Hz.

Photophysical measurements

All the spectroscopic investigations were carried out in spectrofluorimetric grade acetonitrile using fluorimetric Suprasil® quartz cuvettes with a 10.00 mm path length.

Absorption spectroscopy

Absorption spectra were recorded with a Perkin-Elmer Lambda 950 spectrophotometer. All photoluminescence experiments were performed in oxygen-free solution, by removing oxygen through argon bubbling for 20 minutes.

Stern-Volmer quenching experiments

Stern-Volmer experiments were performed at room-temperature in oxygen-free conditions (argon-saturated environment) using 3 ml of acetonitrile solution containing iridium photocatalyst (**6**) (with a concentration of $1.5 \cdot 10^{-5}$ M) and increasing amounts of quencher. The emission lifetimes (τ),

used in the Stern-Volmer experiment, were measured through the time-correlated single photon counting (TCSPC) technique using an HORIBA Jobin Yvon IBH FluoroHub controlling a spectrometer equipped with a pulsed NanoLED ($\lambda_{\text{exc}} = 330 \text{ nm}$; FWHM = 11 nm) as excitation source and a red-sensitive Hamamatsu R-3237-01 PMT (185– 850 nm) as detector. The analysis of the luminescence decay profiles was accomplished with the DAS6 Decay Analysis Software provided by the manufacturer, and the quality of the fitting was assessed with the χ^2 value close to unity and with the residuals regularly distributed along the time axis.

Experimental uncertainties are estimated to be $\pm 2 \text{ nm}$ for absorption peaks and $\pm 10\%$ for τ determinations.

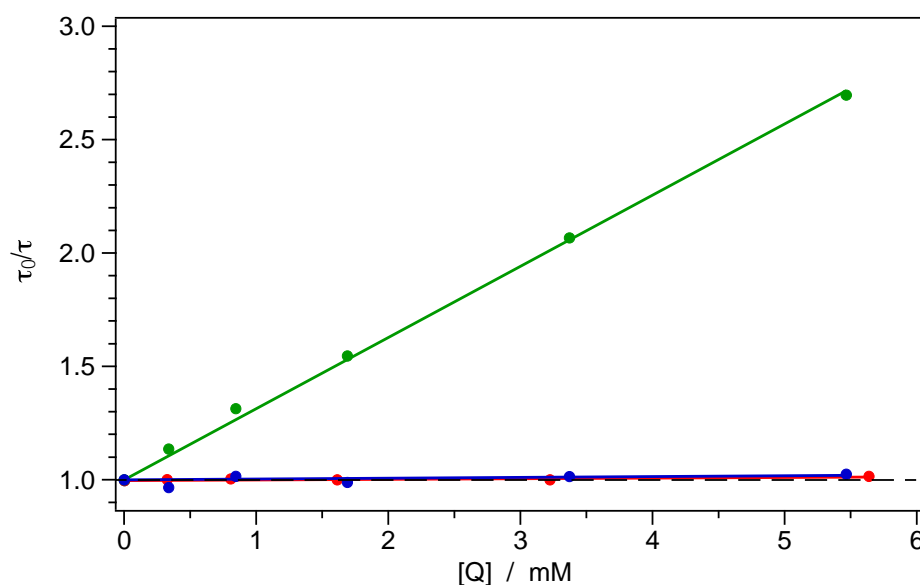


Figure S4. Stern-Volmer plots showing the quenching of the excited-state lifetime (τ) of the iridium (III) photocatalysts **6**, in the presence of increasing amounts of the Michael acceptor **5a** (red), of the pure 1-methylimidazole **MI** (blue) and of the benzyl zinc sulfinate **4a** + **4** · **MI** (green). Quenching is only observed when the benzyl zinc sulfinate is added to the photocatalyst solution. Experiments were carried out in oxygen-free acetonitrile solution at 298 K with a photocatalyst concentration of 0.015 mM, exciting at 330 nm. In the y-axis label, τ_0 is the unquenched excited-state lifetime of the photocatalyst.

Determination of quantum yield

The reaction was carried out in a EtOH:H₂O mixture (1:1, analytical grade ethanol and Milli-Q water) mixture and placed in a Suprasil® quartz cuvette with a 2.00 mm path length. The cuvette was filled with the benzyl zinc sulfinate **4a** (67.6 mg, 0.180 mmol, 3 equiv), the Michael acceptor

5a (12.0 mg, 0.060 mmol, 1 equiv), the iridium photocatalyst **6** (0.66 mg, 0.60 μmol), and 600 μl of the above mentioned solvent mixture. Before irradiating this solution, dissolved oxygen was removed from the cuvette by argon bubbling for 15 minutes.

The reaction mixture was excited at 334 nm for 18 hours, using a 100 W Hg lamp equipped with an appropriate dichroic filter. During this process, the solution was stirred and kept at constant temperature (298 K). The photon flux coming from the lamp to the sample in the cuvette was estimated using the ferrioxalate actinometer (photon flux: 1.3 ± 0.1 nmol/s). In our experimental conditions, all the incident light is quantitatively absorbed by the iridium photocatalyst **6** only. This is because of its high concentration (*i.e.*, $A_{334 \text{ nm}} \approx 2.4$) and because no other molecule added to the reaction mixture absorbs at the excitation wavelength (see Figure S5).

The product formation was determined by $^1\text{H-NMR}$ based on the relative conversion of the Michael acceptor **5a**. After irradiation, the estimated conversion was $(52 \pm 8)\%$, corresponding to (31 ± 8) μmol of product formed.

$$\Phi = \frac{\text{moles of product formed}}{\text{moles of photons absorbed}} = \frac{31 \mu\text{mol}}{1.3 \frac{\text{nmol}}{\text{s}} \cdot 6.48 \cdot 10^4 \text{ s}} = 0.37 \pm 0.09$$

The error on the quantum yield estimation (Φ) was calculated using the general rule for the propagation of error (using the partial-derivatives method).

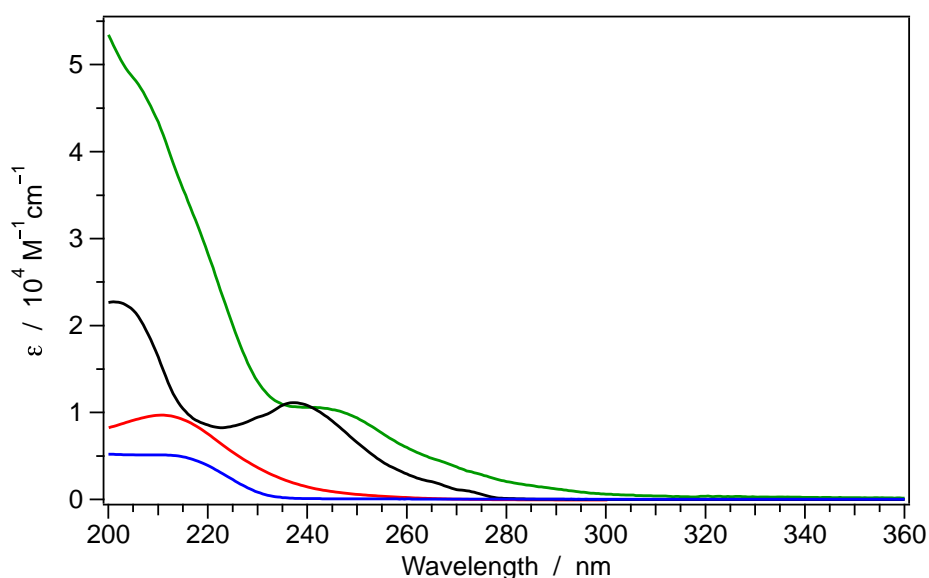
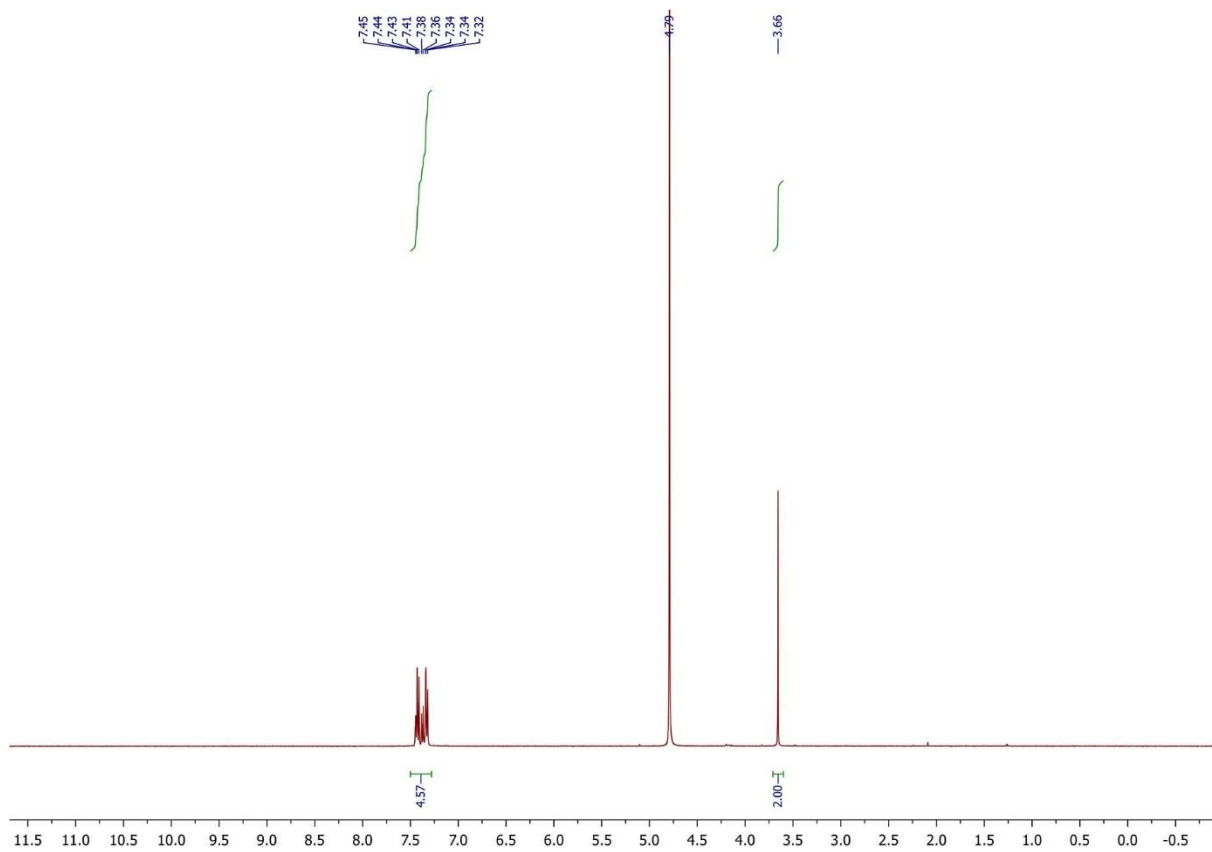
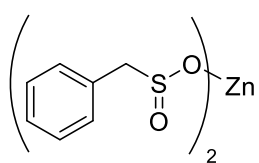


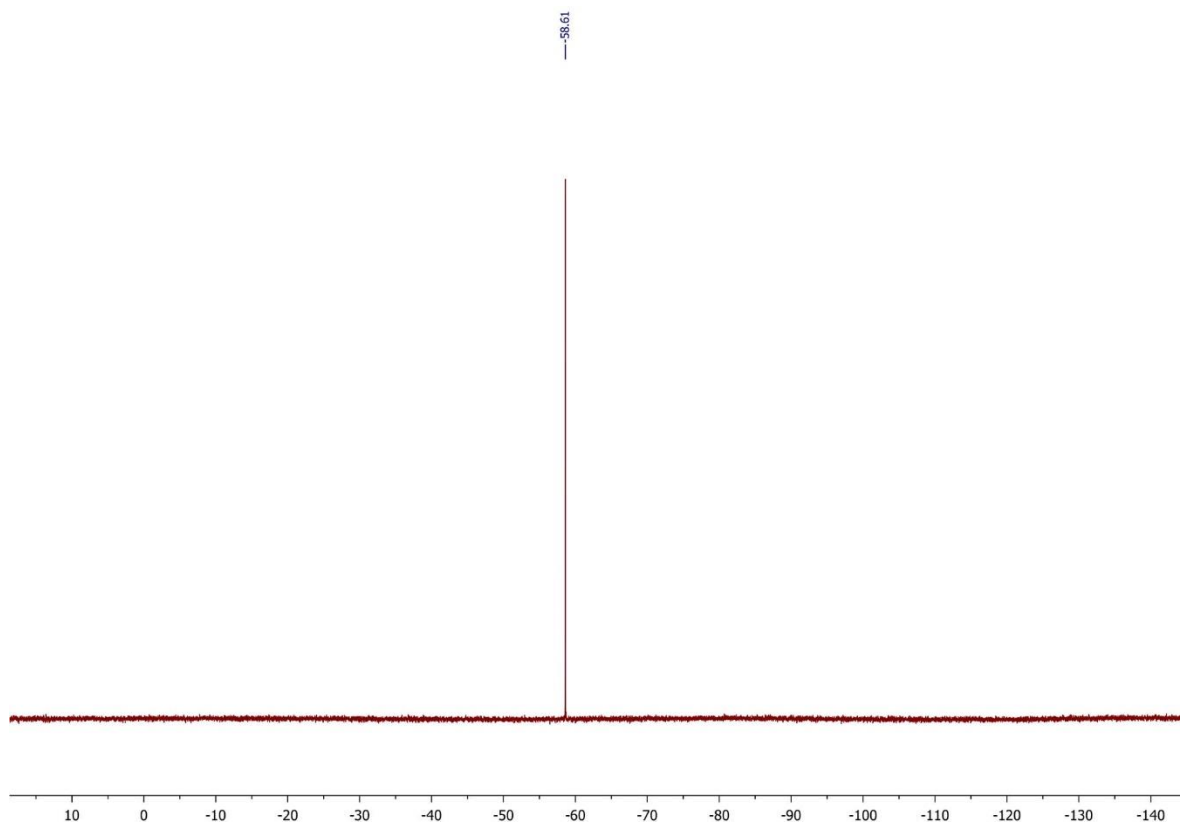
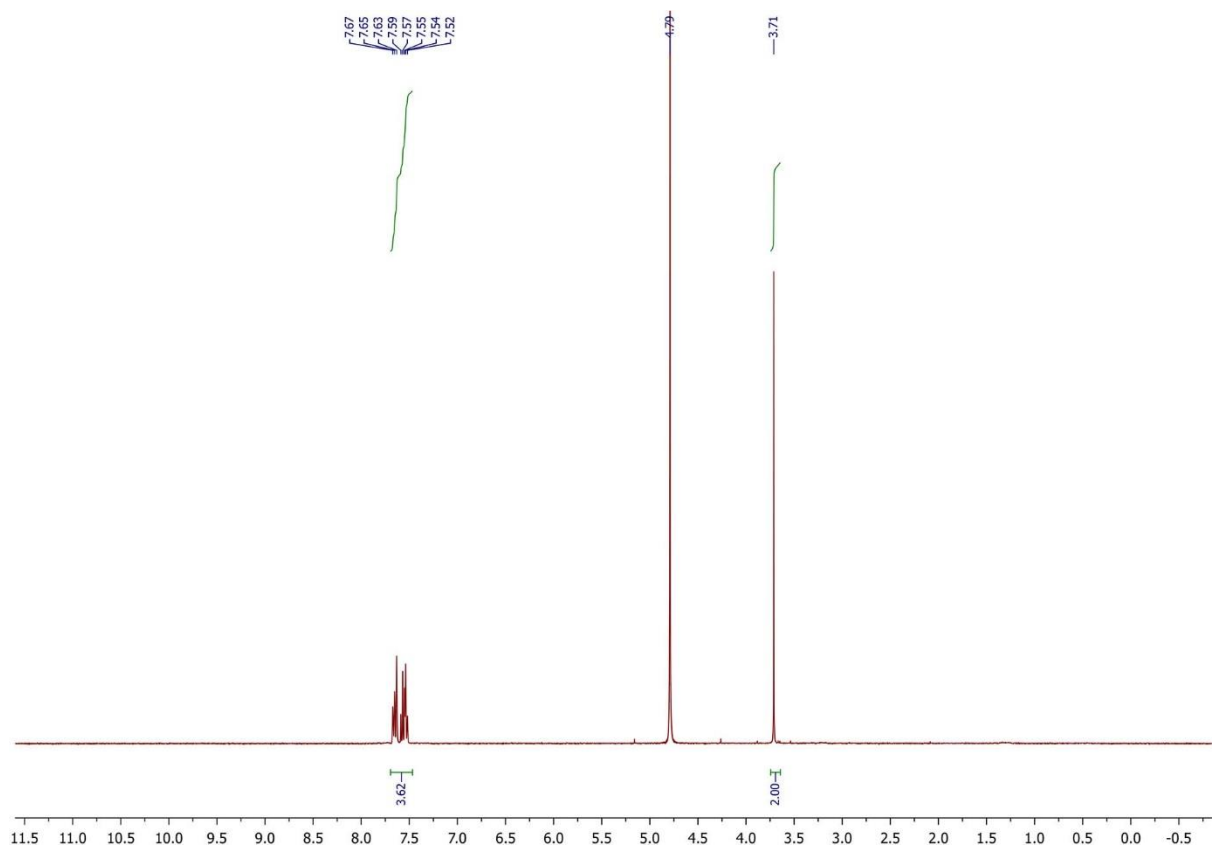
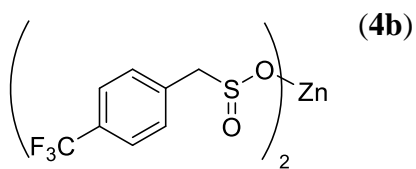
Figure S5. Room-temperature absorption spectra of pristine benzyl zinc sulfinate **4a** in water (black), and of the compounds of the reaction mixtures in acetonitrile (*i.e.*, the Michael acceptor **5a** (red), the pure 1-methylimidazole **MI** (blue) and the radical precursor **4a** + **4 MI** (green)). None of the above-mentioned compound display absorption features at $\lambda > 300$ nm.

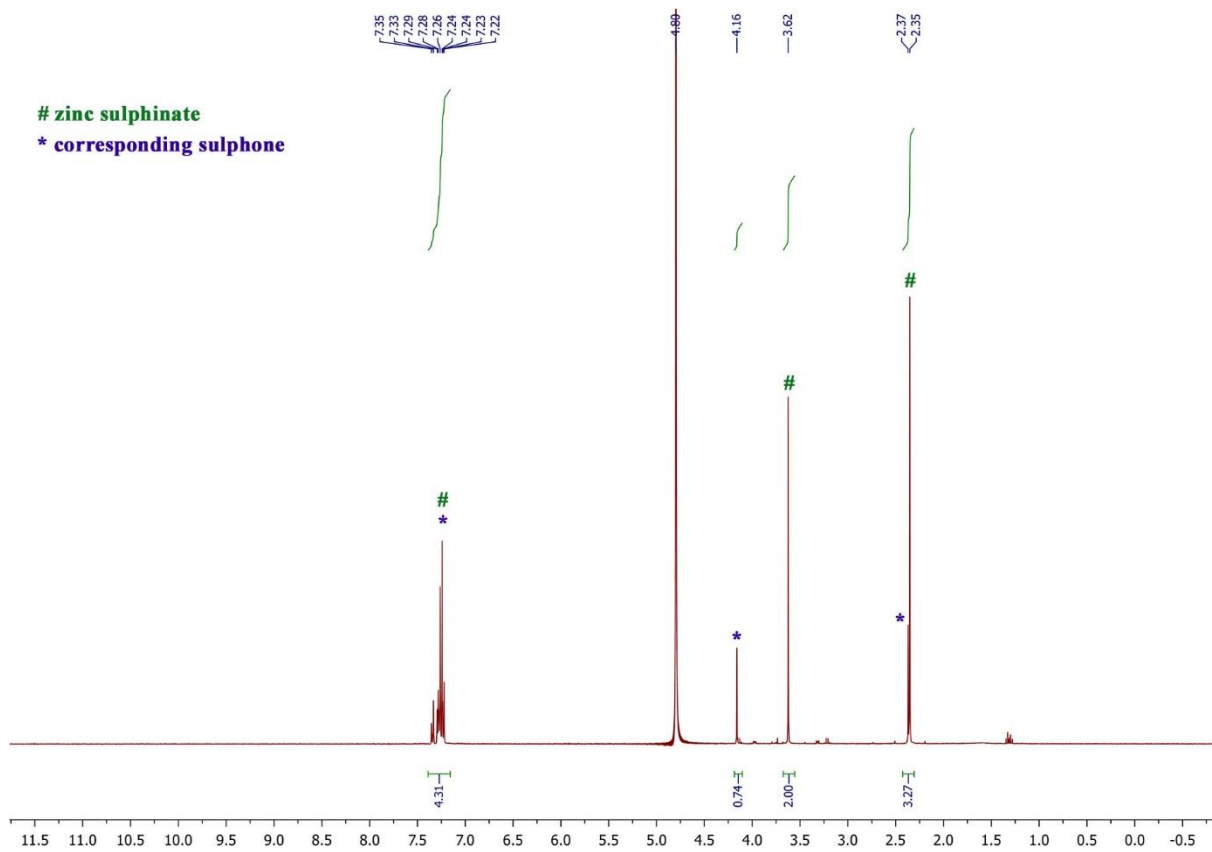
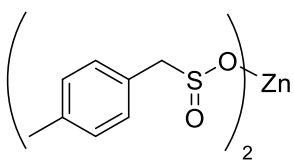
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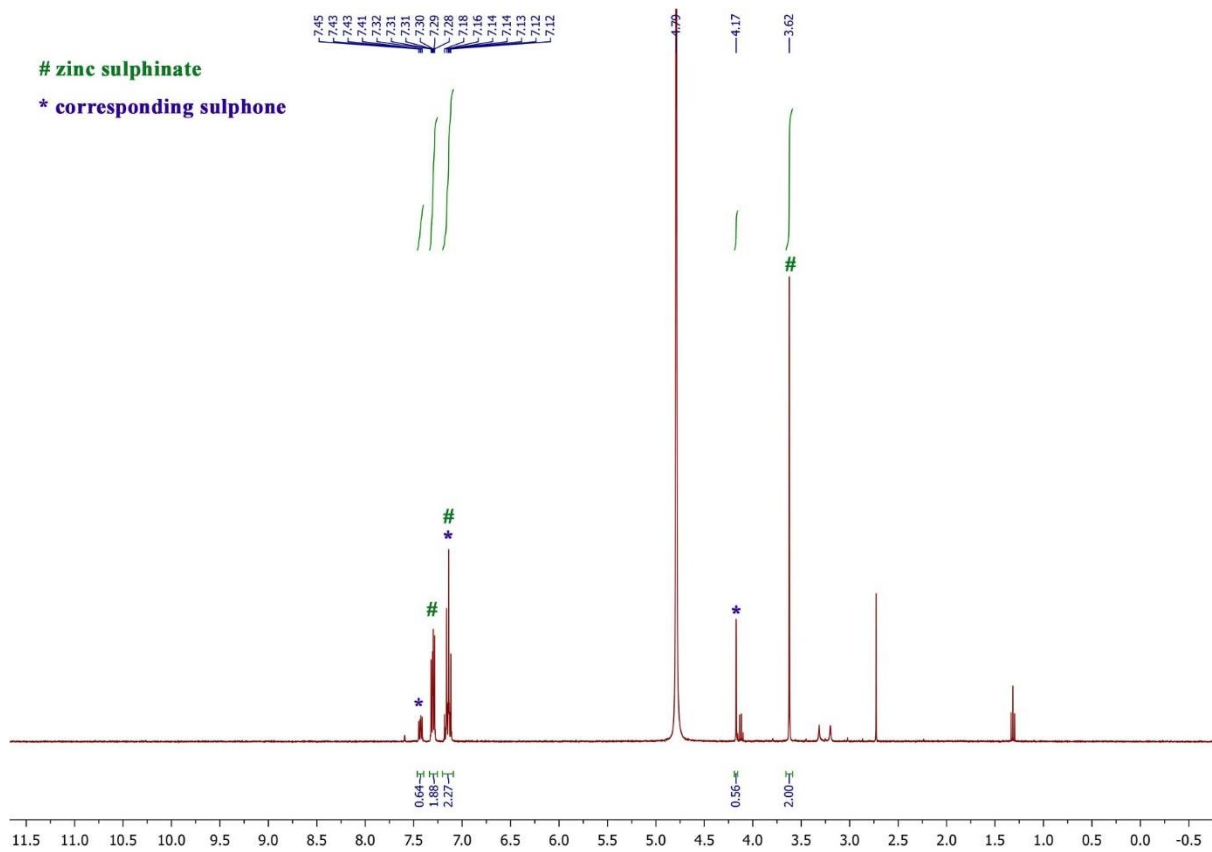
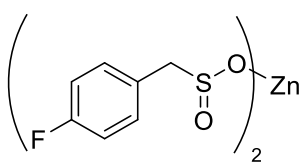
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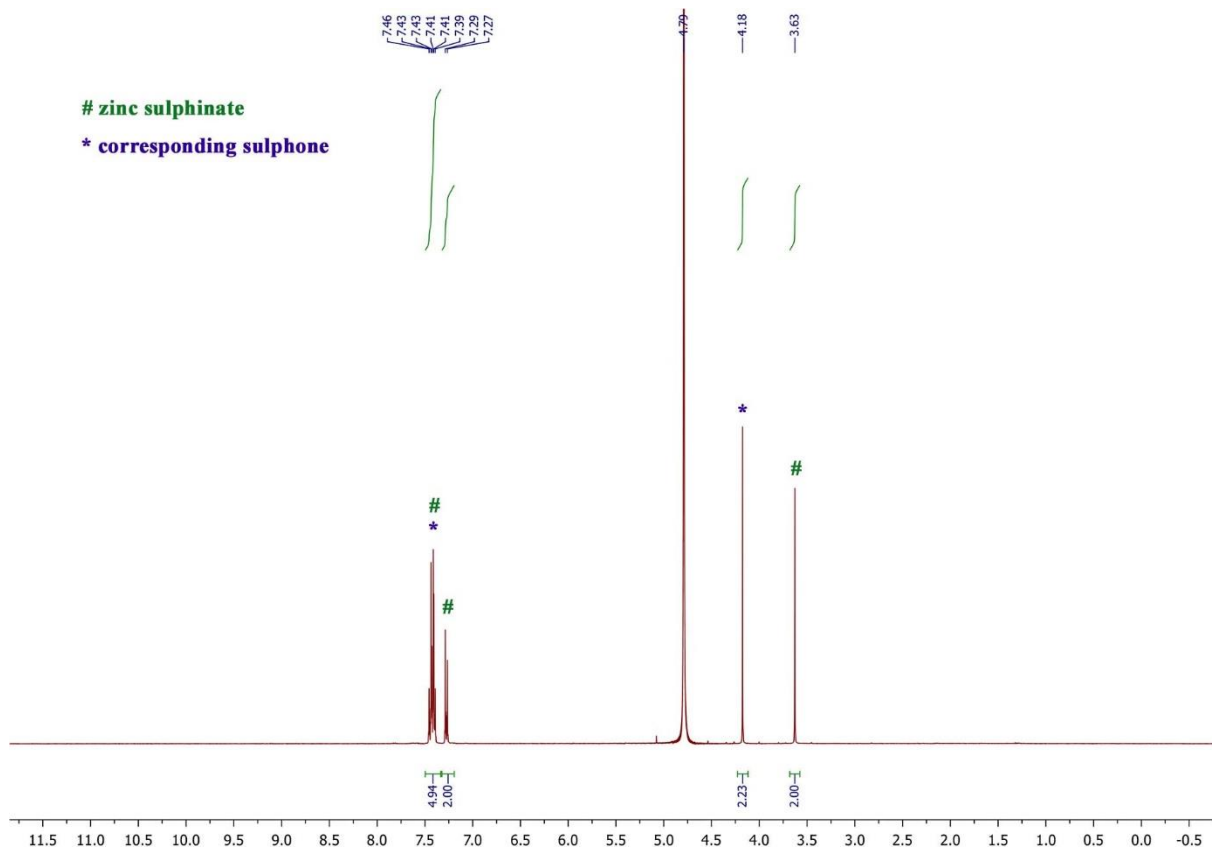
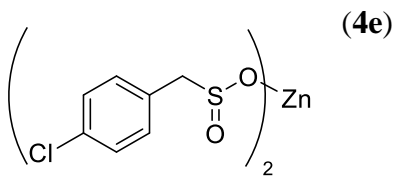
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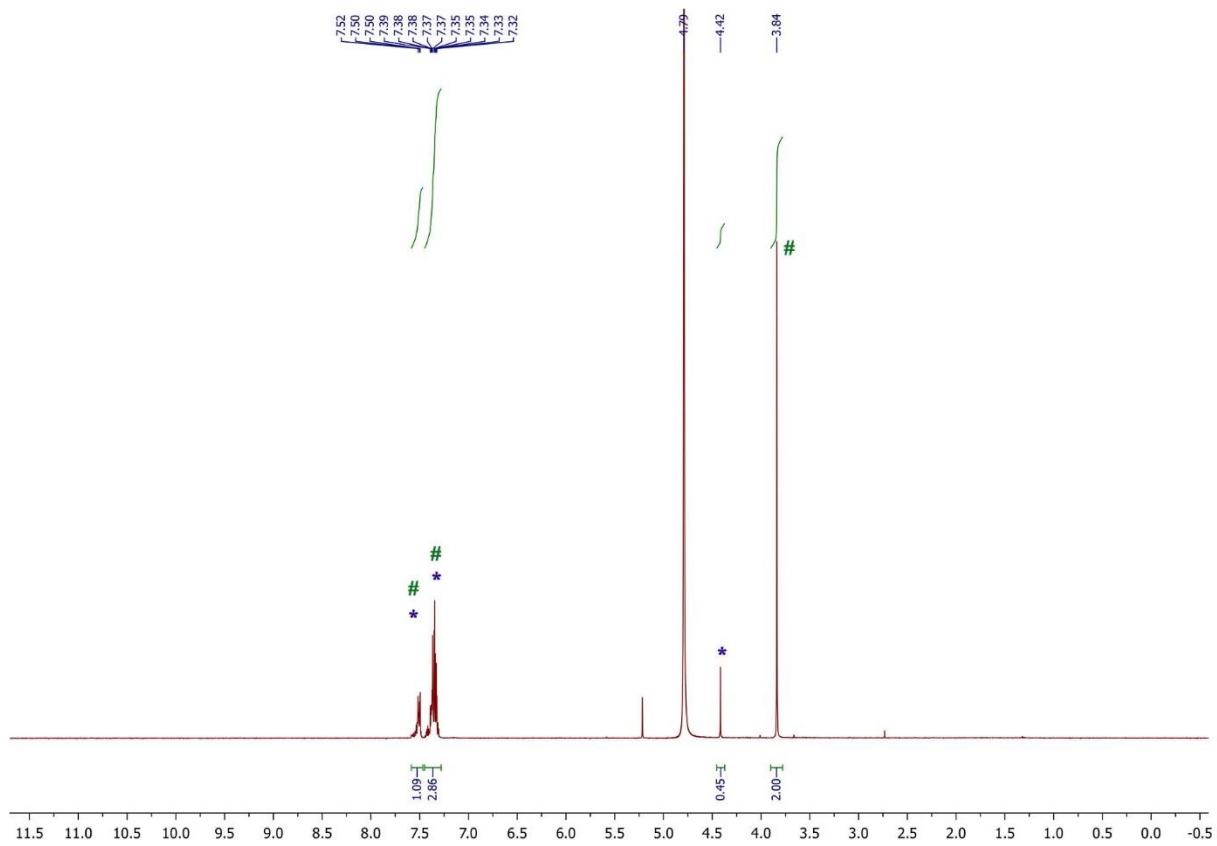
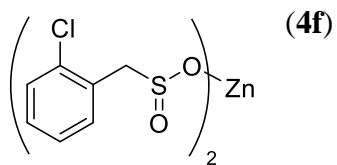


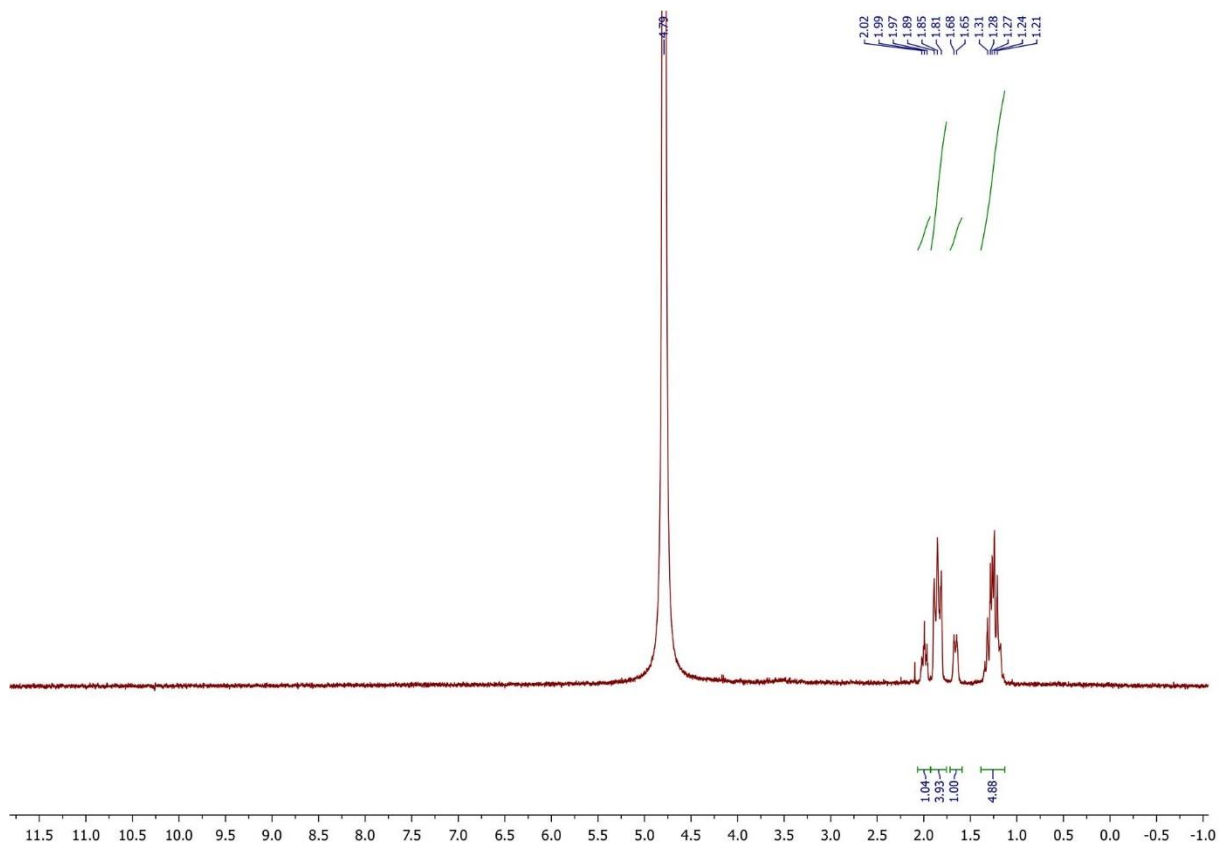
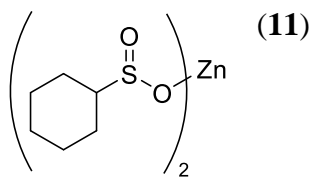






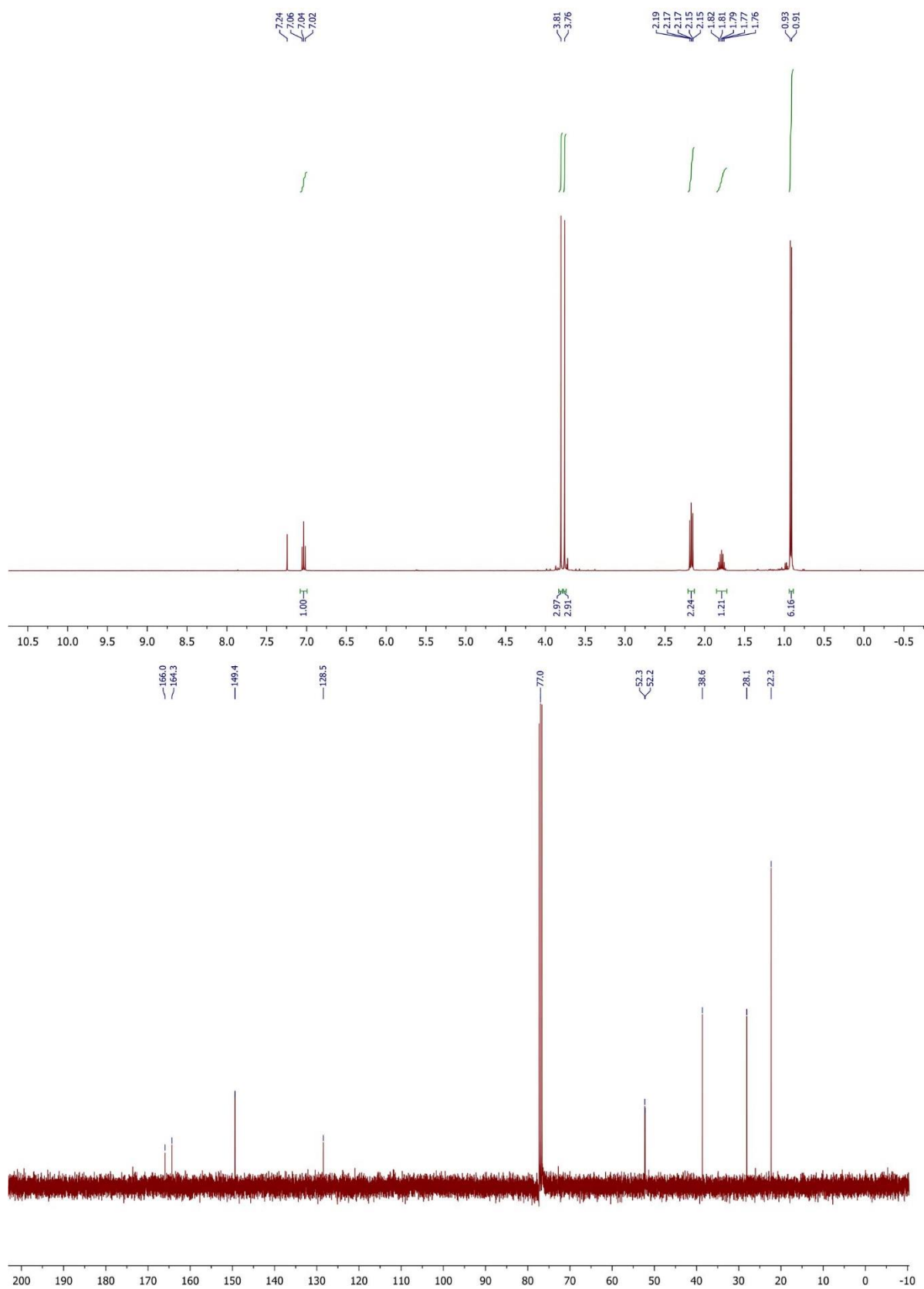
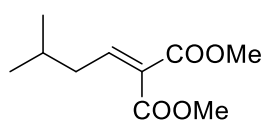


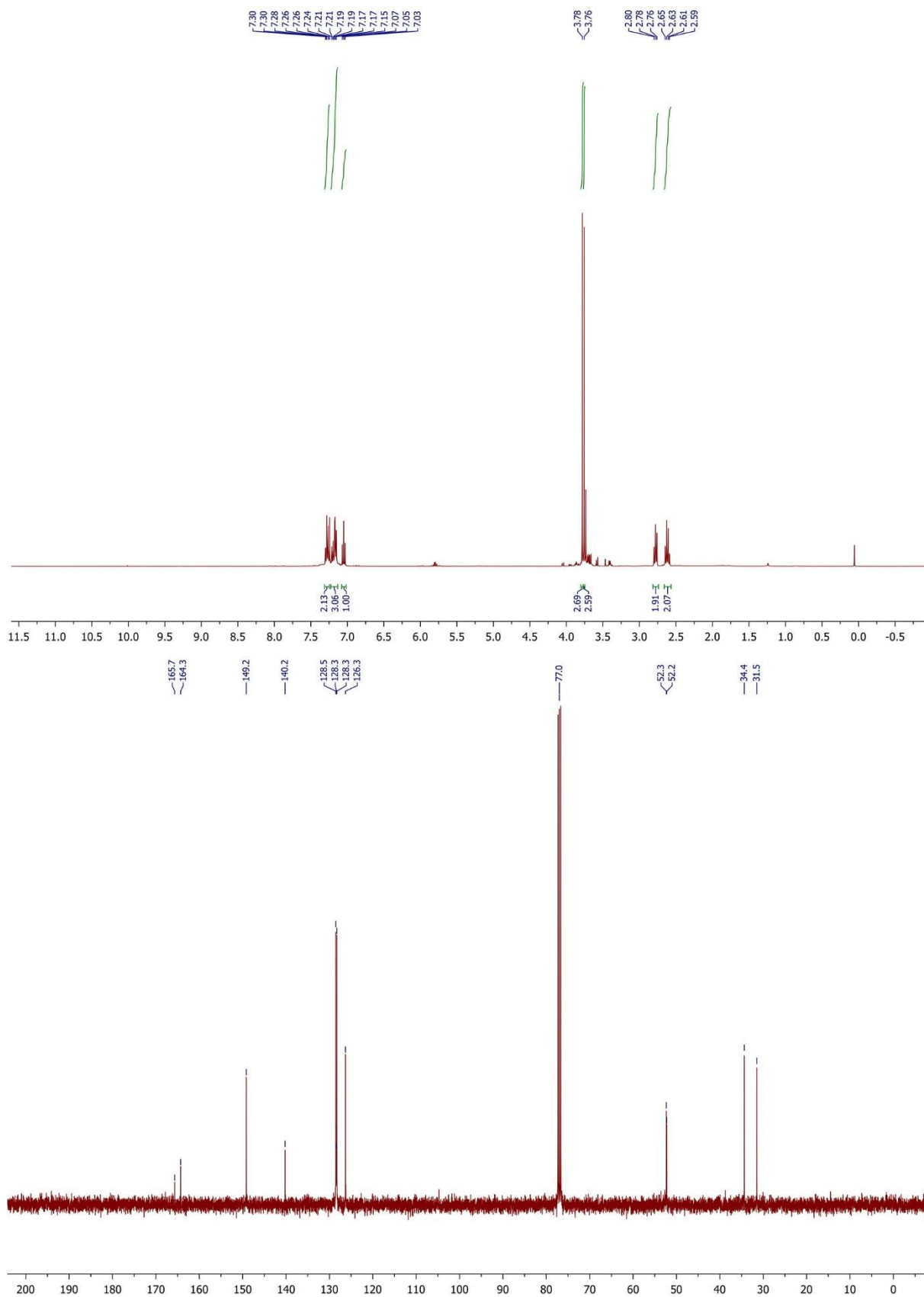
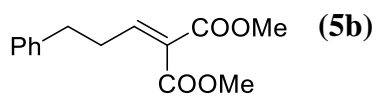


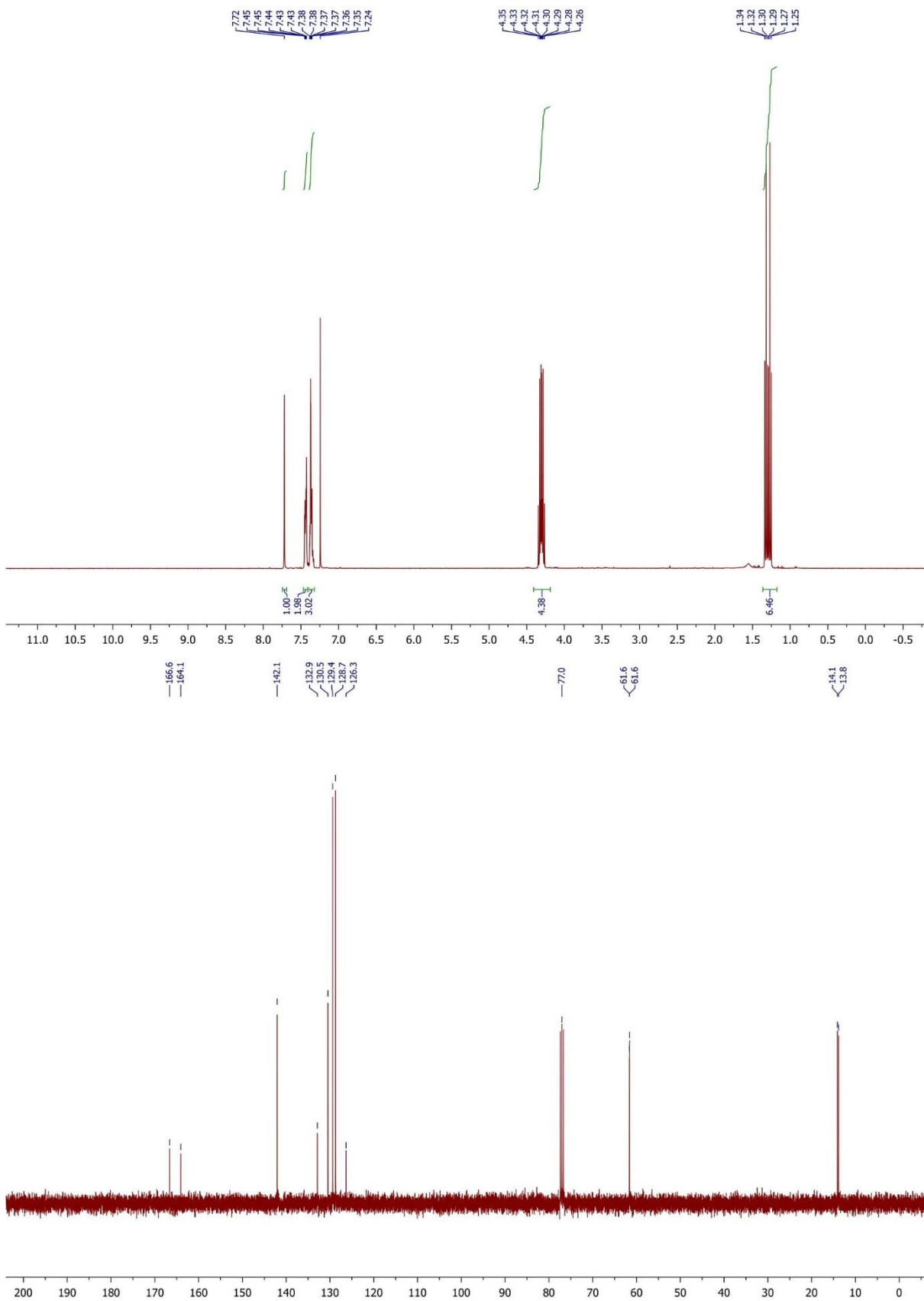
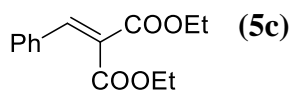


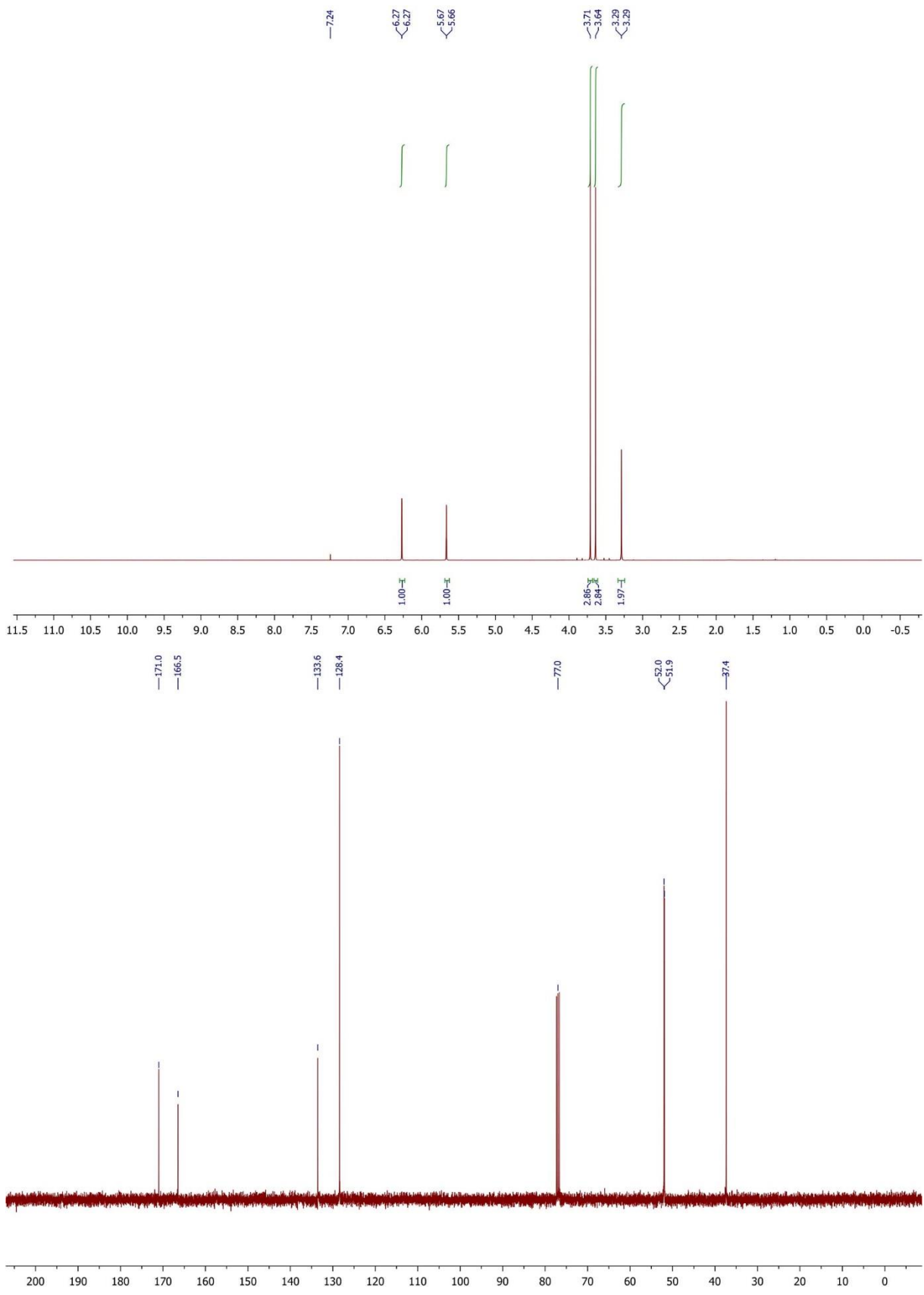
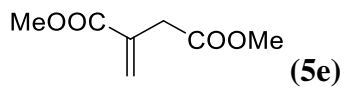
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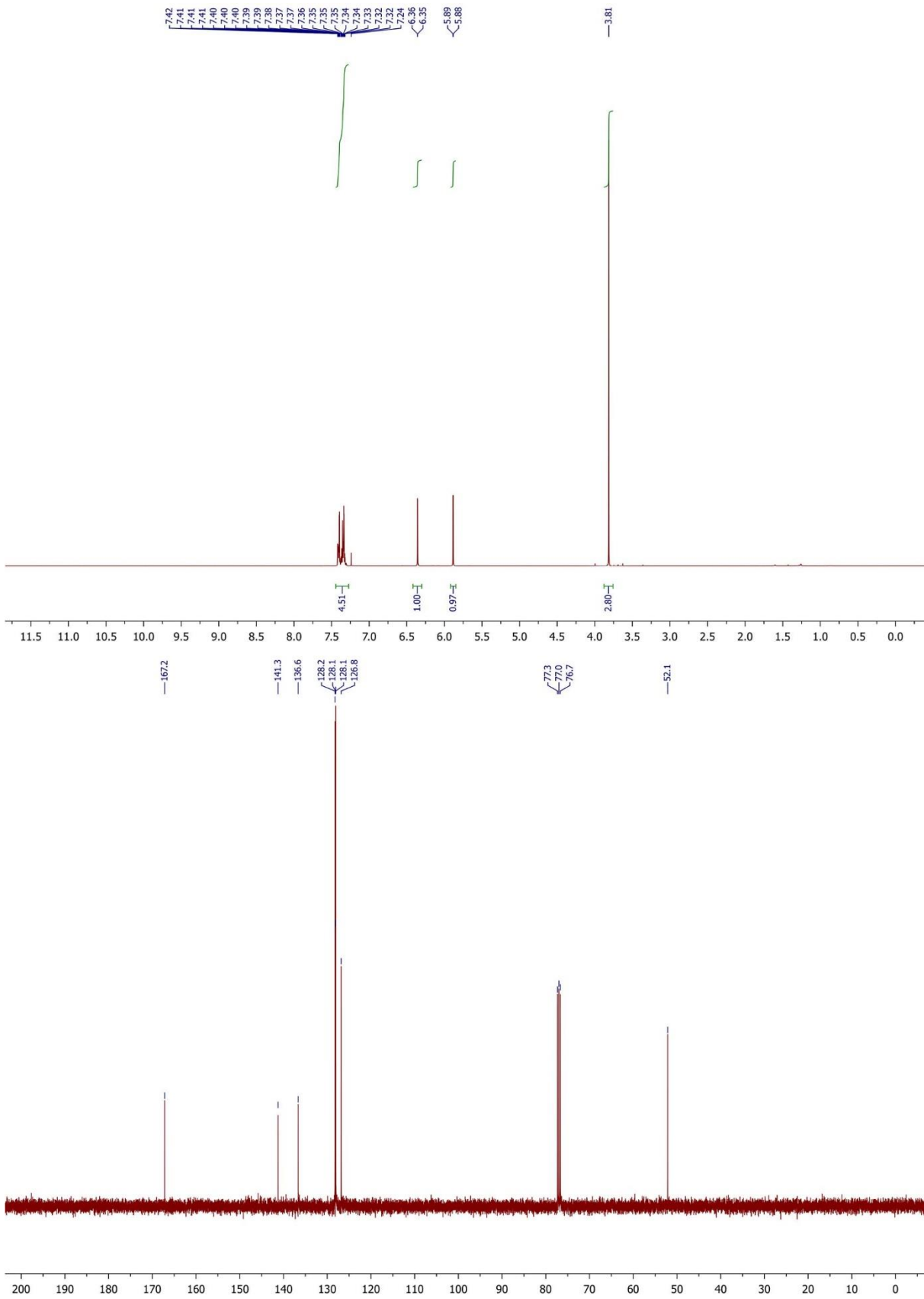
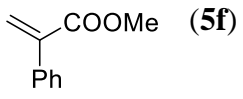
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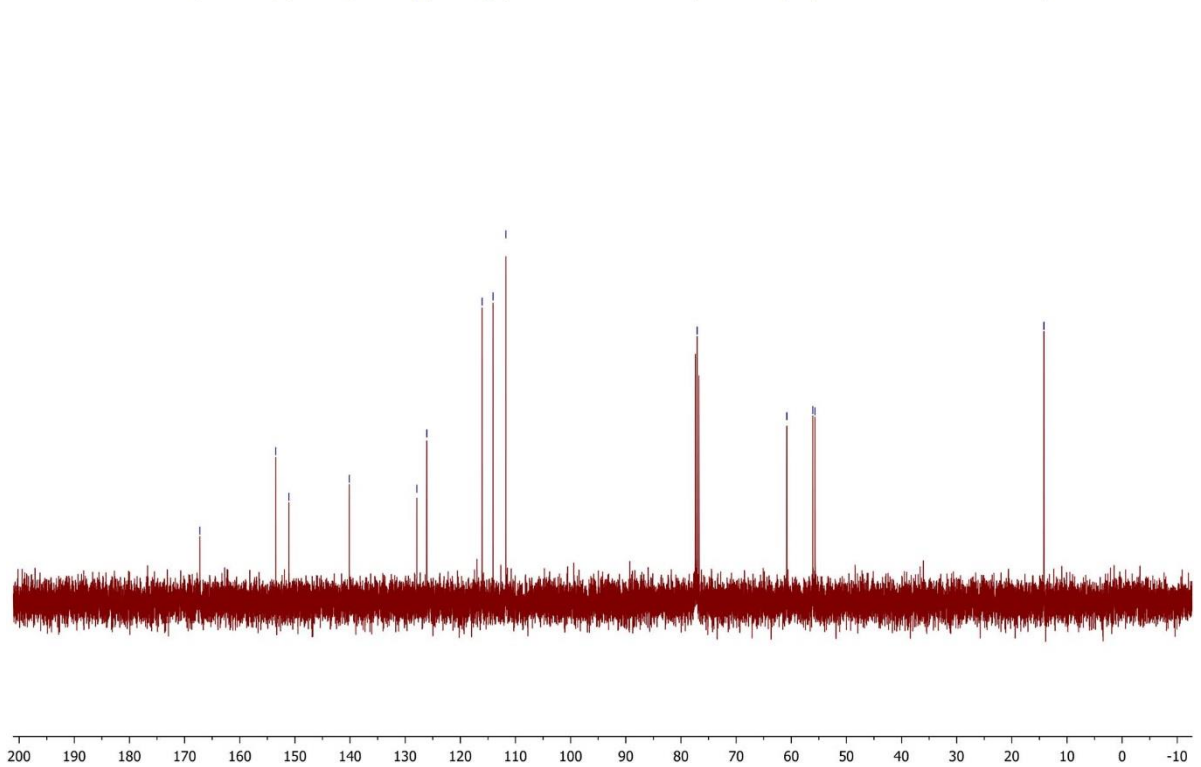
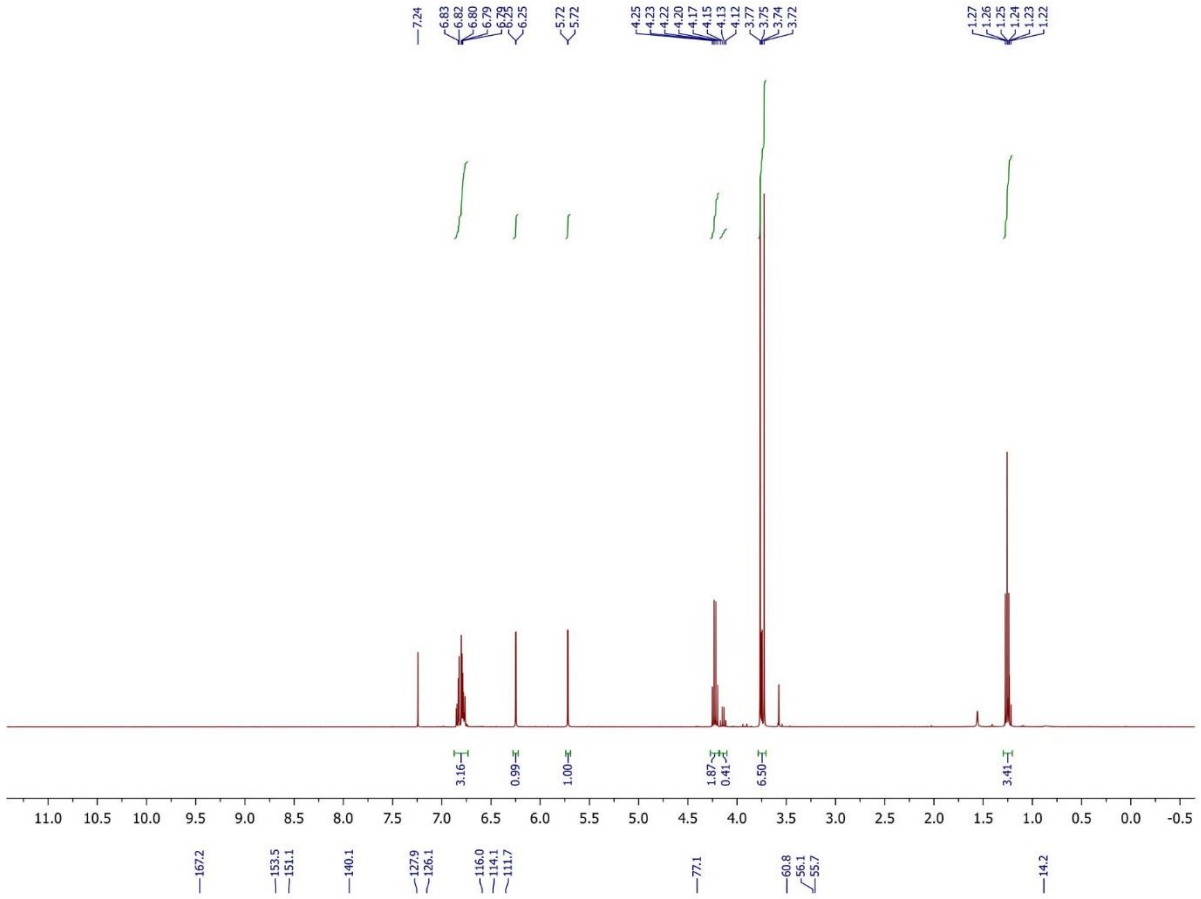
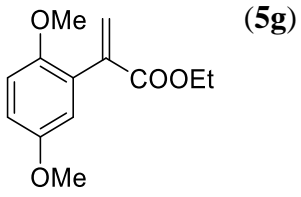


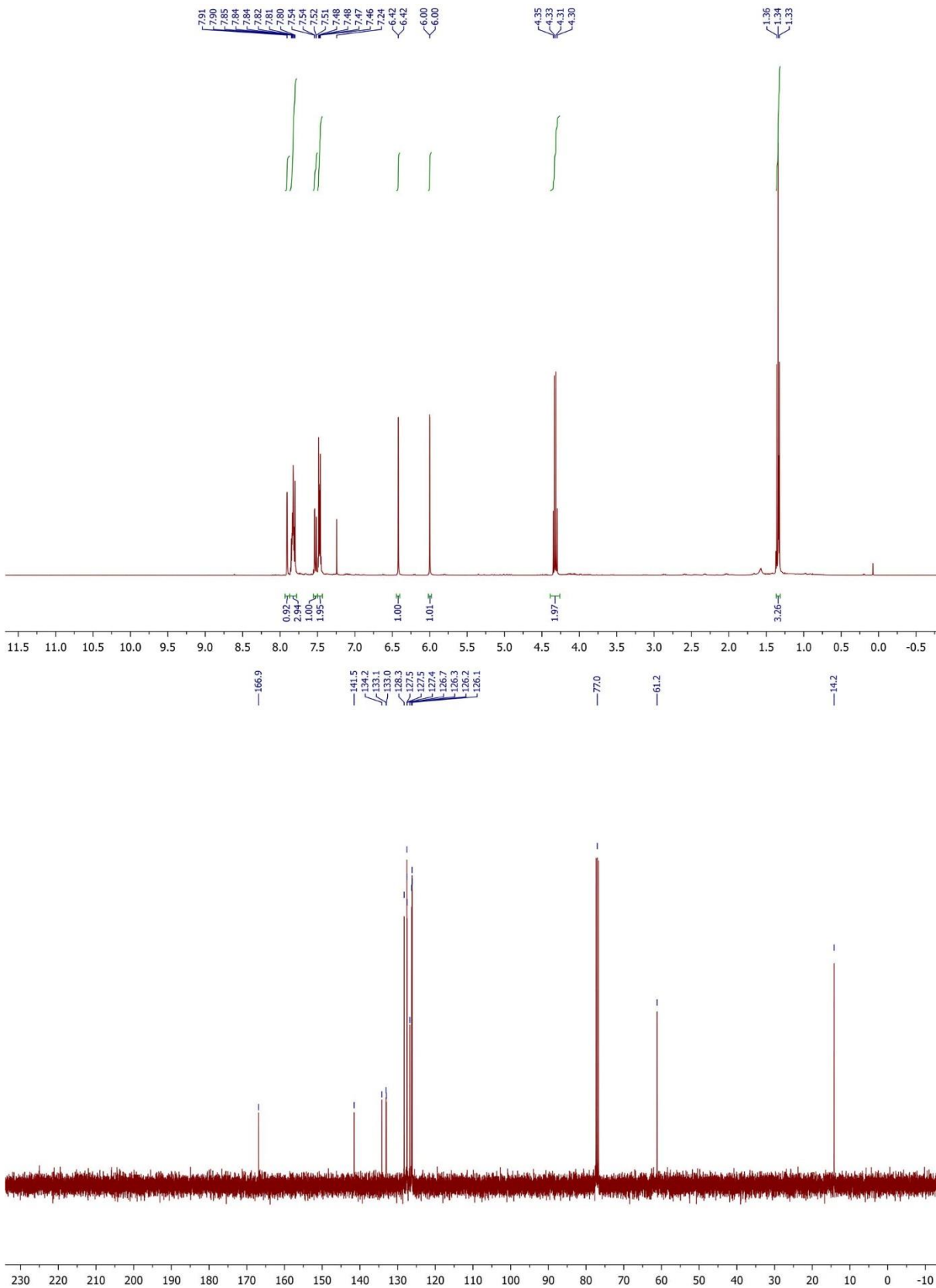
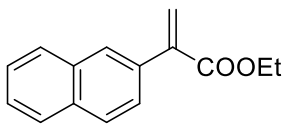


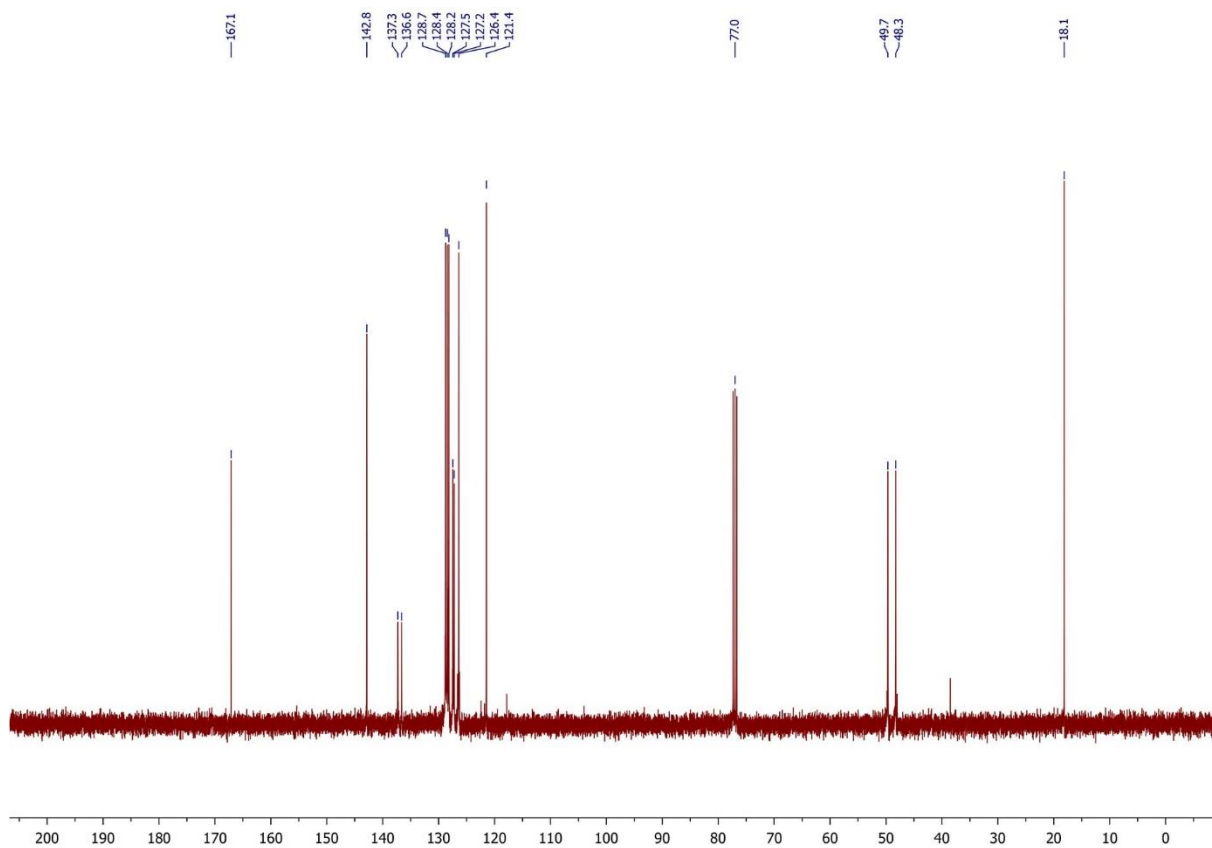
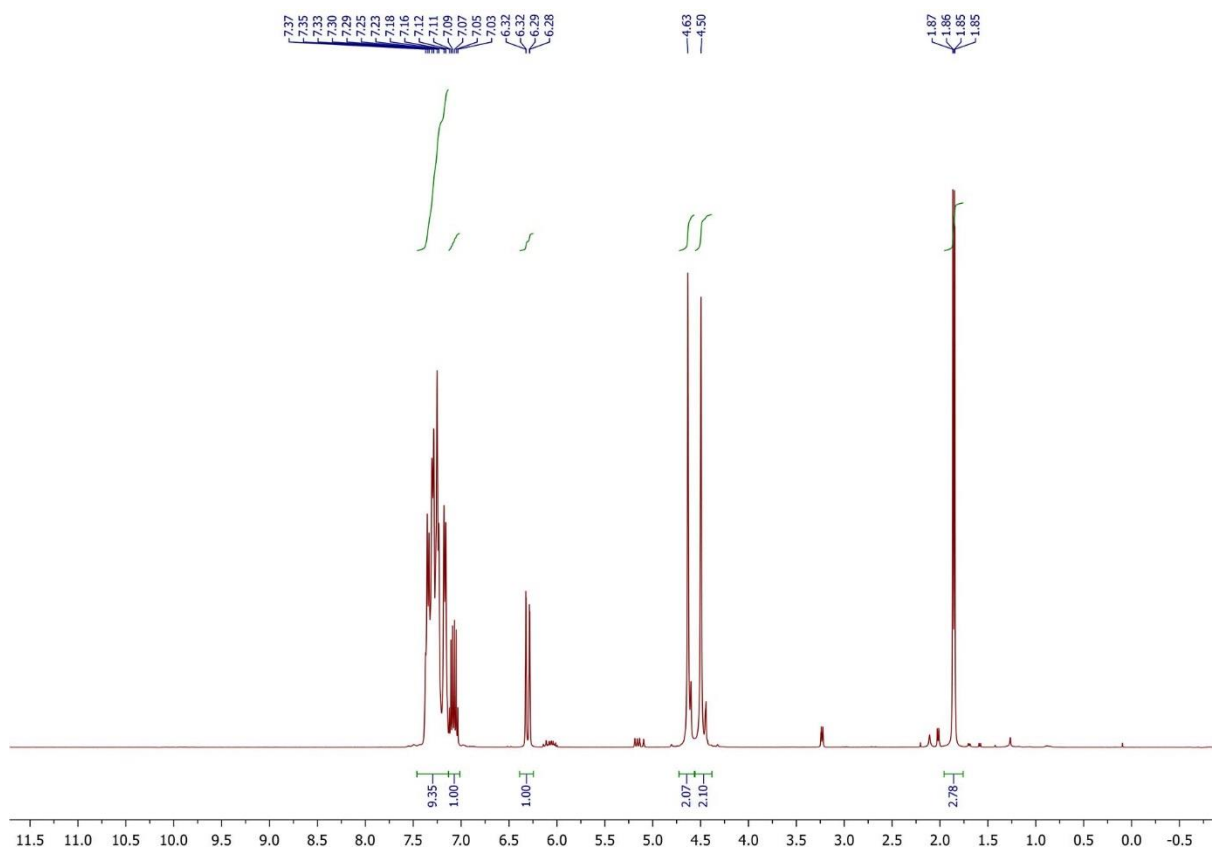
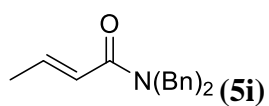


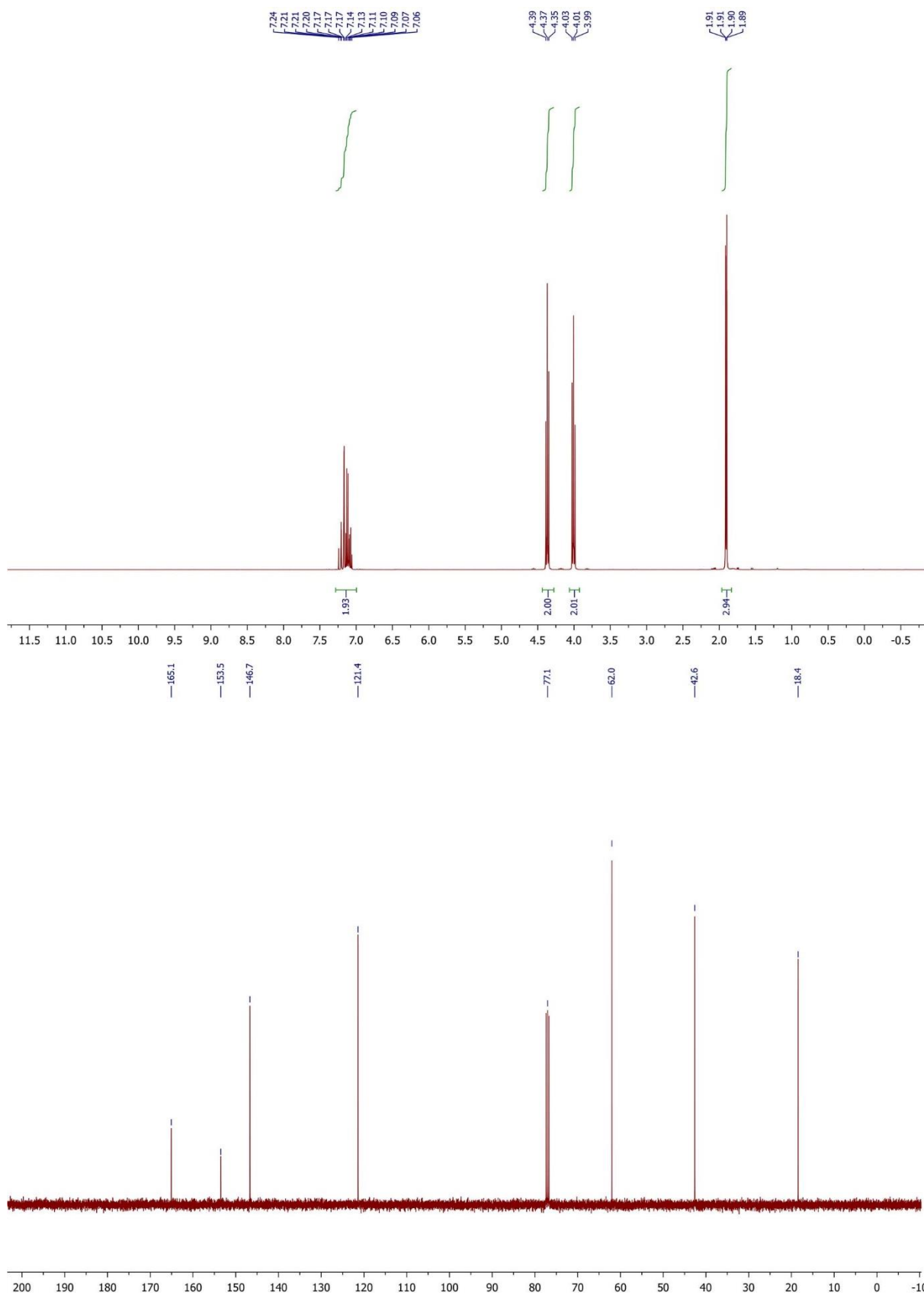
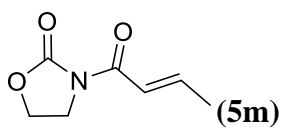


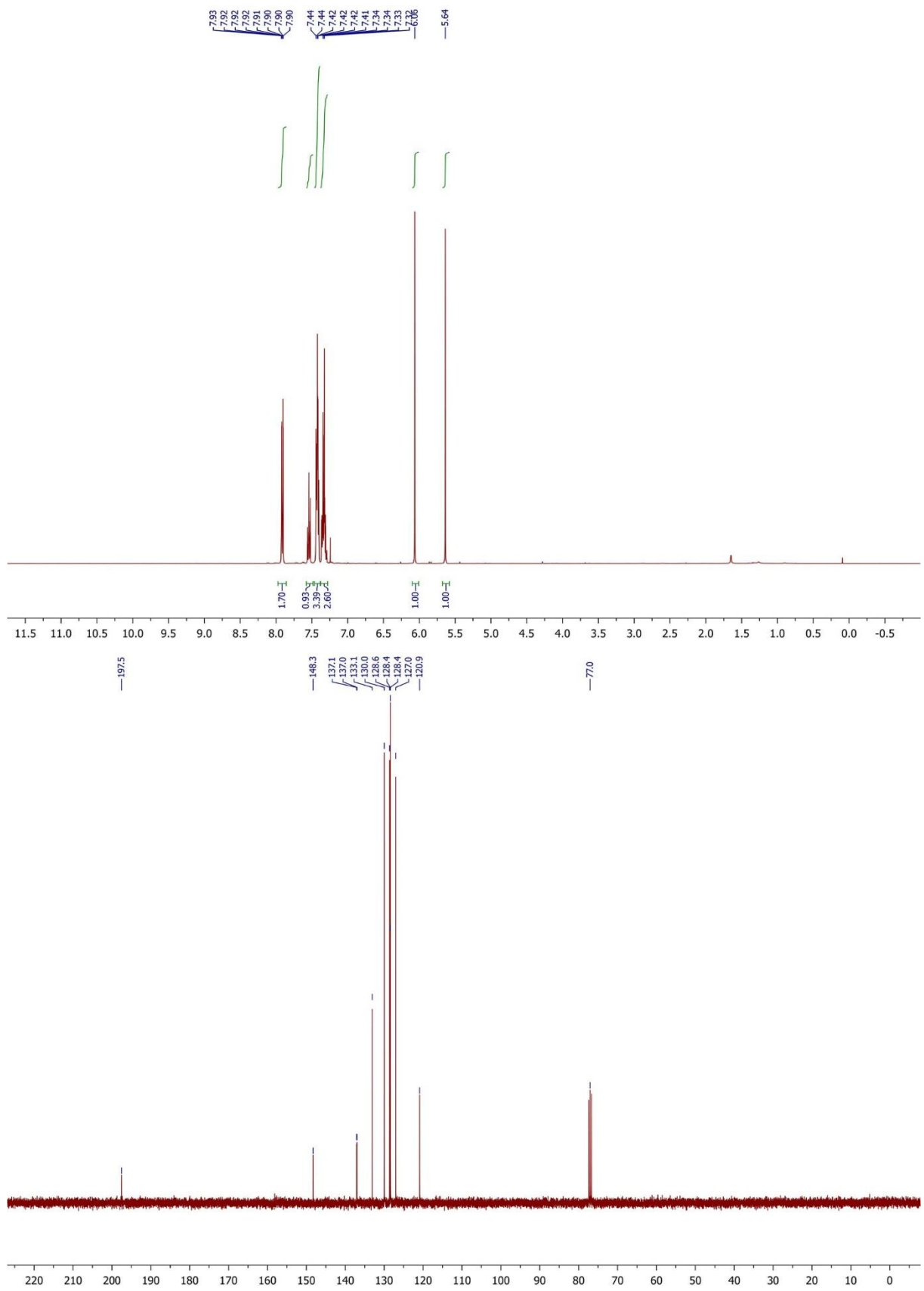
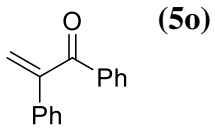


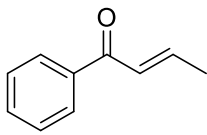




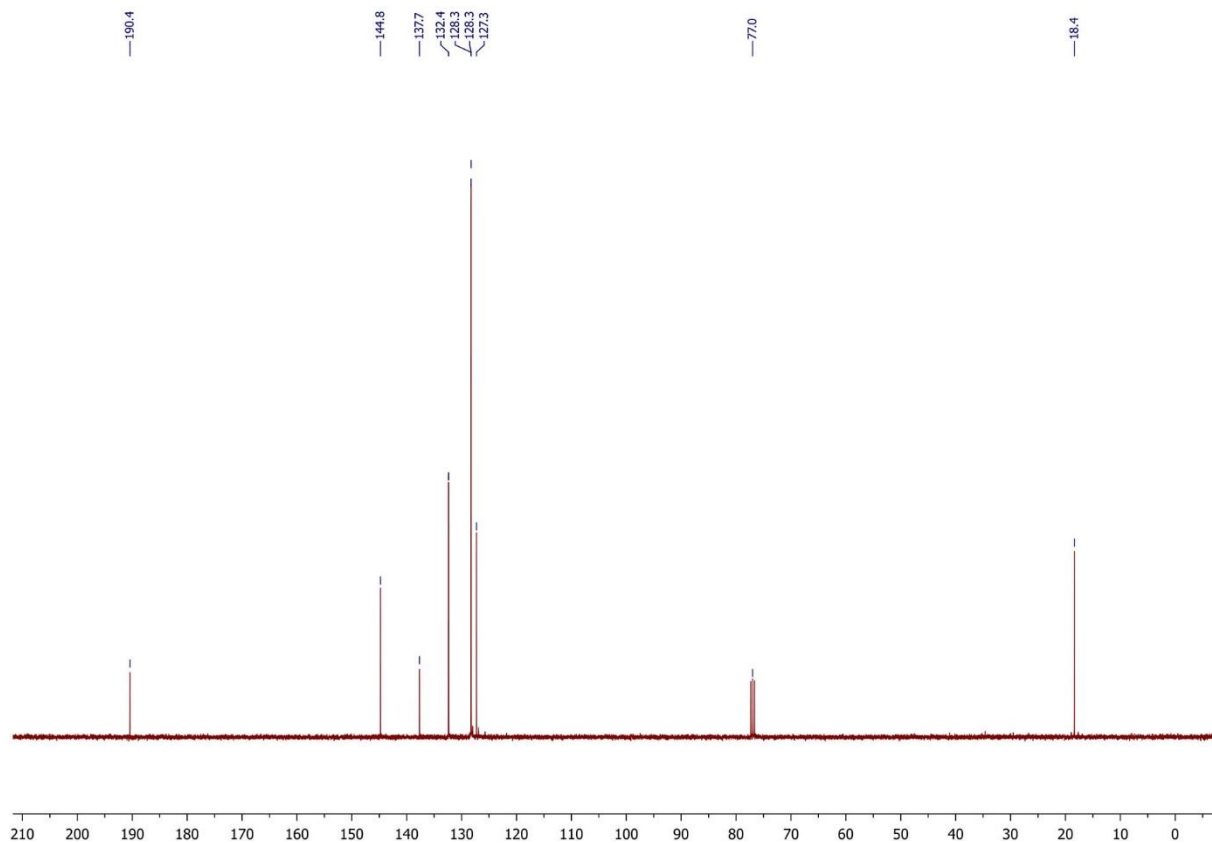
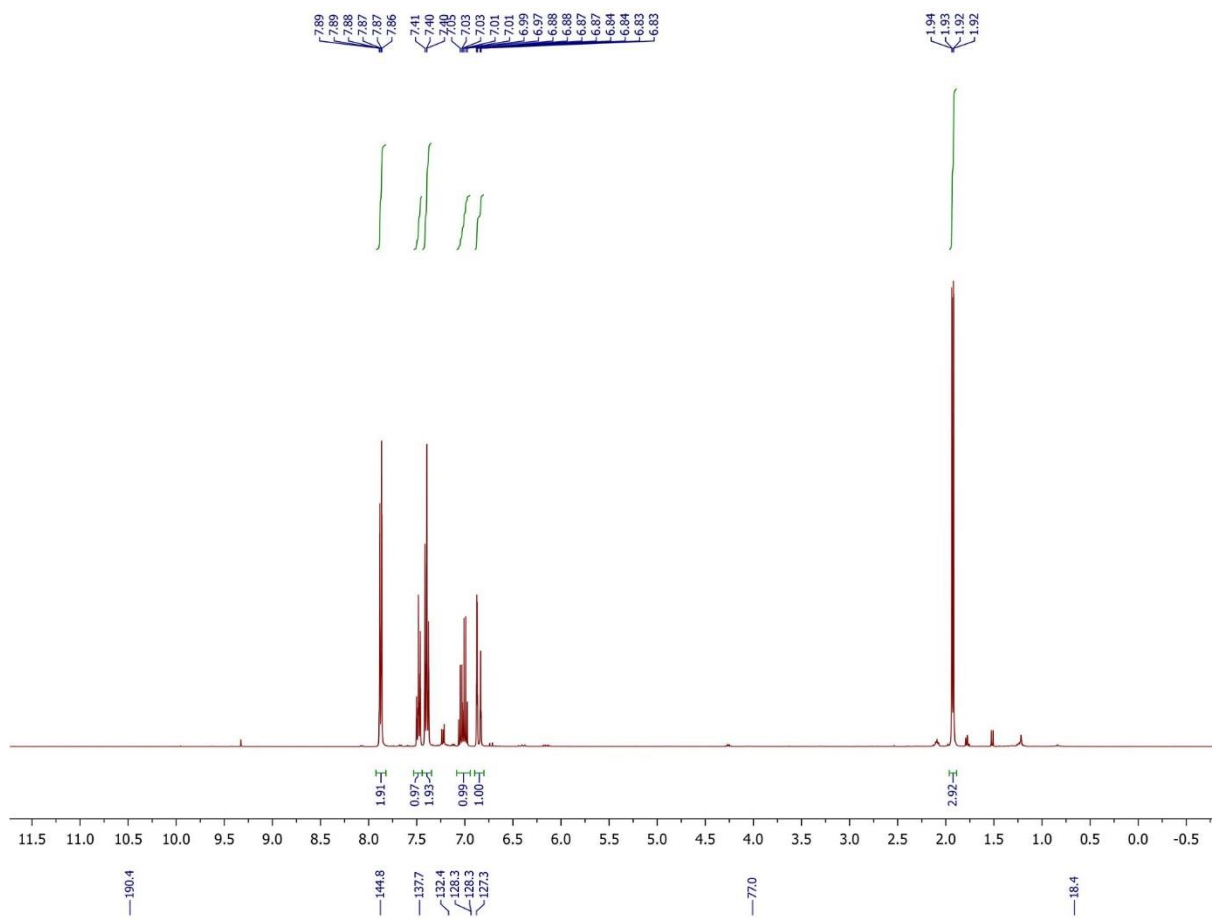




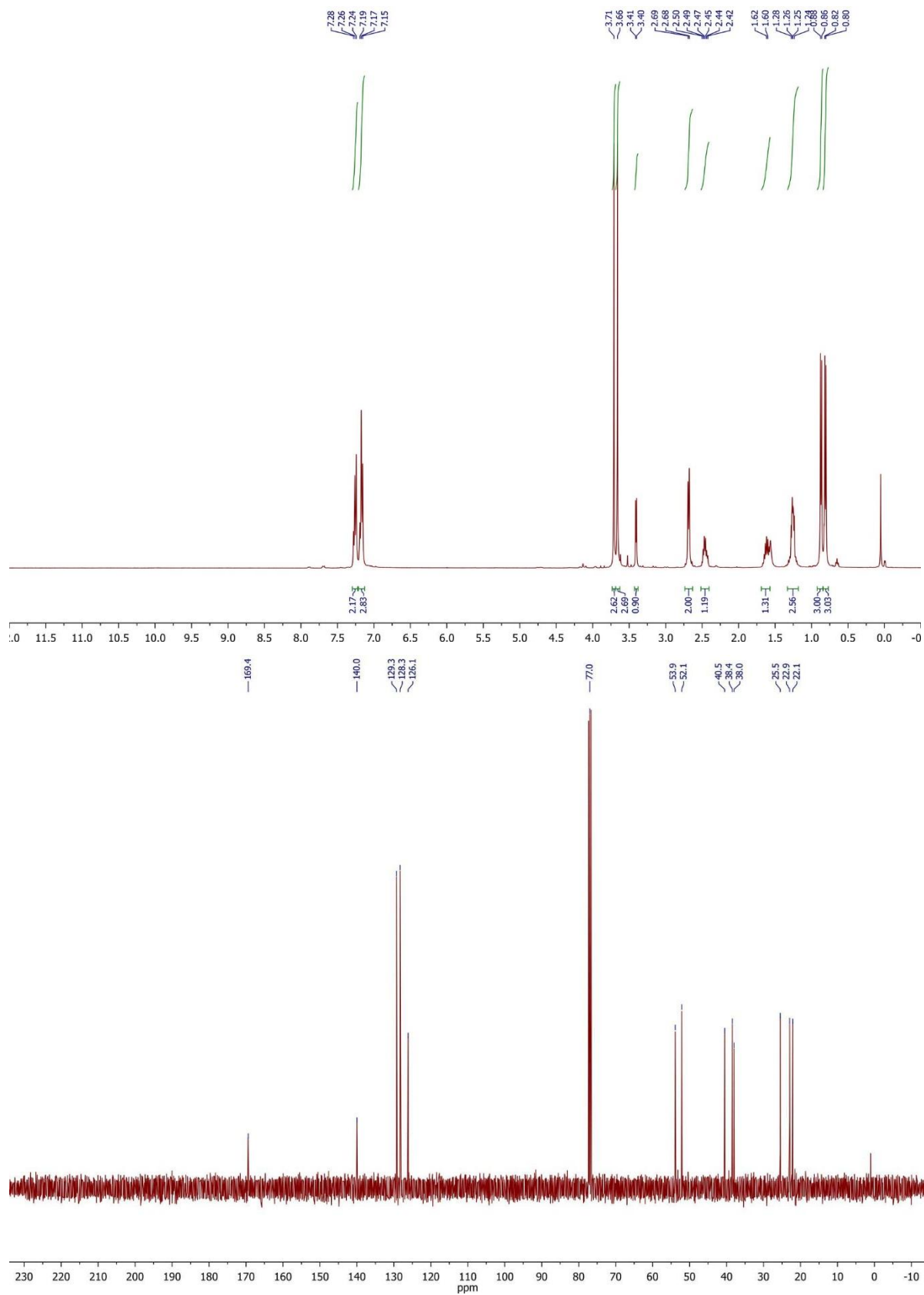
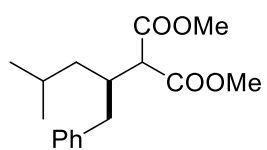


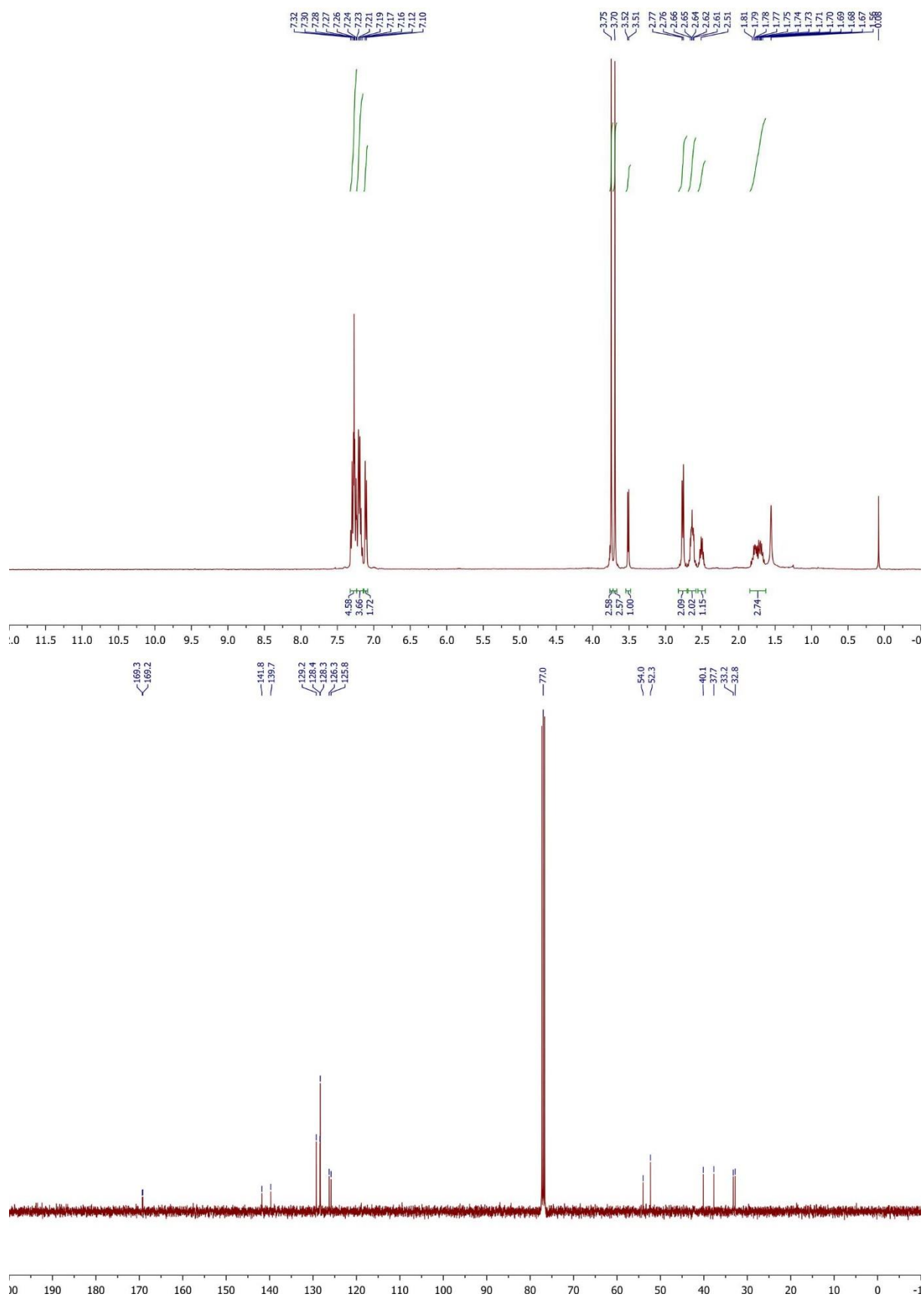
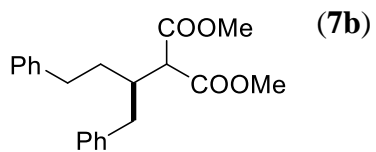


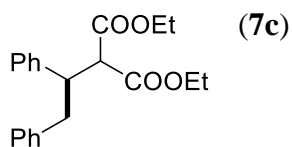
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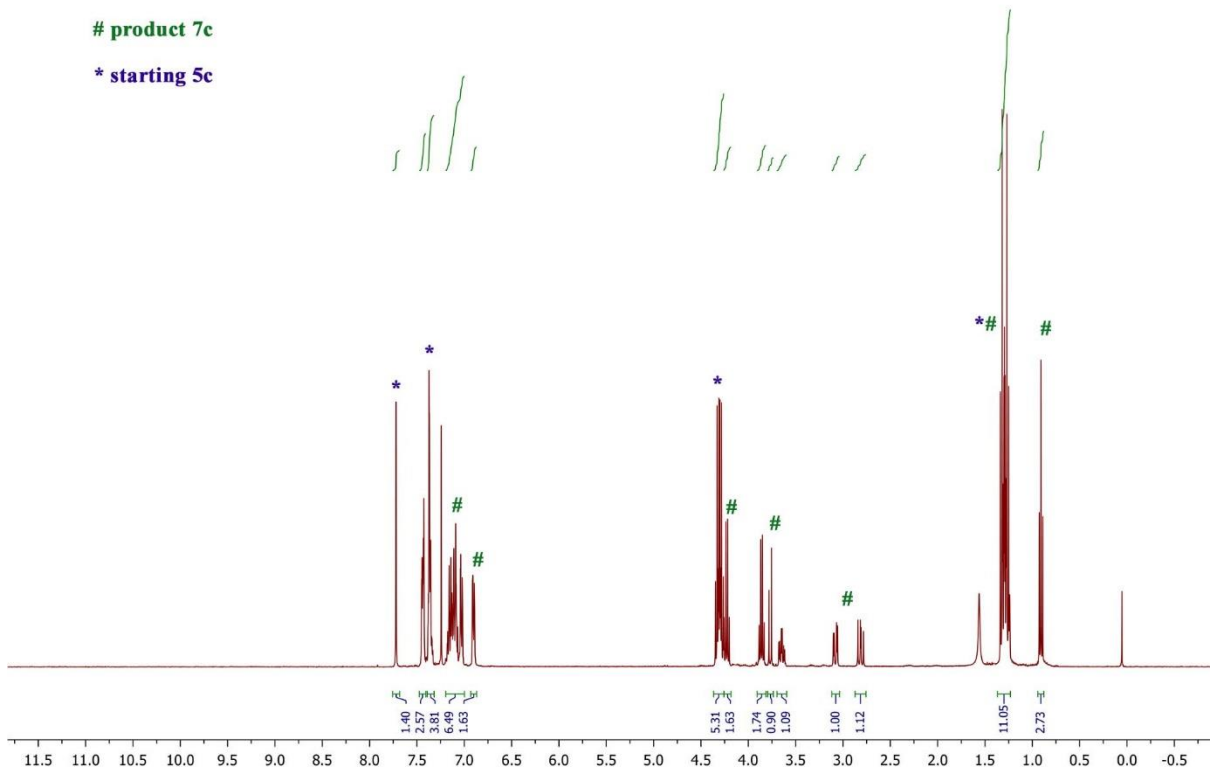




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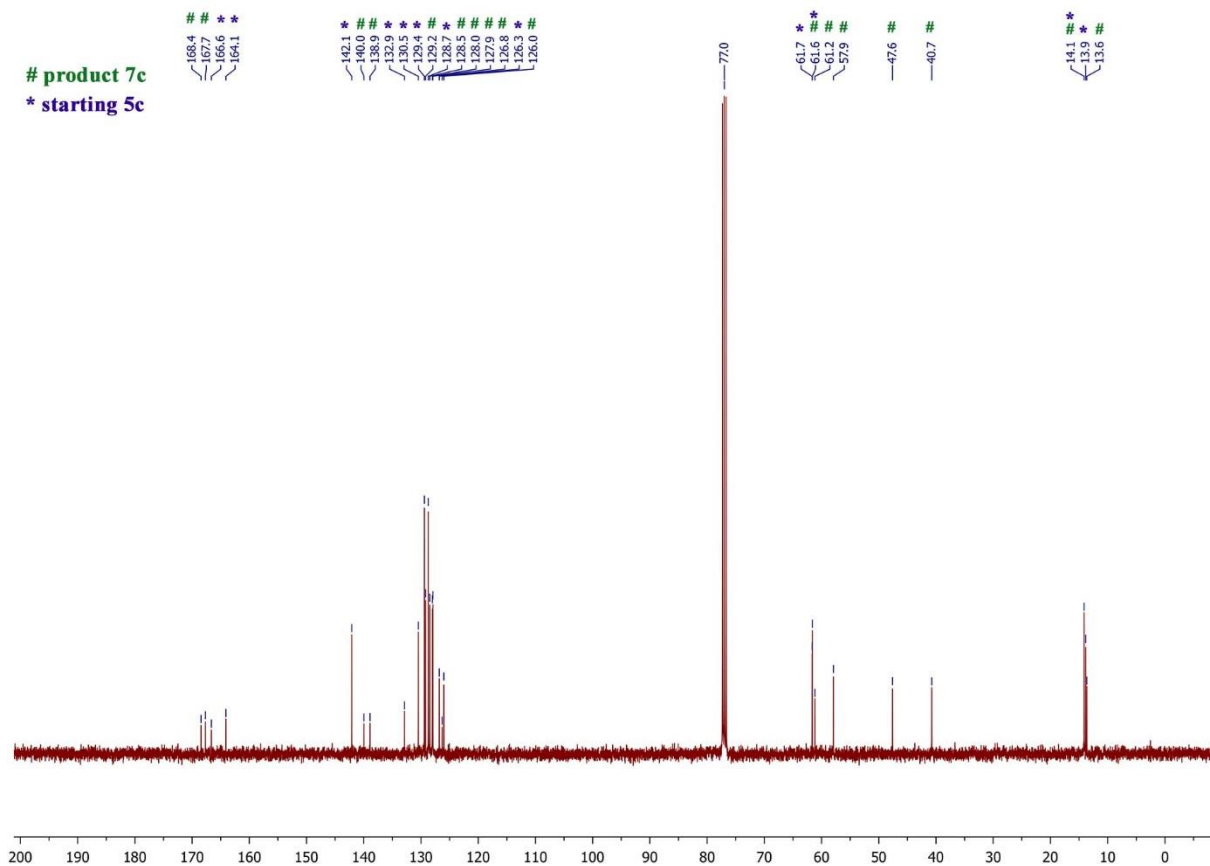
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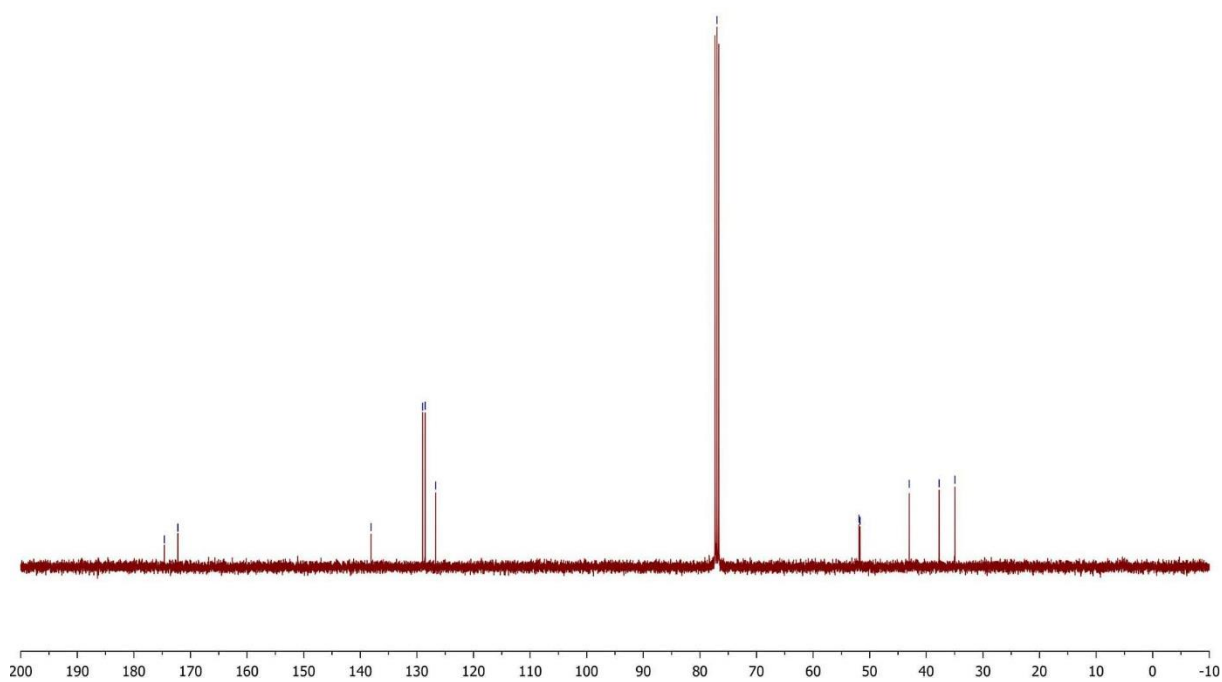
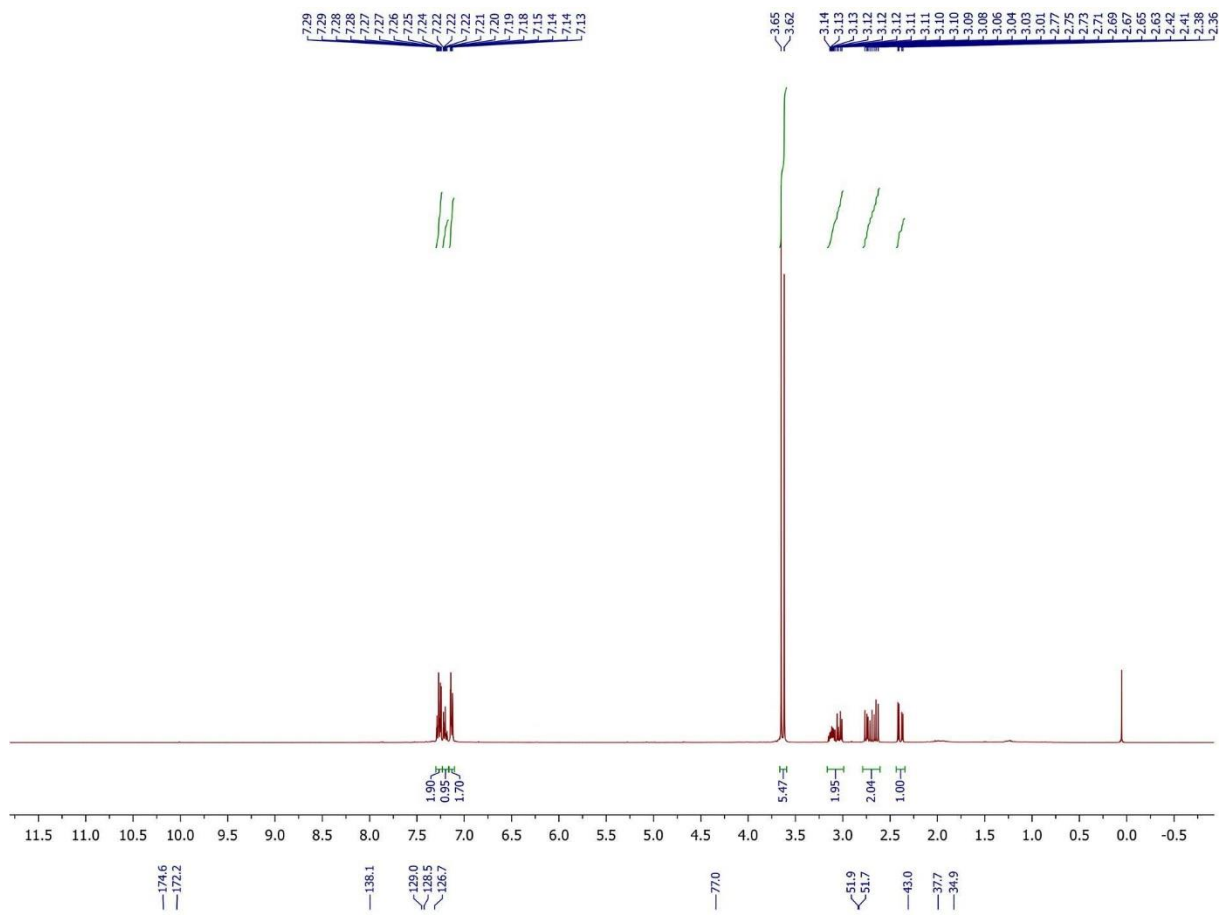
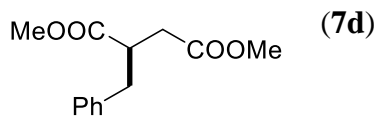
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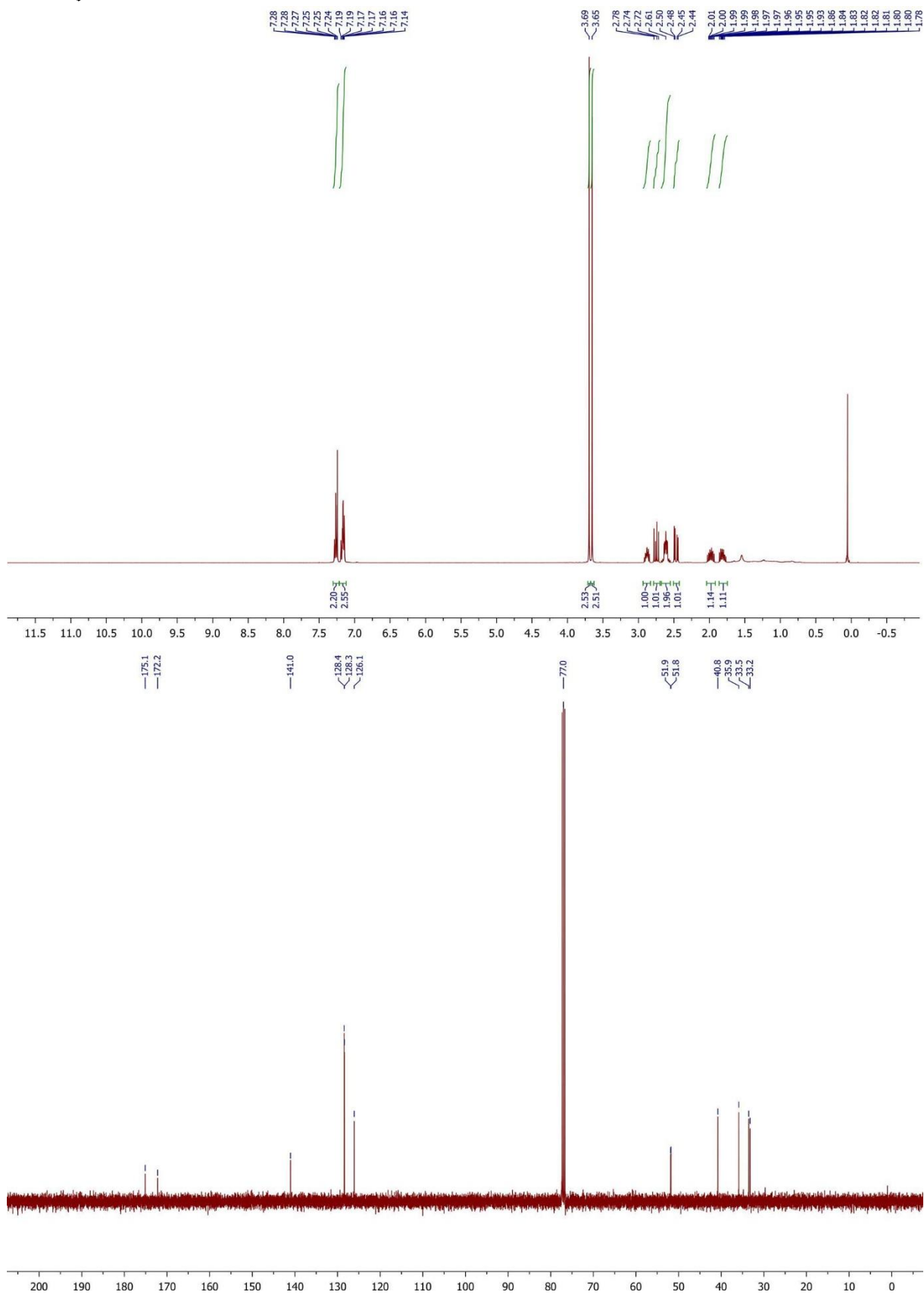
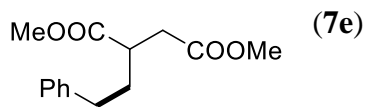


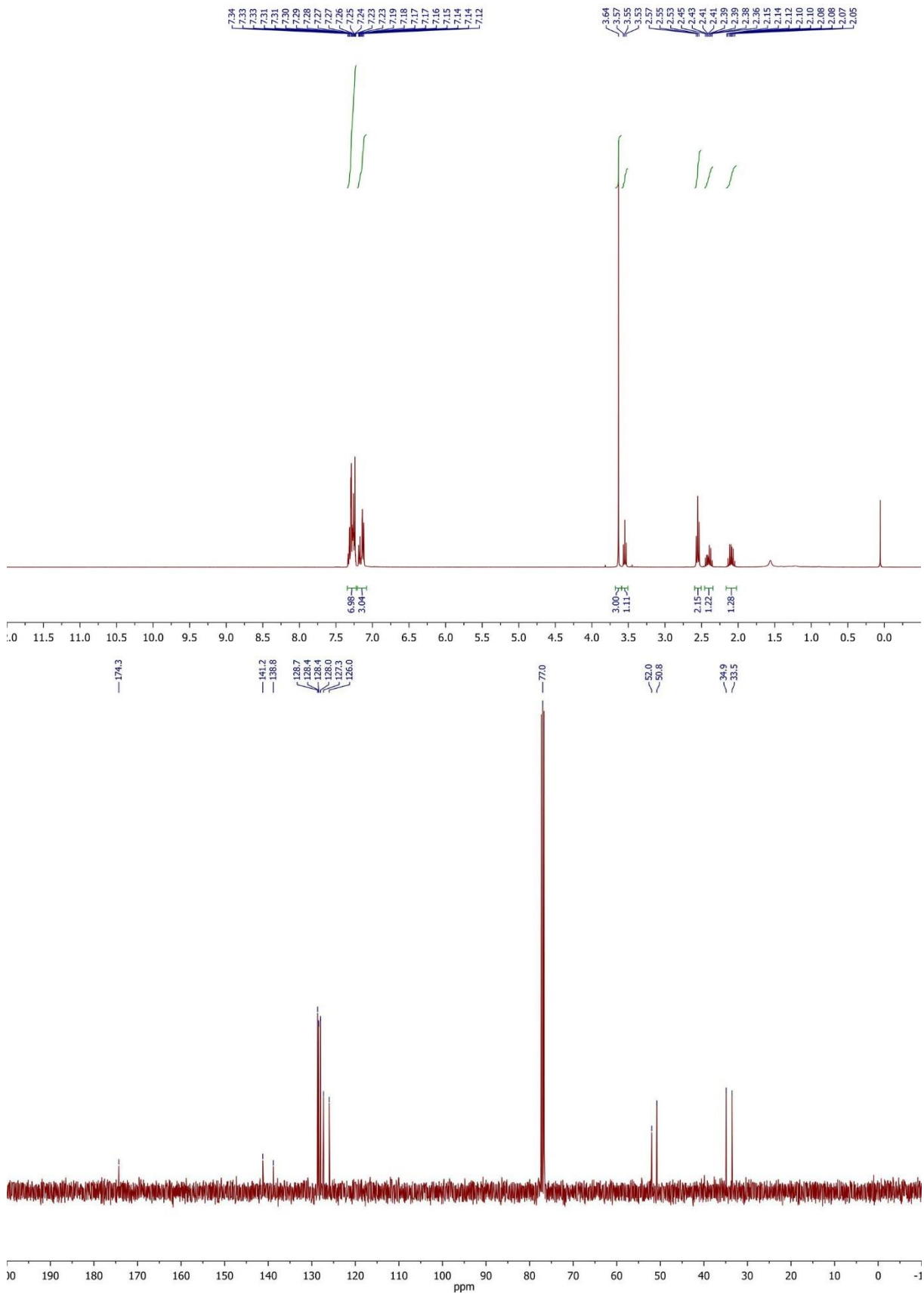
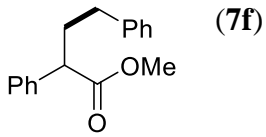
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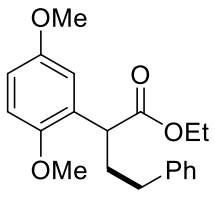
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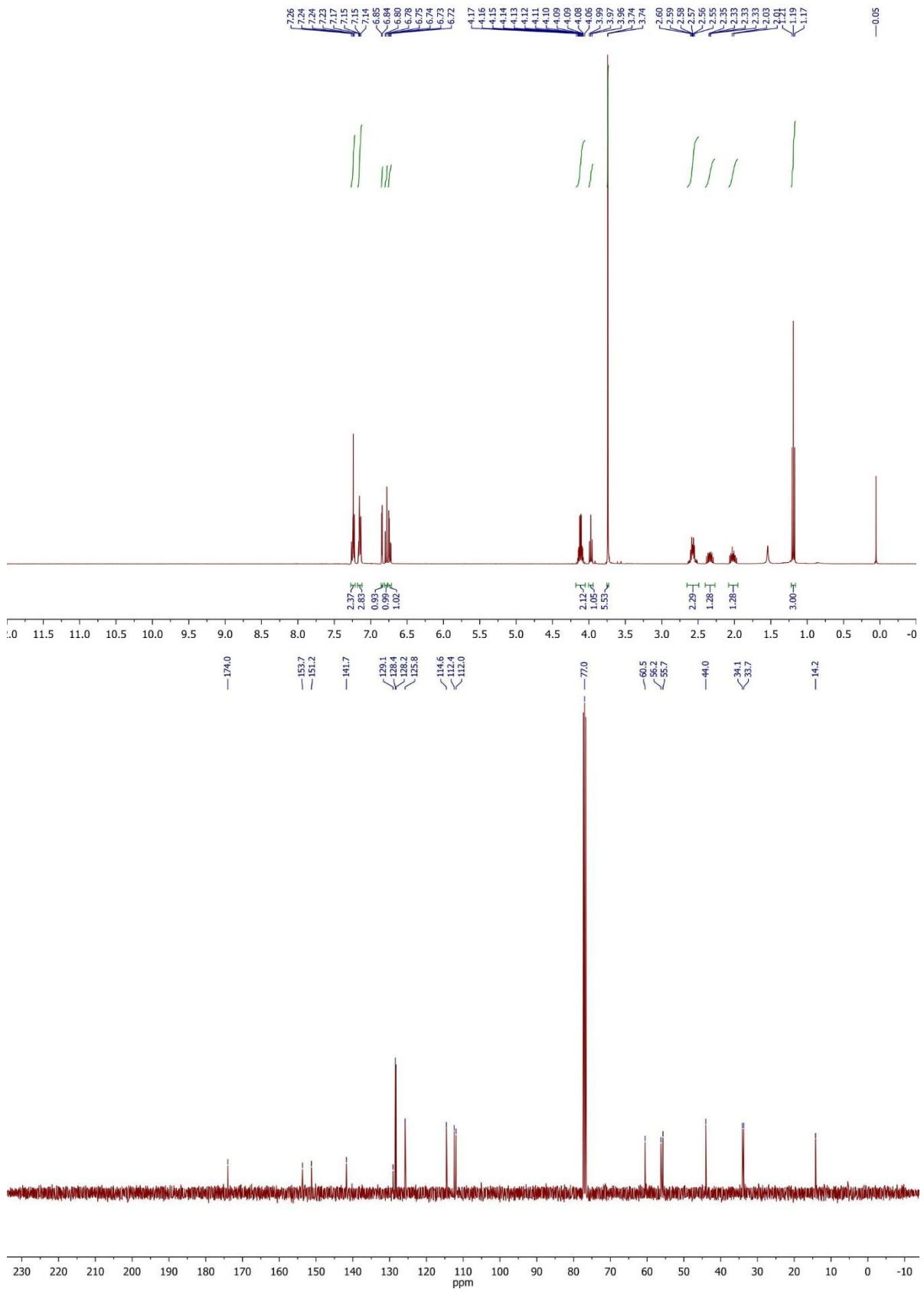


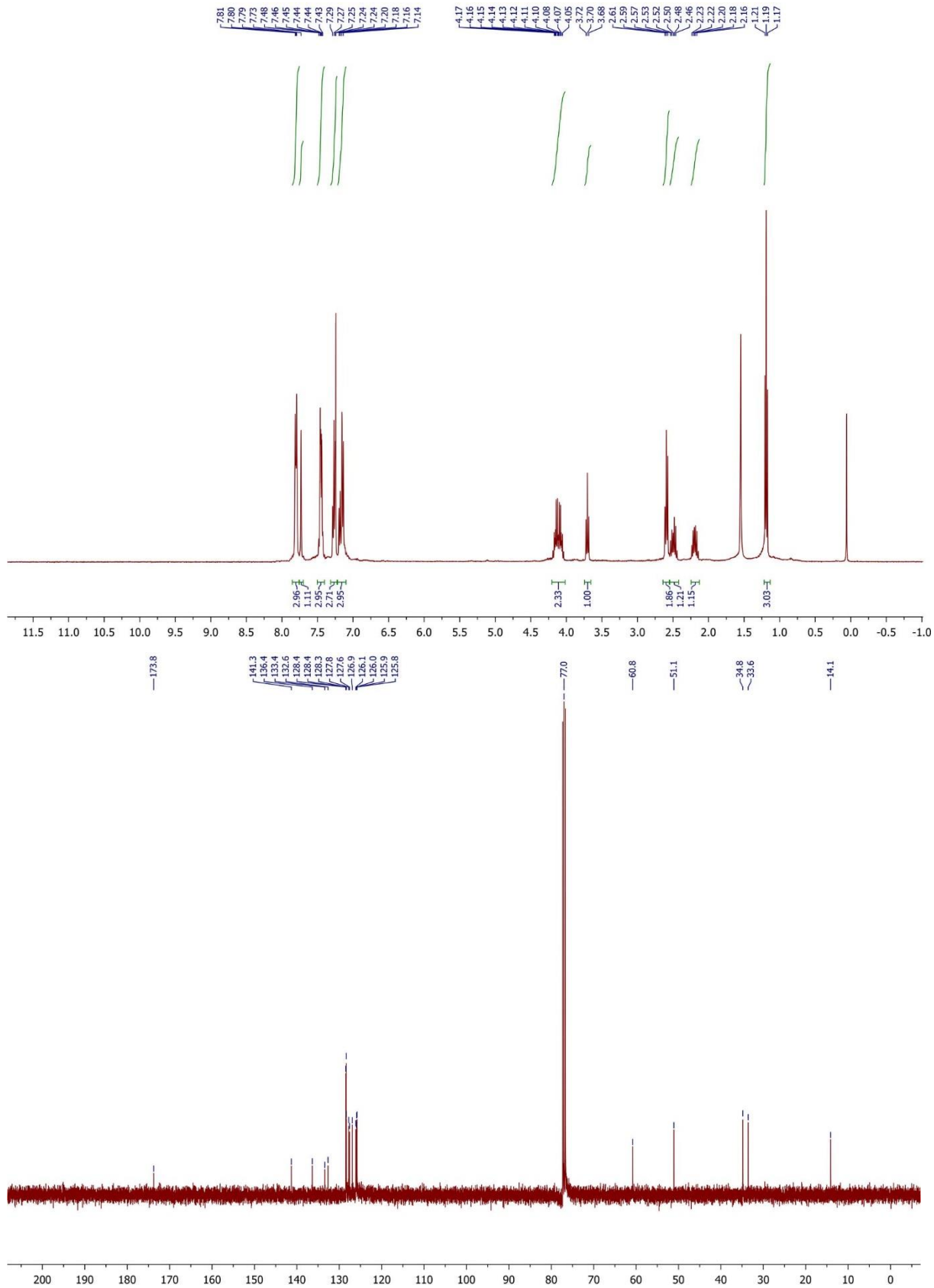
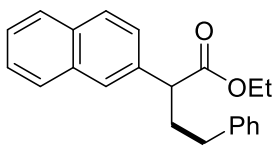


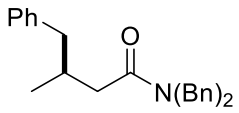




(7g)







(7i)

